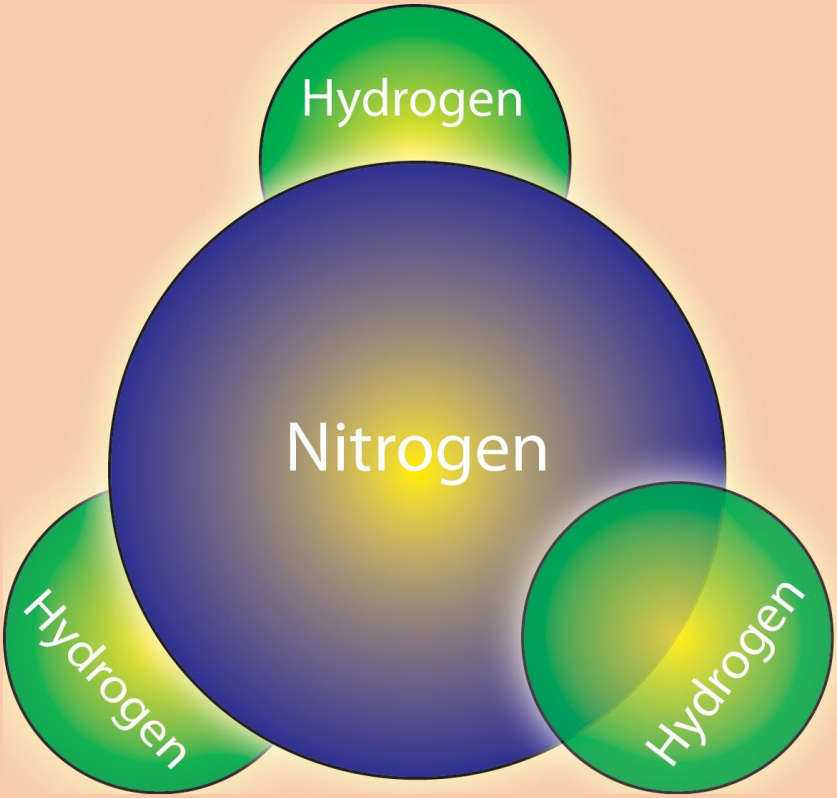
13. AMINES



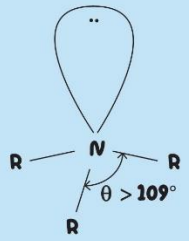
Chemistry Smart Booklet

Theory + NCERT MCQs + Topic Wise Practice MCQs + NEET PYQs

AMINES

STRUCTURE

NH_3	Ammonia
$R\text{-}NH_2$	1° Amine
$R_2\text{-}NH$	2° Amine
R_3N	3° Amine



Pyramidal geometry

PHYSICAL PROPERTIES

PHYSICAL STATE

Lower aliphatic amines are gases, intermediate members are liquid (fishy odour), while higher members are solid.

SOLUBILITY

Lower aliphatic amines are soluble in wate due to H-bonding, while higher amines (> C_6) are insoluble in water.

$$\text{Solubility} \propto \frac{1}{\text{Molecular weight}}$$

BOILING POINT

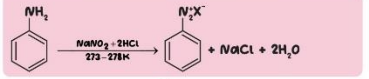
Primary and secondary amines forms intermolecular H-Bonding while tertiary does not.

Primary > Secondary > Tertiary

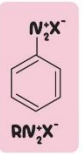
PHYSICAL PROPERTIES

Colourless, soluble in water, decompose in dry state
$C_6H_5N_2^+Cl^-$ is readily soluble in water

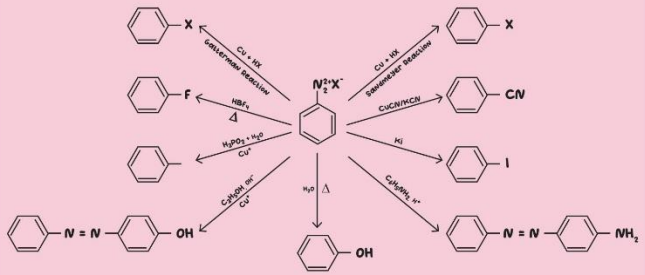
PREPERATION



DIAZONIUM SALTS



CHEMICAL PROPERTIES



PREPARATION

- **Reduction of Nitro Compounds.**

$$RNO_2 \xrightarrow[\text{Or } H_2/Pd]{Sn/HCl \text{ or } Fe/HCl} RNH_2$$

- **Ammonolysis**

$$R-X \xrightarrow{NH_3} R-\overset{+}{N}H_3X^- \xrightarrow{NaOH} R-NH_2 + H_2O + Na^+X^-$$

- **Reduction of Nitriles**

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

- **Reduction of Amides**

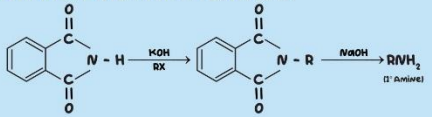
$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R-CH_2-NH_2$$

- **Hoffmann Bromamide Degradation reaction**

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

One carbon less amine is formed as compared to amides

- **Gabriel Phthalimide Synthesis**



Aromatic primary amines cannot be prepared by this method.

BASIC NATURE

Due to the presence of lone pair on Nitrogen amines are basic.
Factors affecting basicity
(i) Inductive effect
(ii) Solvation effect
(iii) Steric hinderance

IN GASEOUS PHASE

$3° Amine > 2° Amine > 1° Amine > NH_3$

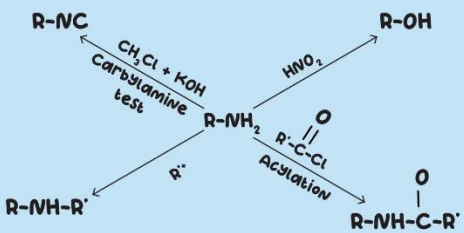
IN AQUEOUS PHASE

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
$(C2H5)2 > (C_2H_5)_2N > (C_2H_5)NH_2 > NH_3$

OVERALL BASICITY ORDER

Aliphatic Amine > Amines > Aromatic Amines

CHEMICAL REACTION



TEST FOR AMINES

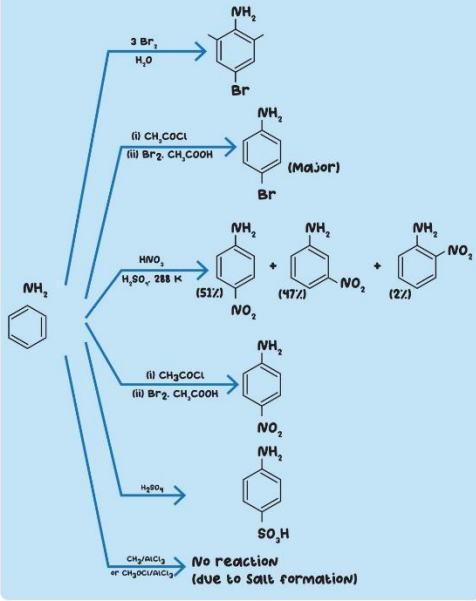
HINSBERG'S TEST

PRIMARY AMINE

SECONDARY AMINE

TERTIARY AMINE

ELECTROPHIC SUBSTITUTION



AMINES

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

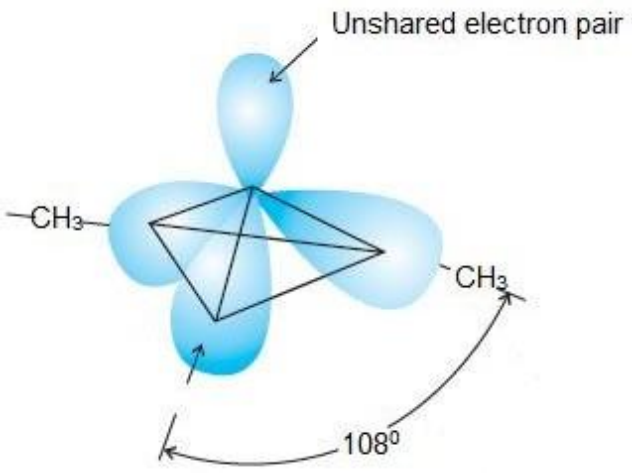
Examples:

(i) CH_3-NH_2

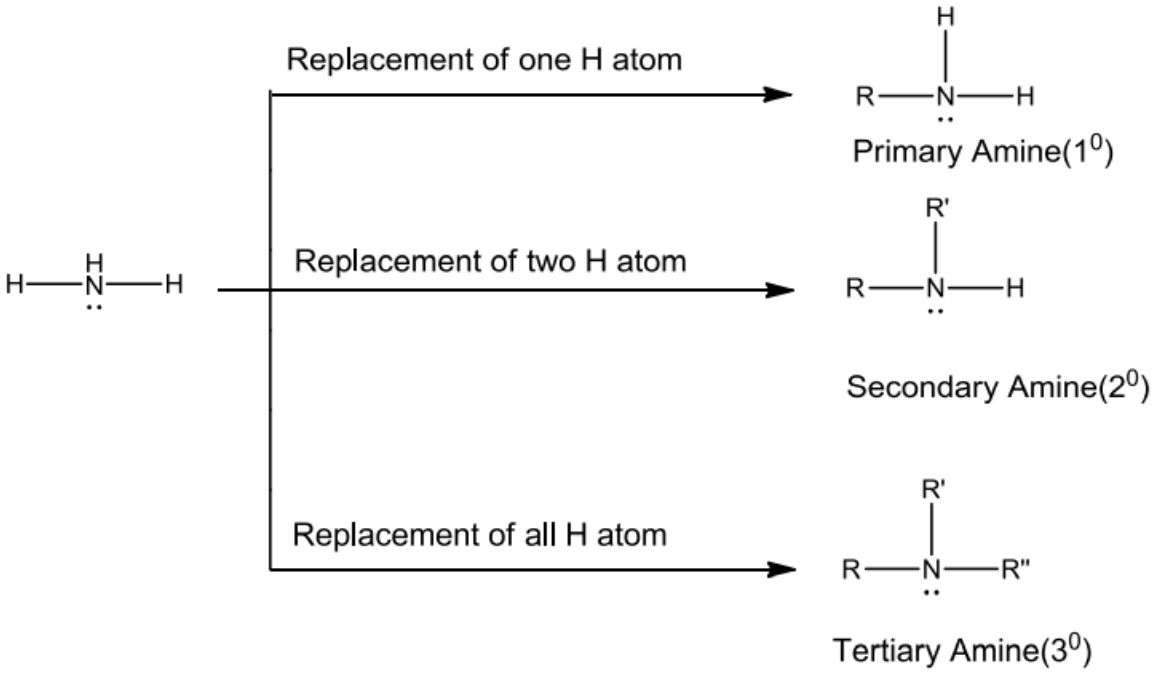
Structure of Amines

- In amines, the nitrogen atom is trivalent and has an unshared pair of electrons. Hence the nitrogen orbitals 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



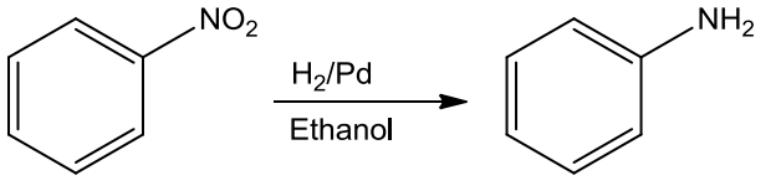
R, R' and R'' can be alkyl or aryl

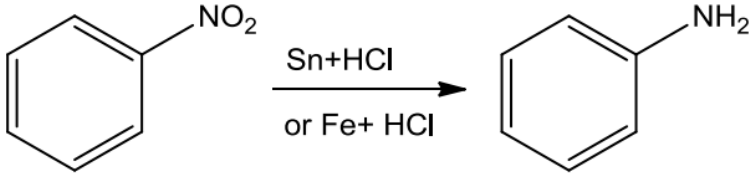
Preparation of Amines

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.

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

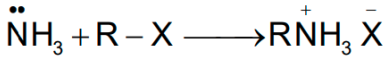




Ammonolysis

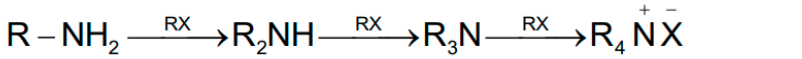
Alkyl halides or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which halogen

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.



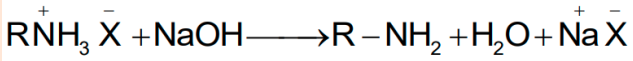
Nucleophile Substituted ammonium salt

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



(1^0) (2^0) (3^0) Quaternary ammonium salt

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

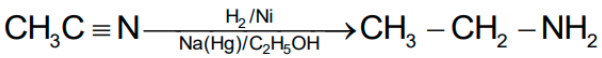


In this method, a mixture of primary, secondary and tertiary and also a quaternary ammonium salt.However a primary amine is prepared by taking large excess of ammonia.

The order of reactivity of halides with amines is RI > RBr > RCl

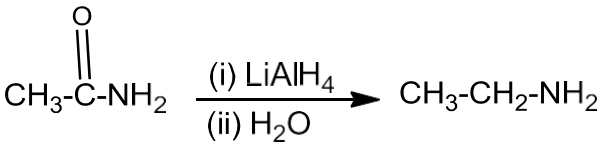
Reduction of Nitriles

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



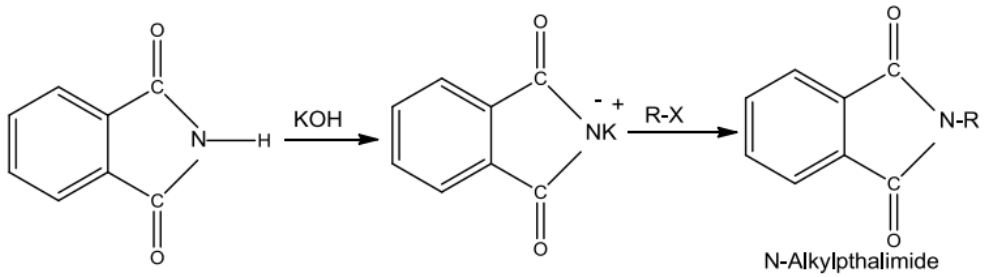
Reduction of Amides

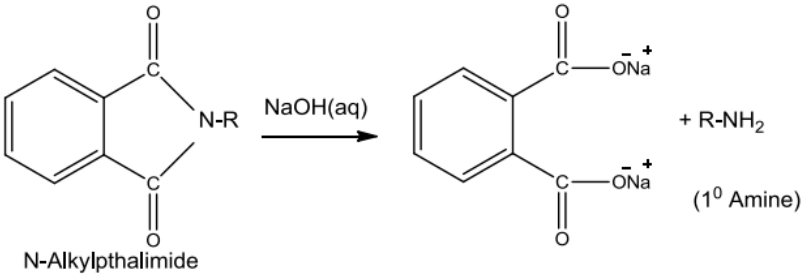
Amides on reducing with $LiAlH_4$ yield amines.



Gabriel pthalimide synthesis

Pthalimide on reacting with ethanolic solution of KOH forms potassium salt of pthalimide which onheating 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.

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 is

  Primary > 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.

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

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

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

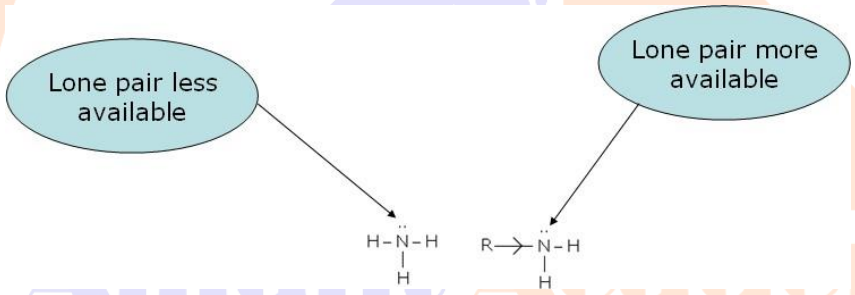
$$K_b = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2]}$$

$$pK_b = -\log K_b$$

- 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.



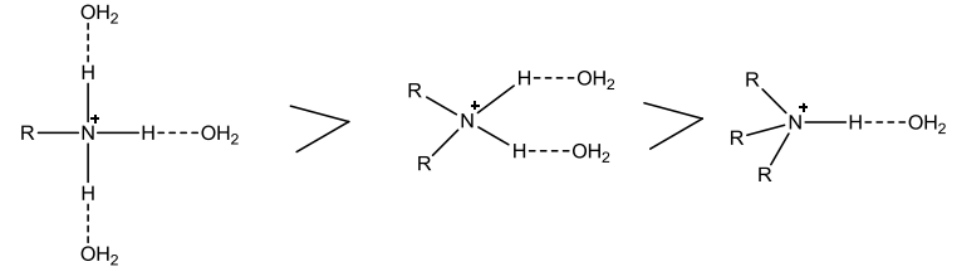
c) Comparison of basic strength of primary, secondary and tertiary amines

- 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.



1^0 Maximum hydration

2^0

3^0 Minimum hydration

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

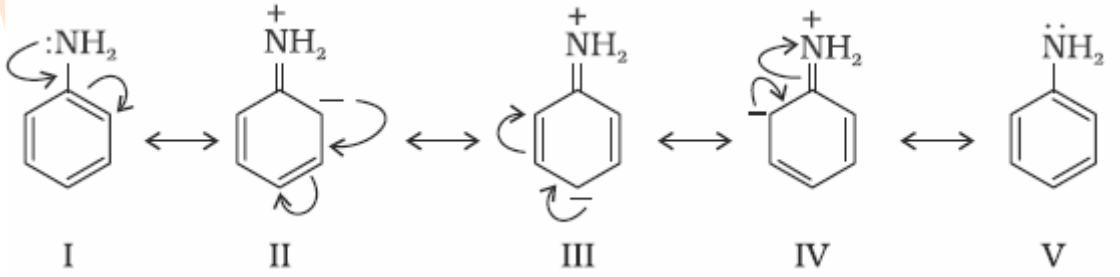
➢ Steric factor

- ✓ 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 groupwhich decides the basic strength of alkyl amines in the aqueous state.

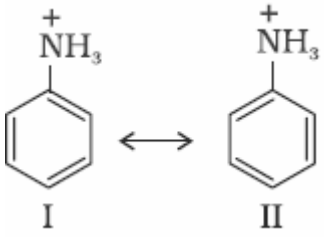
- ✓ When the alkyl group is small like CH_3, there is no steric hindrance to hydrogen bonding. In this case, the order of basicity in aqueous medium is:
$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
- ✓ When the alkyl group is the ethyl group, the group order of basicity in the aqueous medium is $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

➢ 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 ofelectrons 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.



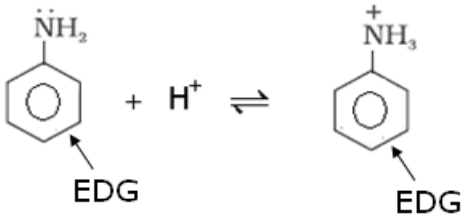
- ✓ Thus, aniline has less tendency to accept a proton to form the anilinium ion.

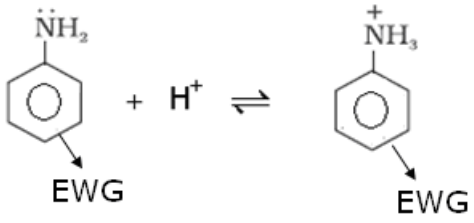
➢ Effect of substituent on the basic character of amines

✓ 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)

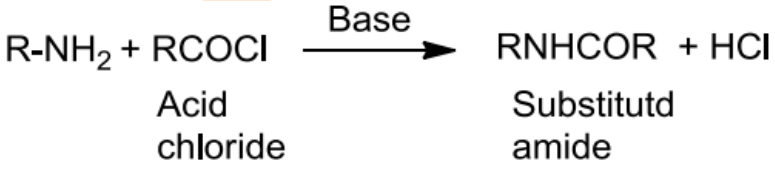
Reaction of Amines

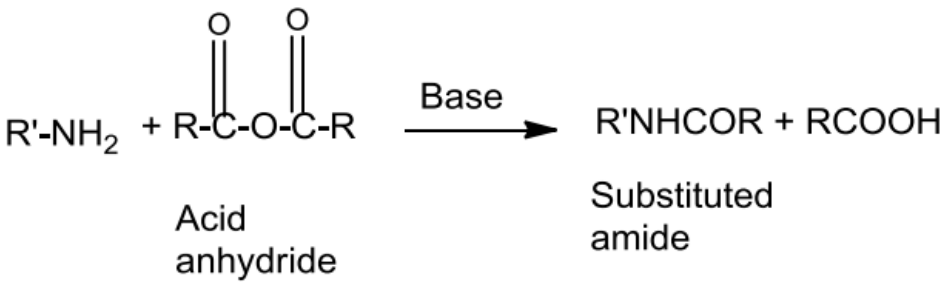
Acylation reaction

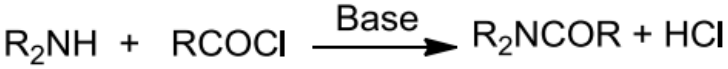
➢ Aliphatic and aromatic primary and secondary amines (which contain replaceable hydrogenatoms) react with acid chlorides, anhydrides and esters to form substituted amide.

➢ 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.







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 which are used in the synthesis of a variety of aromatic compounds.

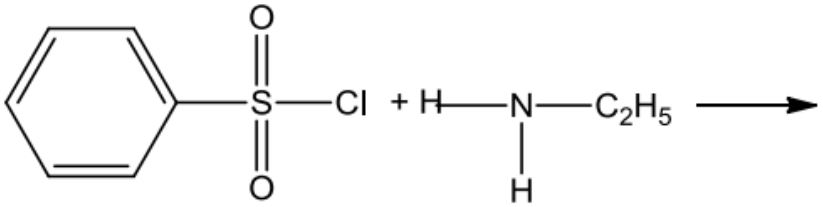
$$C_6H_5-NH_2 \xrightarrow[273-278K]{NaNO_2+HCl} C_6H_5-\overset{+}{N}_2\,Cl^- + NaCl + 2H_2O$$

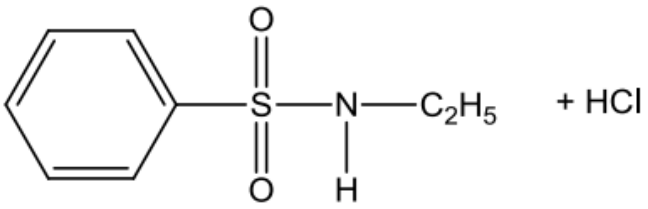
- Secondary and tertiary amines react with nitrous acid in a different manner.

Reaction with arylsulphonyl chloride

Hinsberg's reagent or benzenesulphonyl chloride ($C_6H_5SO_2Cl$) reacts with primary amines andsecondary amines to form sulphonamides.

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

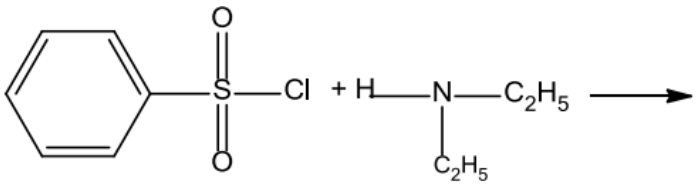


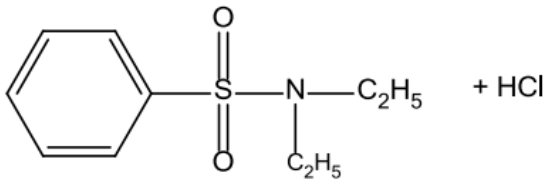


N-ethylbenzenesulphonamide

The hydrogen bonded to nitrogen is strongly acidic due to the presence of strong electronwithdrawing 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.

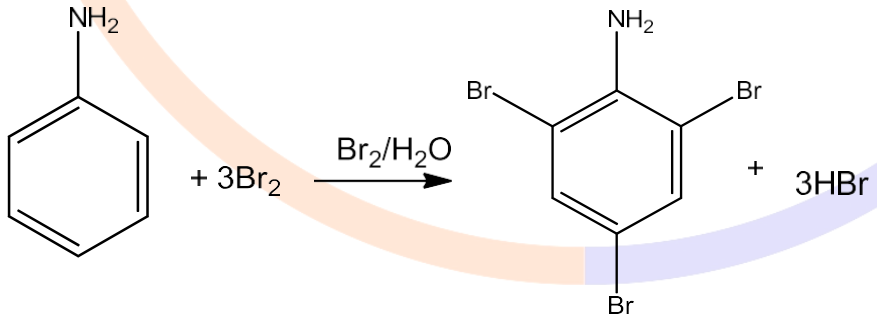
- Tertiary amines do not react with benzenesulphonyl chloride.

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

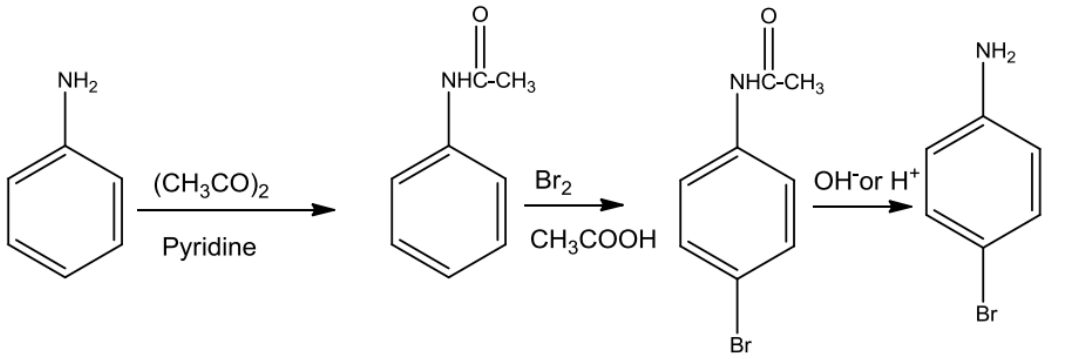
- Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoaniline.



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 aceticanhydride then carrying out the desired substitution followed by the hydrolysis of the substituted amide to the substituted amine.

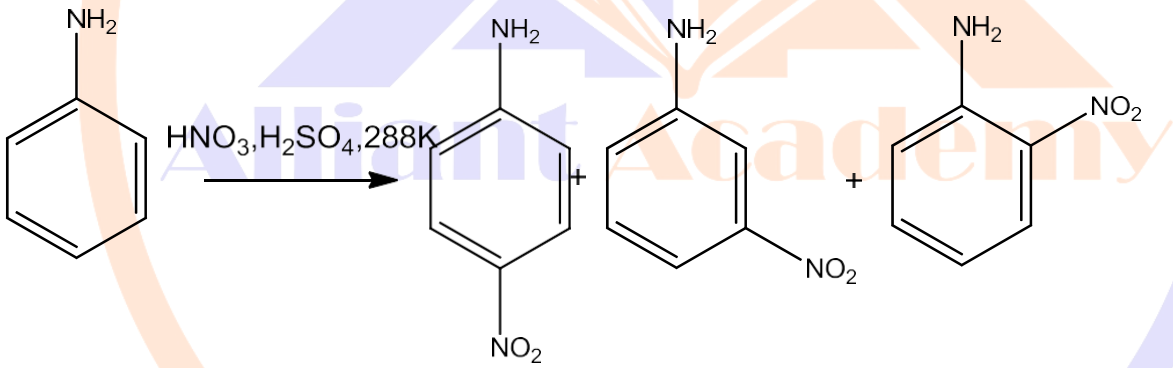


4-Bromoaniline

(b) Nitration

➢ Nitric acid is a nitrating agent plus a good oxidising agent. So direct oxidation of aromatic amines isnot 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.

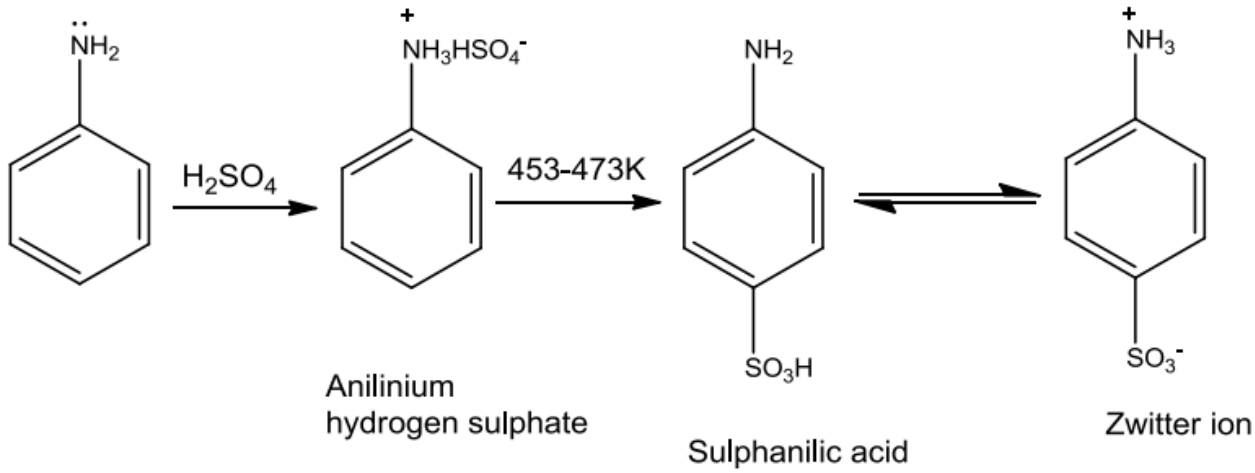


Acetanilide p-nitroacetanilide p-nitroaniline

➢ However if we protect the $-NH_2$ 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 withsulphuric acid at 453-473K gives p-aminobenzene sulphonic acid as the major product.



Anilinium hydrogen sulphate

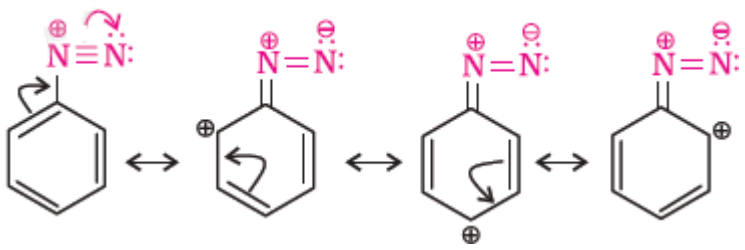
Sulphanilic acid

Zwitter ion

Aniline does not undergo Friedel-Crafts reaction due to salt formation with Lewis acid aluminium chloridewhich 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 $RN_2^+X^-$.
  - ✓ 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

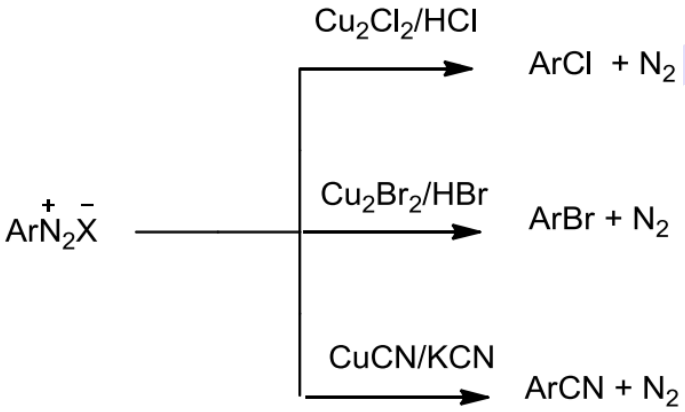
- Benzenediazonium chloride is a colourless crystalline solid.
- It is readily soluble in water and is stable in cold but reacts with warm water.
- It decomposes easily in the dry state.
- Benzenediazonium fluoborate is water insoluble and stable at room temperature.

Chemical Reactions

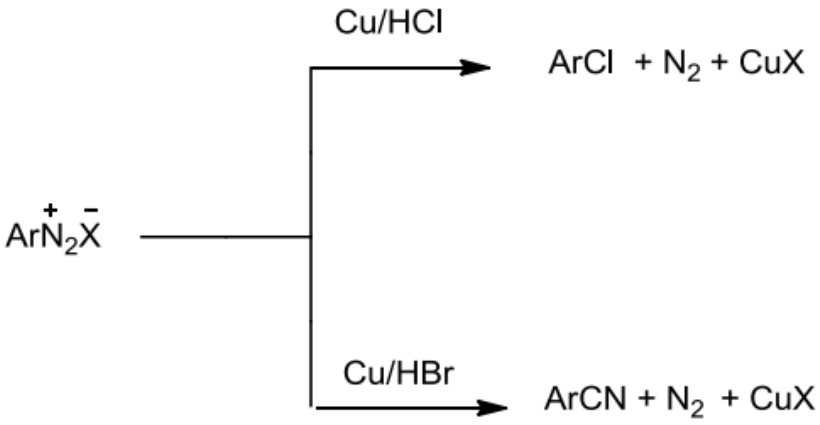
Reactions involving displacement of Nitrogen

➢ 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.

$$ArN_2^+X^- + KI \longrightarrow ArI + KCl + N_2$$

- **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.

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

- **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.

$$ArN_2^+Cl^- + H_3PO_3 + H_2O \longrightarrow Ar\,H + N_2 + H_3PO_3 + HCl$$

$$ArN_2^+Cl^- + CH_3\,CH_2OH \longrightarrow Ar\,H + N_2 + CH_3CHO + HCl$$

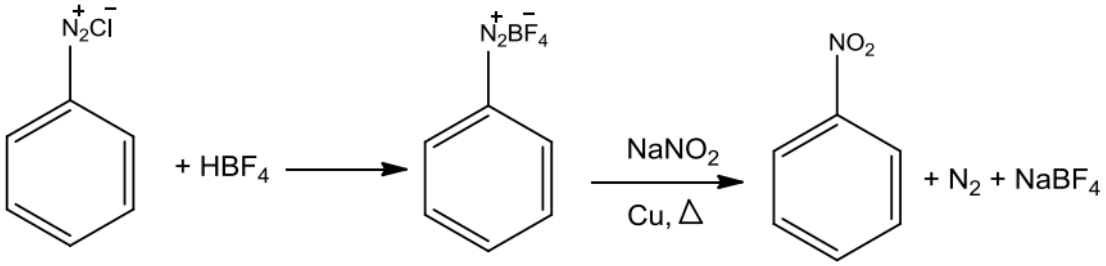
- **Replacement by hydroxyl group:**

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

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

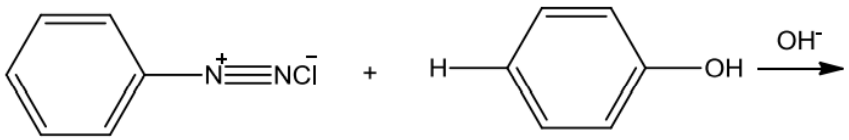
- **Replacement by $-NO_2$ group:**

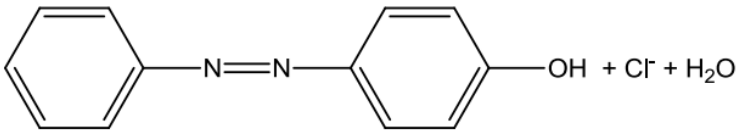
On heating diazonium fluoroborate with aqueous sodium nitrite solution in the presence of copper,the diazonium group is replaced by $-NO_2$ group.



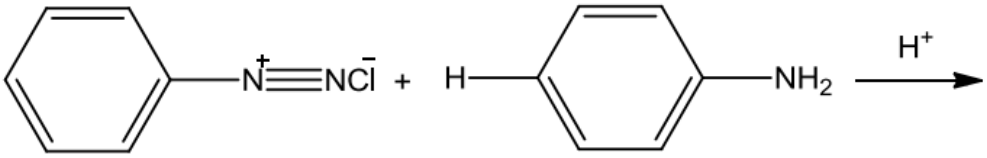
Reactions involving retention of diazo group coupling reactions

- ✓ Benzene diazonium chloride reacts with phenol in which the phenol at its para position is coupledwith 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.

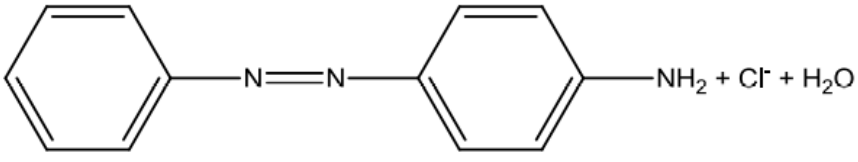




p-hydroxyazobenzene (orange dye)



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 aromaticcompounds which cannot be prepared by direct substitution in benzene or substituted benzene.

NCERT LINE BY LINE QUESTIONS

Introduction

1. Benadryl, a well known antihistamine contains **(NCERT Page-389)**

(a) Primary amino group (b) Amide group

(c) Secondary amino group (d) Tertiary amino group

Topic 1: Structure of Amines, Classification and Nomenclature

2. The total number of electrons around the nitrogen atom in amines are **(NCERT Page-390)**

(a) 8 (b) 7 (c) 4 (d) 3

3. Read the following statements and choose the correct option. **(NCERT Page-390)**

(i) Nitrogen atom in amines is *sp*3-hybridised.

(ii) The geometry of amines is pyramidal.

(iii) The angle C–N–C or C–N–H is slightly more than 109.5°.

(a) (i), (ii) and (iii) (b) (i) and (ii) (c) (i) and (iii) (d) (ii) and (iii)

4. A secondary amine is **(NCERT Page-390)**

(a) a compound with two carbon atoms and an –NH2 group.

(b) a compound containing two –NH2 groups.

(c) a compound in which hydrogens of NH3 have been replaced by two alkyl groups.

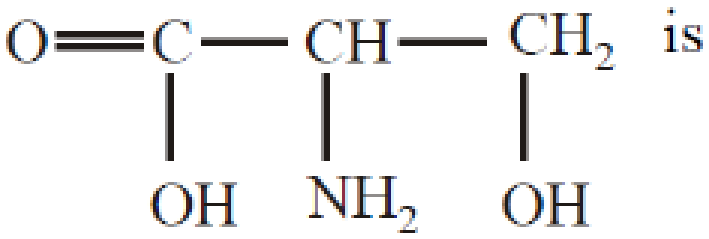
(d) a compound with an –NH2 group on carbon atom in number two position.

RNH_2	R_2NH	R_3N
Primary amine	Secondary amine	Tertiary amine

5. The number of primary amines of formula $C_4H_{11}N$ is : **(NCERT Page-389)**

(a) 1 (b) 3 (c) 4 (d) 2

6. The IUPAC name of the compound having formula, **(NCERT Page-390 & 391)**



is

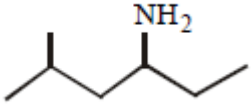
(a) 3-amino-hydroxy propine acid

(b) 2-amino-propan-3-oic acid

(c) amino hydroxy propanoic acid

(d) 2-amino-3-hydroxy propanoic acid

7. What is the IUPAC name of the following compound ? **NCERT Page-390 & 391)**



(a) 2-methyl-4-hexanamine

(b) 5-methyl-3-hexanamine

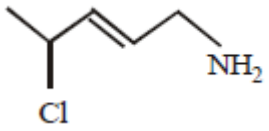
(c) 2-methyl-4-amino hexane

(d) 5-methyl-3-amino hexane

8. The IUPAC name of diethyl isopropyl amine is **(NCERT Page-390 & 391)**

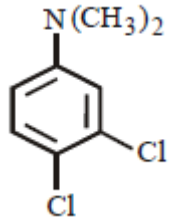
(a) N, N-diethylpropan-2-amine (b) N, N-diethylpropan-1-amine
(c) N, N-diethylisopropylamine (d) N, N-diethylaminopropane

9. IUPAC name of the following compound is **(NCERT Page-390 & 391)**



(a) 2-chloro pentanamine
(b) 4-chloro pentan-1-amine
(c) 4-chloro pent-2-en-1-amine
(d) 2-chloro pent-3-en-5-amine

10. Which of the following is the correct IUPAC name of the compound ?
(NCERT Page-390 & 391)



(a) 1, 2-dichloro-4-(N, N-dimethyl) aniline
(b) Dimethyl – (3, 4-dichlorophenyl) amine
(c) 3, 4-dichloro - N, N-dimethyl aniline
(d) N, N-dimethylamino - 3, 4-dichlorobenzene

Topic 2: Preparation of Amines

11. Which of the following reactions will not give a primary amine?**(NCERT Page-390 & 391)**

(a) $CH_3CONH_2 \xrightarrow{Br_2/KOH}$

(b) $CH_3CN \xrightarrow{LiAlH_4}$

(c) $CH_3NC \xrightarrow{LiAlH_4}$

(d) $CH_3CONH_2 \xrightarrow{LiAlH_4}$

12. Propionamide on Hoffmann degradation gives – **(NCERT Page-394)**
(a) methyl amine (b) ethyl amine
(c) propyl amine (d) ethyl cyanide

13. Gabriel's phthalimide synthesis is used for the preparation of**(NCERT Page-394)**
(a) Primary aromatic amines (b) Secondary amines
(c) Primary aliphatic amines (d) Tertiary amines

14. The reduction of nitro compounds is most preferred in the presence of
(NCERT Page-392)
(a) Pd/H_2 in ethanol (b) Sn + HCl
(c) finely divided Ni (d) iron scrap and HCl.

15. An alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes
(NCERT Page-392)
(a) electrophilic substitution reaction (b) nucleophilic substitution reaction.
(c) free radical mechanism. (d) nucleophilic addition reaction.

16. In the ammonolysis of alkyl halides the halogen atom is replaced by an amino($-NH_2$) group which of the following represent the correct order of reactivity of halides with amines.
(NCERT Page-393)
(a) RBr > RI > RCl (b) RI > RCl > RBr
(c) RI > RBr > RCl (d) RCl > RBr > RI

17. Which of the following will give primary amine only ?**(NCERT Page-392 & 394)**
(i) ammonia + propylchloride
(ii) potassium pthalimide + ethylchloride
(iii) potassium pthalimide + chlorobenzene
(a) (i) and (ii) (b) (i) and (iii)
(c) (ii) and (iii) (d) (i), (ii) and (iii)

18. A primary amine is formed by an amide on treatment with bromine and alkali. The primary amine has **(NCERT Page-394)**
(a) 1 carbon atom less than amide
(b) 1 carbon atom more than amide
(c) 1 hydrogen atom less than amide
(d) 1 hydrogen atom more than amide

19. **Assertion:** Aniline can not be prepared by Gabriel phthalamide reaction while phenyl methyl amine can.
Reason: Aniline is less basic than phenyl methyl aniline
(a) Assertion is true, Reason is true: Reason is a correct explanation for Assertion.
(b) Assertion is true, Reason is true: Reason is not a corret explanation for Assertion.
(c) Assertion is true, Reason is false.
(d) Assertion is false, Reason is true

Topic 3: Physical Properties

20. Amines have **(NCERT Page-395)**
(a) Garlic odour (b) Fishy odour
(c) Jasmine odour (d) Bitter almonds odour

21. Aniline is less soluble in water than ethyl amine due to **(NCERT Page-395)**
(a) resonance stablization of benzene ring
(b) resonance stabilization of anilium ion
(c) more hydrophobic nature of C6H5 group than C2H5 group
(d) more hydrophobic nature of C2H5 group than C6H5 group

22. Which of the following is not characteristic of amines? **(NCERT Page-395)**
(a) They smell like ammonia
(b) They are inflammable in air
(c) They show the property of hydrogen bonding
(d) They are amphoteric in nature

23. Arrange the following compounds in decreasing order of boiling point
(NCERT Page-396)
(a) $(CH_3)_3N < CH_3NHEt < PrNH_2 < PrOH$
(b) $(CH_3)_3N < PrNH_2 < PrOH < MeNHEt$
(c) $PrNH_2 < MeNHEt < Me_3N < PrOH$
(d) $Me_3N < MeNHEt < PrOH < PrNH_2$

24. **Assertion:** Secondary amines have more boiling point than tertiary amines having same mol. wt

Reason: Molecules of secondary amines held with one another by H-bonding.
(a) Assertion is true, Reason is true: Reason is a correct explanation for Assertion.
(b) Assertion is true, Reason is true: Reason is not a correct explanation for Assertion.
(c) Assertion is true, Reason is false.
(d) Assertion is false, Reason is true.

Topic 4: Chemical Reactions

25. Aliphatic amines are.....basic than NH3 but aromatic amines are.....basic than NH_3. **(NCERT Page-399)**

(a) more, less (b) less, more (c) both (a) and (b) (d) None of these

26. Substitution of one alkyl group by replacing hydrogen of primary amines **(NCERT Page-397)**

(a) increases the base strength (b) decreases the base strength
(c) remains the same (d) None of the above

27. High basicity of Me2NH relative to Me3N in aqueous solution is attributed to: **(NCERT Page-399)**

(a) effect of solvent (b) inductive effect of Me
(c) shape of Me2NH (d) shape of Me3N

28. The correct order of basicity of the following compounds **(NCERT Page-399)**

(a) B > A > C (b) A > B > C (c) C > A > B (d) C > B > A

29. Which of the following factors affect the basic strength of amine? **(NCERT Page-398 & 399)**

(i) Inductive effect (ii) Steric hinderance
(iii) Solvation effect (iv) Solubility in organic solvents.
(a) (i) and (iv) (b) (i), (ii) and (iii) (c) (ii) and (iii) (d) (ii) and (iv)

30. Which of the following statements about primary amines is **'False'** ? **(NCERT Page-399)**

(a) Alkyl amines are stronger bases than aryl amines
(b) Alkyl amines react with nitrous acid to produce alcohols
(c) Aryl amines react with nitrous acid to produce phenols
(d) Alkyl amines are stronger bases than ammonia

31. The compound obtained by heating a mixture of a primary amine and chloroform with ethanolic potassium hydroxide (KOH) Is **(NCERT Page-401)**

(a) an alkyl cyanide (b) a nitro compound
(c) an alkyl isocyanide (d) an amide

32.

$$R-NH_2 + \underset{\text{(excess)}}{CH_3COCl} \longrightarrow A$$

(NCERT Page-400)

The product (A) will be –

(a) $RNHCOCH_3$ (b) $RN(COCH_3)_2$
(c) $\overset{+}{R}N(COCH_3)_3Cl^-$ (d) $R-CONH_2$

33. In the reaction, **(NCERT Page-401)**

$$RNH_2 \xrightarrow{HNO_2} ROH + H_2O + A\uparrow ; \text{A is}$$

(a) NH_3 (b) N_2 (c) O_2 (d) CO_2

34. The amine that does not react with acetyl chloride is **(NCERT Page-400)**
(a) CH_3NH_2 (b) $(CH_3)_2NH$ (c) $(CH_3)_3N$ (d) None of these

35. In order to distinguish between C_2H_5–NH_2 and C_6H_5–NH_2, which of the following reagent is useful **(NCERT Page-401)**
(a) Hinsberg's reagent (b) HNO_2 (c) $CHCl_3$ + KOH (d) NaOH

36. Strong activating effect of –NH2 group is reduced by using**(NCERT Page-403)**
(a) CH_3COCl (b) CH_3Cl (c) CH_3ONa (d) CH_3–CHO

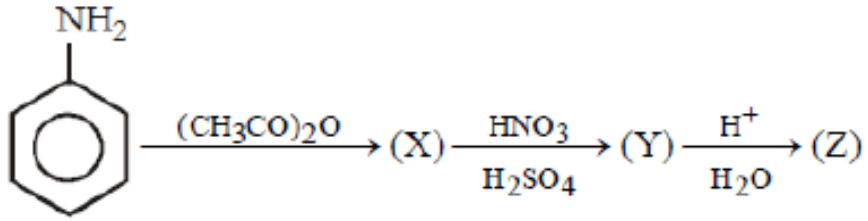
37. When bromination of aniline is carried out by protecting–NH2. The product is **(NCERT Page-402)**
(a) *o*-bromoaniline (b) 2, 4, 6 tribromoaniline
(c) *p*-bromoaniline (d) mixture of *o*-and *p*-bromoanilines

38. Hinsberg's method to separate amines is based on the use of **(NCERT Page-401)**
(a) benzene sulphonyl chloride (b) benzene sulphonic acid
(c) ethyl oxalate (d) acetyl chloride

39. Arrange the following in increasing order of their basic strength? **(NCERT Page-399)**
p–nitroaniline(1); *m*–nitroaniline (2); 2,4,6–trimethylaniline(3); 3–methylanline (4).
(a) 1, 3, 2, 4 (b) 2, 3, 4, 1 (c) 3, 1, 2, 4 (d) 1, 2, 4, 3

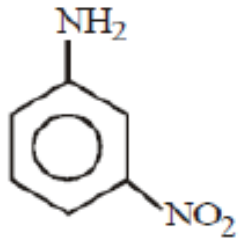
40. **Assertion :** Nitrating mixture used for carrying out nitration of benzene consists of conc. HNO_3 + conc. H_2SO_4.
Reason : In presence of H_2SO_4, HNO_3 acts as a base and produces NO_2+ ions.
(a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
(b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
(c) Assertion is correct, reason is incorrect
(d) Assertion is incorrect, reason is correct.

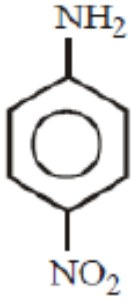
41.

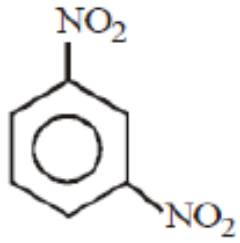


(NCERT Page-402)

Product Z of the reaction is

(a) 

(b) 

(c) 

(d) 

42. Correct order of increasing basic character is **(NCERT Page-399)**

(a) $NH_3 < PhNH_2 < Et_2NH < EtNH_2 < Et_3N$

(b) $PhNH_2 < NH_3 < Et_3N < Et_2NH$

(c) $PhNH_2 < NH_3 < Et_2NH < Et_3N$

(d) $Et_3N < PhNH_2 < Et_2NH < NH_3$

43. **Assertion:** After acylation of aniline, benzene nucleus becomes more reactive towards electrophile.

Reason: After acylation electron density inside benzene ring decreases.

(a) Assertion is true, Reason is true: Reason is a correct explanation for Assertion.

(b) Assertion is true, Reason is true: Reason is not a correct explanation for Assertion.

(c) Assertion is true, Reason is false.

(d) Assertion is false, Reason is true

Topic 5: Methods of Preparation of Diazonium Salts

44. Diazonium salt is obtained when aniline reacts with : **(NCERT Page:404)**

(a) cold NaOH (b) $NaNO_2$ and HCl (0–5°C)

(c) $SnCl_2$ at 10°C (d) N_2O at (0 – 5°C)

45. In the diazotization of arylamines with sodium nitrite and hydrochloric acid, an excess of hydrochloric acid is used primarily to **(NCERT Page:404)**

(a) supress the concentration of free aniline available for coupling

(b) supress hydrolysis of phenol

(c) ensure a stoichiometric amount of nitrous acid

(d) neutralise the base liberated

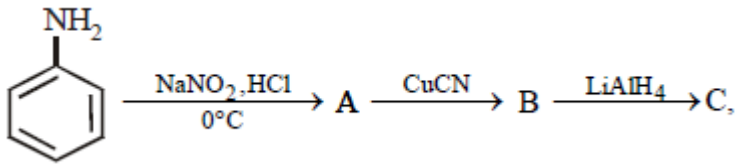
Topic 6: Properties of Diazonium Salts

46. Azo dye is prepared by the coupling of phenol and **(NCERT Page:406)**

(a) benzene diazonium chloride (b) *o*-nitroaniline

(c) benzoic acid (d) chlorobenzene

47. In the reaction sequence **(NCERT Page:405)**



the product 'C' is:

(a) benzonitrile (b) benzaldehyde

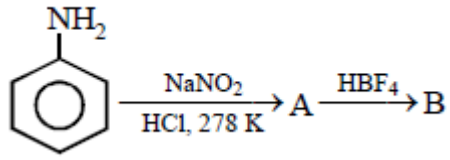
(c) benzoic acid (d) benzylamine

48. Which of the following reagents will convert *p*-methylbenzenediazonium chloride into *p*-cresol? **(NCERT Page:406)**

(a) Cu powder (b) H_2O

(c) H_3PO_2 (d) C_6H_5OH

49. In the chemical reactions, **(NCERT Page:406)**



the compounds 'A' and 'B' respectively are

(a) nitrobenzene and fluorobenzene

(b) phenol and benzene

(c) benzene diazonium chloride and fluorobenzene

(d) nitrobenzene and chlorobenzene

50. Match the columns

Column-I	**Column-II**
(A) $ArN_2^+Cl^- \longrightarrow ArOH$	(p) HBF_4 / $NaNO_2$
(B) $ArN2+Cl^- \longrightarrow ArNO_2$	(q) H_2O
(C) $ArN_2Cl^- \longrightarrow ArH$	(r) HBF_4
(D) $ArN_2+Cl^- \longrightarrow ArF$	(s) CH_3CH_2OH

(a) A – (q), B – (p), C – (s), D – (r)

(b) A – (s), B – (p), C – (q), D – (r)

(c) A – (q), B – (s), C – (p), D – (r)

(d) A – (q), B – (s), C – (r), D – (p)

51. Match the columns

Column-I	**Column-II**
(A) Benzene sulphonyl	(p) Zwitter ion chloride
(B) Sulphanilic acid	(q) Hinsberg reagent
(C) Alkyl diazonium salts	(r) Dyes
(D) Aryl diazonium salts	(s) Conversion to alcohols

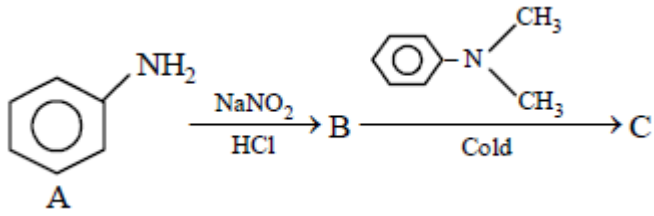
(a) A – (s), B – (q), C – (r), D – (p)

(b) A – (q), B – (p), C – (s), D – (r)

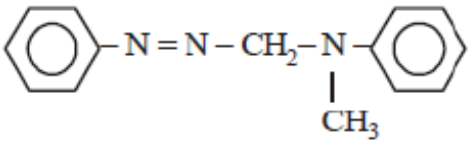
(c) A – (r), B – (s), C – (p), D – (q)

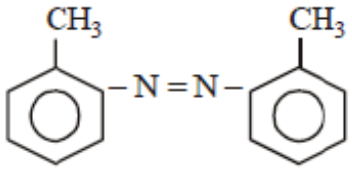
(d) A – (s), B – (p), C – (r), D – (q)

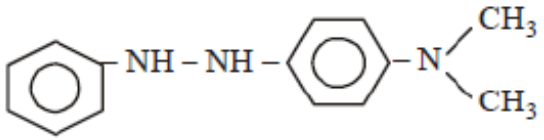
52. In a reaction of aniline-A coloured product C was obtained **(NCERT Page:406)**

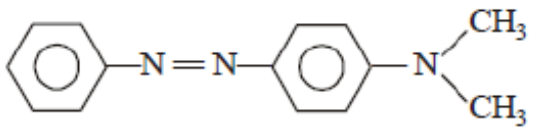


The structure of C would be :

(a) 

(b) 

(c) 

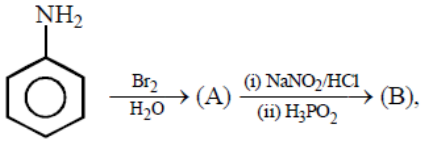
(d) 

TOPIC WISE PRACTICE QUESTIONS

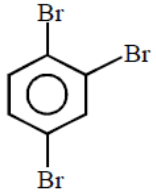
TOPIC 1: Amines and Amides

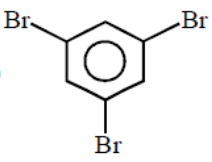
1. Which of the following arylamines will not form a diazonium salt on reaction with sodium nitrite in hydrochloric acid?

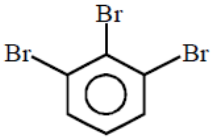
1) *m*-Ethylaniline
2) *p*-Aminoacetophenone
3) 4-Chloro-2-nitroaniline
4) N-Ethyl-2-methylaniline

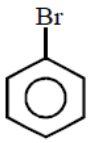
2. 

Product (B) in this reaction is:

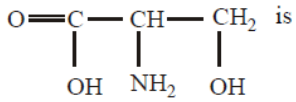
(a) 

(b) 

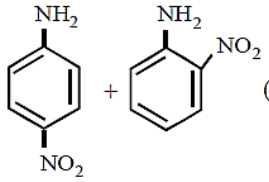
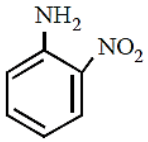
(c) 

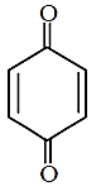
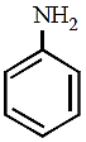
(d) 

3. The total number of electrons around the nitrogen atom in amines are
   1) 8 2) 7 3) 4 4) 3
4. The reagent that reacts with nitromethane to form methylhydroxylamine is
   1) Zn/HCl 2) Zn/NH_4Cl 3) Zn/NaOH 4) Sn/HCl
5. Conversion of benzene diazonium chloride to chlorobenzene is an example of which of the following reactions?
   1) Claisen 2) Friedel-craft 3) Sandmeyer 4) Wurtz
6. Read the following statements and choose the correct option.
   (i) Nitrogen atom in amines is sp^3-hybridised. (ii) The geometry of amines is pyramidal.
   (iii) The angle C–N–C or C–N–H is slightly more than 109.5°.
   1) (i), (ii) and (iii) 2) (i) and (ii) 3) (i) and (iii) 4) (ii) and (iii)
7. Secondary amines could be prepared by
   1) reduction of nitriles. 2) Hofmann bromamide reaction.
   3) reduction of amides. 4) reduction of isonitriles.
8. Which of the following statement is not correct?
   1) Methylamine is more basic than NH_3.
   2) Amines form hydrogen bonds.
   3) Ethylamine has higher boiling point than propane.
   4) Dimethylamine is less basic than methylamine.
9. The strongest base among the following is
   1) phenylmethanamine 2) N-methylmethanamine 3) ethanamine 4) methanamine
10. The IUPAC name of the compound having formula,



is
   1) 3-amino-hydroxy propine acid 2) 2-amino-propan-3-oic acid
   3) amino hydroxy propanoic acid 4) 2-amino-3-hydroxy propanoic acid
11. Which of the following reagents will convert *p*-methylbenzenediazonium chloride into *p*-cresol?
   1) Cu powder 2) H_2O 3) H_3PO_2 4) C_6H_5OH
12. Benzamide on reaction with $POCl_3$ gives
   1) aniline 2) chlorobenzene 3) benzylamine 4) benzonitrile
13. The general formula of quaternary ammonium compound is
   1) $R–NH_2$ 2) R_3N 3) $R_4N^+ X^-$ 4) NH_4X
14. Aniline is separated from a mixture by :
   1) fractional crystallisation 2) fractional distillation
   3) vacuum distillation 4) steam distillation
15. The number of primary amines of the formula $C_4H_{11}N$ is :
   1) 1 2) 3 3) 4 4) 2
16. The conversion of acetophenone to acetanilide is best accomplished by using :
   1) Beckmann rearrangement 2) Curtius rearrangement
   3) Lossen rearrangement 4) Hofmann rearrangement
17. Intermediates formed during reaction of $RCONH_2$ with Br_2 and KOH are
   1) RCONHBr and RNCO 2) RNHCOBr and RNCO
   3) RNHBr and RCONHBr 4) $RCONBr_2$
18. Aniline when treated with conc. HNO_3 gives

(a)  (b) 

(c)  (d) 

19. Gabriel's phthalimide synthesis is used for the preparation of
1) Primary aromatic amines 2) Secondary amines
3) Primary aliphatic amines 4) Tertiary amines

20. For alkylation of ammonia which of the following is not used?
1) CH_3–X 2) CH_3–CH_2–X 3) $(CH_3)_2CH$–X 4) $(CH_3)_3C$–X

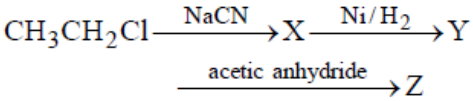
21. Treatment of ammonia with excess of ethyl iodide will yield
1) diethylamine 2) ethylamine 3) triethylamine 4) tetraethylammonium iodide

22. Which of the following gives primary amine on reduction?
1) $CH_3CH_2NO_2$ 2) $CH_3CH_2 - O - N = O$ 3) $C_6H_5N = NC_6H_5$ 4) CH_3CH_2NC

23. The reduction of nitro compounds is most preferred in the presence of
1) Pd/H_2 in ethanol 2) Sn + HCl 3) finely divided Ni 4) iron scrap and HCl.

24. Which is formed when $(CH_3)_4$ NOH is heated?
1) CH_3NH_2 2) $C_2H_5NH_2$ 3) $(CH_3)_3N$ 4) $(CH_2)_3N$

25. The correct order of increasing basicity in aqueous solution is
1) $NH_3 < C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2 < (C_2H_5)_3N$
2) $C_6H_5NH_2 < NH_3 < (C_2H_5)_3N < C_2H_5NH_2 < (C_2H_5)_2NH$
3) $C_6H_5NH_2 < NH_3 < C_2H_5NH_2\,(C_2H_5)_3N < (C_2H_5)_2NH$ 4) None of the above

26. 

Z in the above reacting sequence is
1) $CH_3CH_2CH_2NHCOCH_3$ 2) $CH_3CH_2CH_2NH_2$
3) $CH_3CH_2CH_2CONHCH_3$ 4) $CH_3CH_2CH_2CONHCOCH_3$

27. In the ammonolysis of alkyl halides the halogen atom is replaced by an amino($–NH_2$) group which of the following represent the correct order of reactivity of halides with amines.
1) RBr > RI > RCl 2) RI > RCl > RBr 3) RI > RBr > RCl 4) RCl > RBr > RI

28. A primary amine is formed by an amide on treatment with bromine and alkali. The primary amine has
1) 1 carbon atom less than amide 2) 1 carbon atom more than amide
3) 1 hydrogen atom less than amide 4) 1 hydrogen atom more than amide

29. Amines have
1) Garlic odour 2) Fishy odour 3) Jasmine odour 4) Bitter almonds odour

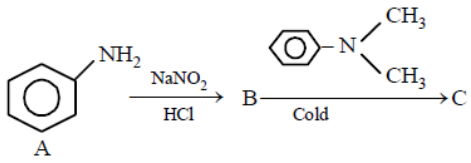
30. In the diazotisation of arylamines with sodium nitrite and hydrochloric acid, an excess of hydrochloric acid is used primarily to
1) supress the concentration of free aniline available for coupling.
2) supress hydrolysis of phenol.
3) ensure a stoichiometric amount of nitrous acid.

4) neutralise the base liberated.

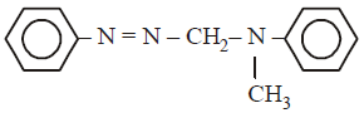
31. The indicator that is obtained by coupling the diazonium salt of sulphanilic acid with N, N-dimethylaniline is

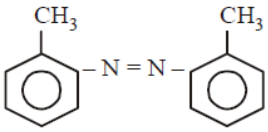
1) phenanthroline 2) methyl orange 3) methyl red 4) phenolphthalein

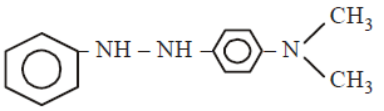
32. In a reaction of aniline a coloured product C was obtained.

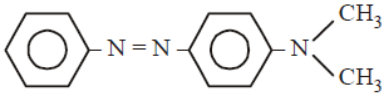


The structure of C would be :

(a) 

(b) 

(c) 

(d) 

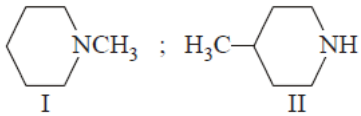
33. Aniline is less soluble in water than ethyl amine due to

1) resonance stablization of benzene ring 2) resonance stabilization of anilium ion

3) more hydrophobic nature of C_6H_5 group than C_2H_5 group

4) more hydrophobic nature of C_2H_5 group than C_6H_5group

34. Predict about the relative boiling point of the following two amines.



1) Boiling point of I > II. 2) Boiling point of II > I.

3) Both should have equal boiling points. 4) It can't be predicted.

35. Identify Z in the following sequence of reactions –

$$CH_3COONH_4 \xrightarrow{\Delta} X \xrightarrow{P_2O_5} Y \xrightarrow{H_2O/H} Z$$

(a) $CH_3-CH_2-CO-NH_2$ (b) CH_3-CN

(c) $(CH_3CO)_2O$ (d) CH_3-COOH

36. Which of the following is not characteristic of amines?

1) They smell like ammonia 2) They are inflammable in air

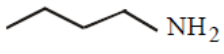
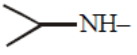
3) They show the property of hydrogen bonding 4) They are amphoteric in nature

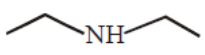
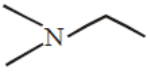
37. Substitution of one alkyl group by replacing hydrogen of primary amines

1) increases the base strength 2) decreases the base strength

3) remains the same 4) None of the above

38. Among the following isomeric $C_4H_{11}N$ amines, one having the lowest boiling point

(a)  (b) 

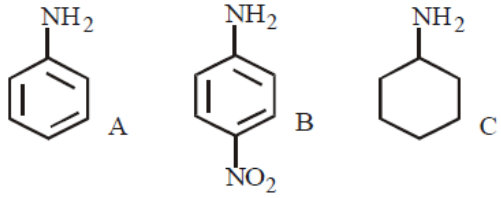
(c)  (d) 

39. The conjugate base of $(CH_3)_2NH^+_2$ is

1) $(CH_3)_2NH$ 2) $(CH_3)_2N^+$ 3) $(CH_3)_3N^+$ 4) $(CH_3)_2N^-$

40. High basicity of Me_2NH relative to Me_3N in aqueous solution is attributed to
1) effect of solvent 2) inductive effect of Me 3) shape of Me_2NH 4) shape of Me_3N

41. The correct order of basicity of the following compounds



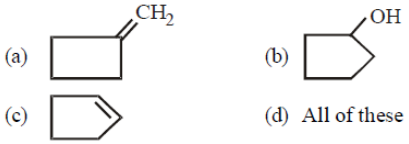
1) B > A > C 2) A > B > C 3) C > A > B 4) C > B > A

42. In the reaction,

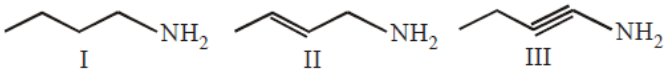
$$RNH_2 \xrightarrow{HNO_2} ROH + H_2O + A\uparrow ; \text{ A is}$$

(a) NH_3 (b) N_2 (c) O_2 (d) CO_2

43. The cyclobutyl methylamine with nitrous acid gives



44. The correct order of decreasing basic character of the three aliphatic primary amines is

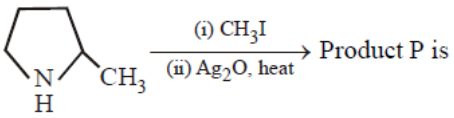


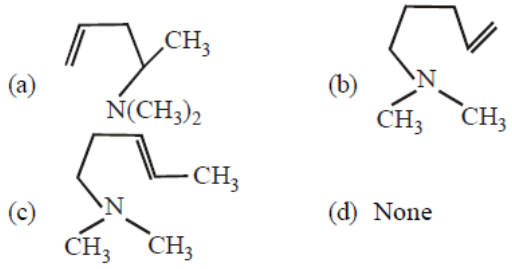
1) I > II > III 2) III > II > I 3) I > II ≈ III 4) I = II ≡ III

45. An organic amino compound reacts with aqueous nitrous acid at low temperature to produce an oily nitrosoamine. The compound is
1) CH_3NH_2 2) $CH_3CH_2NH_2$ 3) $CH_3CH_2NHCH_2CH_3$ 4) $(CH_3CH_2)_3N$

46. Strong activating effect of $-NH_2$ group is reduced by using
1) CH_3COCl 2) CH_3Cl 3) CH_3ONa 4) CH_3-CHO

47.





TOPIC 2: Cyanides and Isocyanides

48. Reaction of ethyl amine with alkaline chloroform leads to the formation of carbylamine reaction. This reaction involves the attack of an electrophile on ethyl amine, the electrophile is
1) H_3O^+ 2) H^+ 3) RNH_3^+ 4) : CCl_2

49. Ethyl isocyanide on hydrolysis in acidic medium generates
1) propanoic acid and ammonium salt. 2) ethanoic acid and ammonium salt.
3) methylamine and ethanoic acid. 4) ethylamine and methanoic acid.

50. Methyl cyanide is less basic than methylamine because
1) there is a triple bond between carbon and nitrogen atoms.
2) molecular weight is higher than methylamine.

3) the lone pair of electrons in nitriles belongs to *sp*-orbital and lone pair of electrons in amines belongs to sp^3 -orbital.
4) None of these.

51. In the reaction: $R-C\equiv N+4[H]\xrightarrow{X}RCH_2NH_2$ X can be:

1) $LiAlH_4$ 2) H_2SO_4 3)Ni 4) 2KBr

52. Hydrolysis of phenyl isocyanide forms:

1) Benzoic acid 2) Formic acid 3) Acetic acid 4) None of these

53. $C_6H_5C\equiv N$ and $C_6H_5N\overset{\rightarrow}{=}C$ exhibit which type of isomerism?

1) Position 2) Functional 3) Dextroisomerism 4) Position isomerism

54. Butanenitrile may be prepared by heating

1) propyl alcohol with KCN 2) butyl alcohol with KCN
3) butyl chloride with KCN 4) propyl chloride with KCN

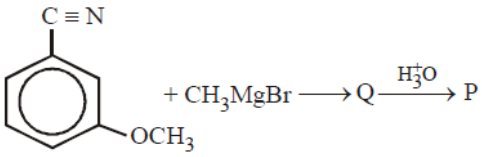
55. Consider the following sequence of reactions :

$$\text{Compound[A]}\xrightarrow{\text{Reduction}}\text{[B]}\xrightarrow{HNO_2}CH_3CH_2OH$$

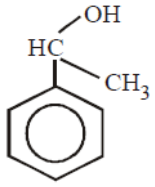
The compound [A] is

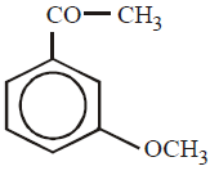
(a) CH_3CH_2CN (b) CH_3NO_2
(c) CH_3NC (d) CH_3CN

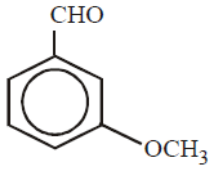
56.

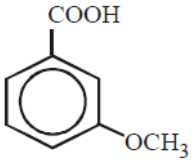


The product 'P' in the above reaction is

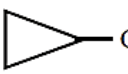
(a) 

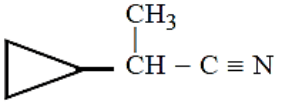
(b) 

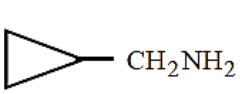
(c) 

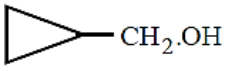
(d) 

57.

In the reaction  $CH_2CN\xrightarrow[NaNH_2,NH_3,-80°C]{CH_3Br}$ the products obtained are

(a) 

(b) 

(c) 

(d) None of these

TOPIC 3: Nitroalkanes and Alkyl Nitrites

58. A nitro alkane reacts with HONO to give insoluble product in alkali which turns blue on treatment with an alkali. The nitro alkane is

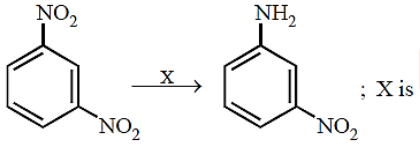
(a) $CH_3CH_2NO_2$ (b) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2NO_2$

(c) $(CH_3)_2CHNO_2$ (d) $(CH_3)_3CNO_2$

59. Acetanilide on nitration followed by alkaline hydrolysis mainly gives –

1) *o*-Nitroaniline 2) *p*-Nitroaniline 3) *m*-Nitroaniline 4) 2, 4, 6-Trinitroaniline

60. In the reaction :

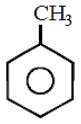


; X is

(a) SiC (b) H_2SO_4

(c) $KMnO_4$ (d) NH_4HS

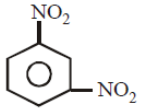
61. Which of the following will be easily nitrated?

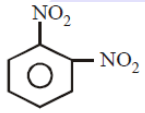
(a) 

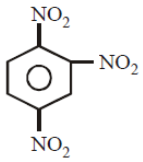
(b) 

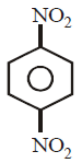
(c) CH_3NO_2 (d) $C_6H_5NO_2$

62. Nitrobenzene, on reaction with fuming nitric acid at 90°C, gives

(a) 

(b) 

(c) 

(d) 

63. In the series of reaction

$$C_6H_5NH_2 \xrightarrow[0-5^\circ C]{NaNO_2/HCl} X \xrightarrow[H_2O]{HNO_2} Y + N_2 + HCl,$$

X and Y are respectively

(a) $C_6H_5-N=N-C_6H_5, C_6H_5N_2^+Cl^-$

(b) $C_6H_5N_2^+Cl^-, C_6H_5-N=N-C_6H_5$

(c) $C_6H_5N_2^+Cl^-, C_6H_5NO_2$

(d) $C_6H_5NO_2, C_6H_6$

64. The consituent of the powerful explosive RDX is formed during the nitration of

1) toluene 2) phenol 3) glycerol 4) urotropine

65. Tautomerism will be exhibited by

1) $(CH_3)_3CNO$ 2) $(CH_3)_2NH$ 3) R_3CNO_2 4) RCH_2NO^2

66. Nitrobenzene on electrolytic reduction in strongly acidic medium gives

1) aniline 2) *p*-aminophenol 3) *m*-nitroaniline 4) nitrosobenzene

67. Hydrolysis of $CH_3CH_2NO_2$ with 85% H_2SO_4 gives

1) CH_3CH_2OH 2) C_2H_6 3) $CH_3CH=NOH$ 4) CH_3COOH

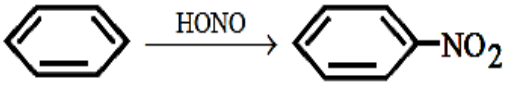
68. Primary nitro compounds react with nitrous acid to form nitrolic acids which dissolve in NaOH giving

1) yellow solution 2) blue solution 3) colourless solution 4) red solution

69. Which of the following reactions is not feasible?

(a) $ICH_2COOC_2H_5 + AgNO_2 \xrightarrow[\text{ether}]{0^\circ C} O_2NCH_2COOC_2H_5 + AgI$

(b) $(CH_3)_3CNH_2 \xrightarrow[\text{acetone + water}]{KMnO_4} (CH_3)_3C - NO_2$

(c) 

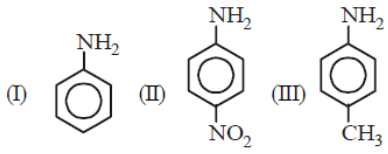
(d) All the above are feasible

70. Dynamite is a mixture of:
1) Nitroglycerine + Saw dust. 2) Nitroglycerine + HCl.
3) Hydrogen bomb + H_2SO_4. 4) Glycerine + H_2SO_4.

NEET PREVIOUS YEARS QUESTIONS

1. Nitration of aniline in strong acidic medium also gives *m*-nitroaniline because **[2018]**
1) Inspite of substituents nitro group always goes to only *m*-position.
2) In electrophilic substitution reactions, amino group is meta directive.
3) In acidic (strong) medium aniline is present as anilinium ion.
4) In absence of substituents, nitro group always goes to *m*-position.

2. The correct increasing order of basic strength for the following compounds is : **[2017]**



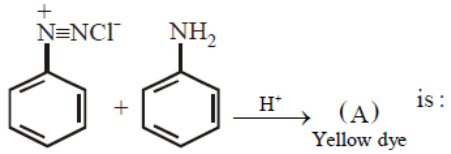
1) III < I < II 2) III < II < I 3) II < I < III 4) II < III < I

3. Which of the following reactions is appropriate for converting acetamide to methanamine? **[2017]**
1) Hoffmann bromamide reaction 2) Stephens reaction
3) Gabriels phthalimide synthesis 4) Carbylamine reaction

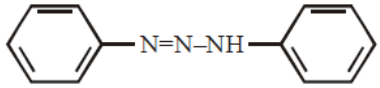
4. The correct statement regarding the basicity of arylamines is [2016]
1) Arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalized by interaction with the aromatic ring p electron system.
2) Arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalized by interaction with the aromatic ring p electron system.
3) Arylamines are generally more basic than alkylamines because of aryl group.
4) Arylamines are generally more basic than alkylamines, because the nitrongen atom in arylamines is sp-hybridized.

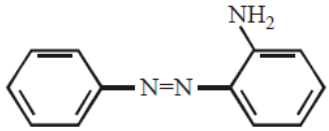
5. The electrolytic reduction of nitrobenzene in strongly acidic medium produces :- **[2015]**
1) Azoxybenzene 2) Azobenzene 3) Aniline 4) p-Aminophenol

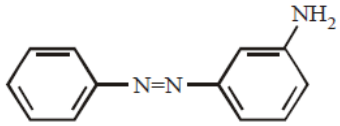
6. In the following reaction, the product **(A)** **[2014]**

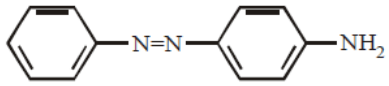


is :

(a) 

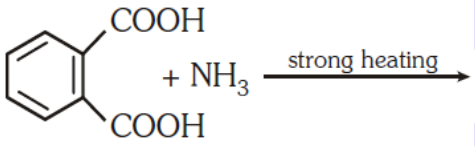
(b) 

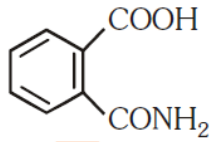
(c) 

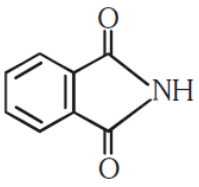
(d) 

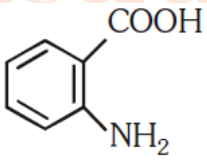
7. The correct order of the basic strength of methyl substituted amines in aqueous solution is :- **[2019]**
(1) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$ (2) $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$
(3) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$ (4) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$

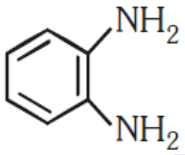
8. The major product of the following reaction is : **[2019]**



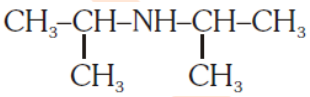
(1) 

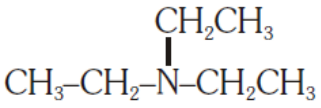
(2) 

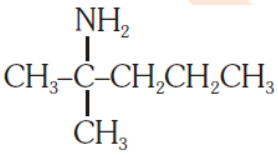
(3) 

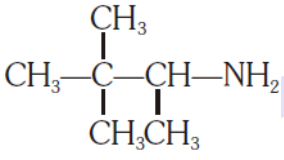
(4) 

9. The amine that reacts will Hinsberg's reagent to give an alkali insoluble product is :- **[2019-ODISSA]**

(1) 

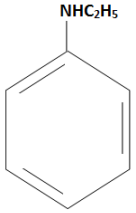
(2) 

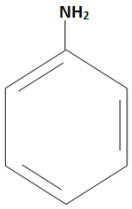
(3) 

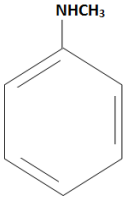
(4) 

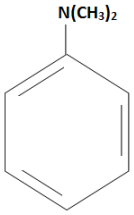
10. Reaction of propanamide with ethanolic sodium hydroxide and bromine will give **[2020-COVID]**
(1) Ethylamine (2) Methylamine (3) Propylamine (4) Aniline

11. Which of the following amine will give the carbylamine test? **[2020]**

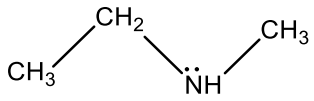
1) 

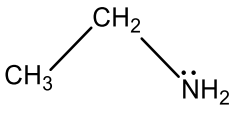
2) 

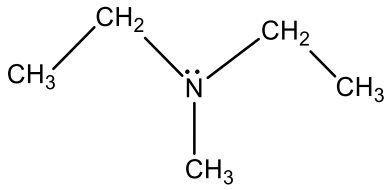
3) 

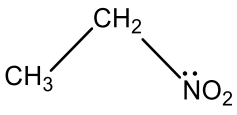
4) 

12. Identify the compound that will react with Hinsberg's reagent to give a solid which dissolves in alkali. **[NEET-2021]**

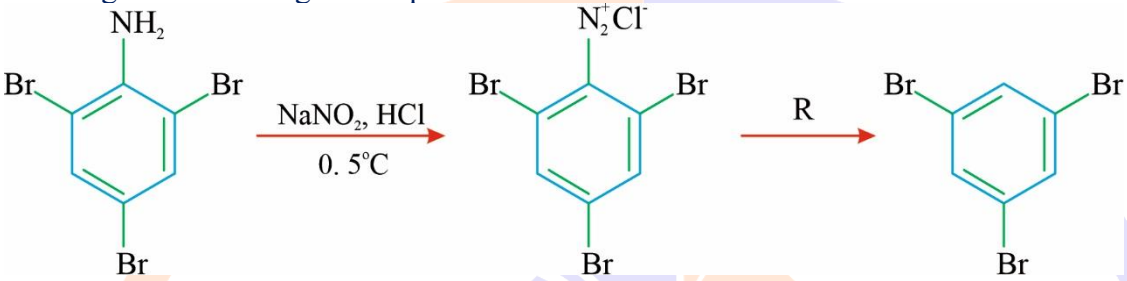
1) 

2) 

3) 

4) 

13. The reagent 'R' in the given sequence of chemical reaction is : **[NEET-2021]**



1) CH_3CH_2OH 2) HI 3) CuCN/KCN 4) H_2O

14. Given below are two statements: **[NEET-2022]**

Statement I: Primary aliphatic amines react with HNO_2 to give unstable diazonium salts.

Statement II: Primary aromatic amines react with HNO_2 to form diazonium salts which are stable even above 300 K.

In the light of the above statements, choose the most appropriate answer from the options given below:

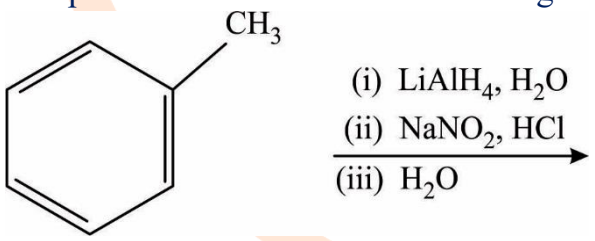
(1) Both Statement 1 and Statement II are correct

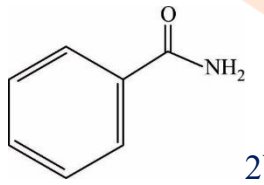
(2) Both Statement I and Statement II are incorrect.

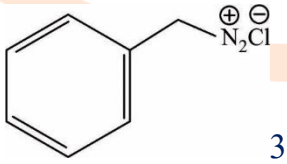
(3) Statement I is correct but Statement II is incorrect.

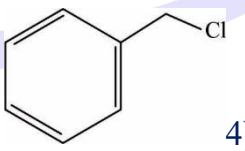
(4) Statement I is incorrect but Statement II is correct

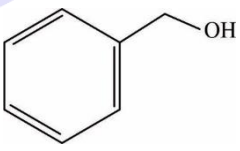
15. The product formed from the following reaction sequence is **[NEET-2022]**



1) 

2) 

3) 

4) 

NCERT LINE BY LINE QUESTIONS – ANSWERS

1 (d)	2.(a)	3. (b)	4. (c)	5. (c)	6. (d)	7. (b)	8. (a)	9. (c)	10. (c)
11. (c)	12. (b)	13. (c)	14. (d)	15. (b)	16. (c)	17. (a)	18. (a)	19. (b)	20. (b)
21. (c)	22. (d)	23. (a)	24. (a)	25. (a)	26. (a)	27. (a)	28. (c)	29. (b)	30. (c)
31. (c)	32. (a)	33. (b)	34. (c)	35. (b)	36. (a)	37. (d)	38. (a)	39. (d)	40. (a)
41. (b)	42. (b)	43. (d)	44. (b)	45. (a)	46. (a)	47. (d)	48. (b)	49. (c)	50. (a)
51. (b)	52. (d)								

TOPIC WISE PRACTICE QUESTIONS - ANSWERS

1) 4	2) 2	3) 1	4) 2	5) 3	6) 2	7) 4	8) 4	9) 2	10) 4
11) 2	12) 4	13) 3	14) 4	15) 3	16) 1	17) 1	18) 3	19) 3	20) 4
21) 4	22) 1	23) 4	24) 3	25) 2	26) 1	27) 3	28) 1	29) 2	30) 1
31) 2	32) 4	33) 3	34) 2	35) 4	36) 4	37) 1	38) 4	39) 1	40) 1
41) 3	42) 2	43) 4	44) 1	45) 3	46) 1	47) 2	48) 4	49) 4	50) 3
51) 1	52) 2	53) 2	54) 4	55) 4	56) 2	57) 1	58) 3	59) 2	60) 4
61) 1	62) 1	63) 3	64) 4	65) 4	66) 2	67) 4	68) 4	69) 3	70) 1

NEET PREVIOUS YEARS QUESTIONS-ANSWERS

1) 3	2) 3	3) 1	4) 1	5) 4	6) 4	7) 1	8) 2	9) 1	10) 1
11) 2	12) 2	13) 1	14) 3	15) 4					

NCERT LINE BY LINE QUESTIONS – SOLUTIONS

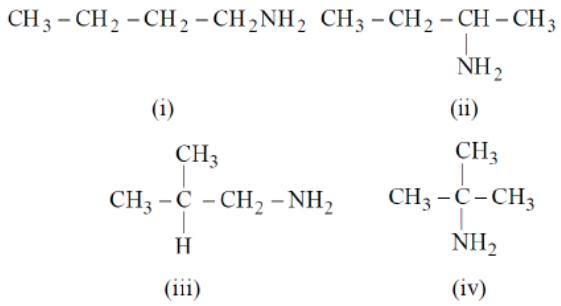
1 (d) Tertiary amino group

2.(a)

3. (b) The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. Due to the presence of unshared pair of electrons, the angle C–N–E, (where E is C or H) is less than 109.5°.

4. (c)

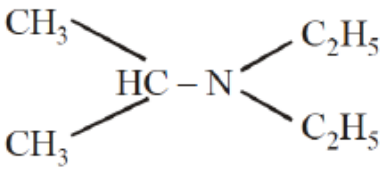
5. (c) 1° amines have –NH2 group in their structure, 4 primary amines are possible for $C_4H_{11}N$.



6. (d)

7. (b) The compound contains longest chain of 6C atoms and amino group. Hence it is an alkanamine.

8. (a)



N, N- Diethylpropan - 2-amine

9. (c)

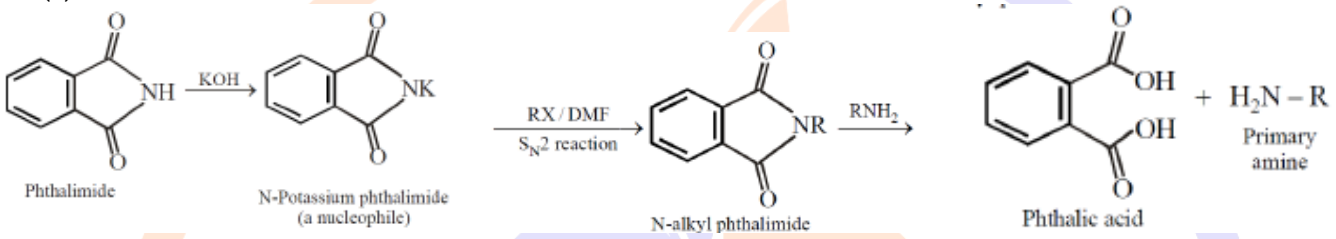
10. (c) The compound is derivative of aniline

11. (c) CH_3NC (methyl isocyanide) on reduction with LiAlH4 gives secondary amine

12. (b)

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + KOH \xrightarrow{\Delta} CH_3-CH_2-\ddot{N}H_2$$

13. (c)



14. (d) Reduction with iron scrap and hydrochloric acid is preferred because FeCl2 formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

15. (b)

16. (c)

17. (a)

18. (a) The reaction is Hoffmann bromamide reaction

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

$R-NH_2$ contains one carbon less than $R-\overset{\overset{O}{\|}}{C}-NH_2$

19. (b) Aromatic amines can not be prepared by Gabriel Phthalimide reaction.

20. (b) Amines possess fishy smell

21. (c)

22. (d) Amines are basic in nature

23. (a) B.P. ¼ Intermolecular forces of attractions like HBonding.

24. (a) B.P. number of H-Bonds

25. (a)

26. (a) Secondary amine is more basic than primary amine.

27. (a) Secondary amines are more basic than tertiary amines due to stabilisation of 2° amine by hydrogen bonding with solvent molecule.

28. (c) Aliphatic amines are more basic than aromatic amines.
Resonance decreases the basic character due to delocalisation of shared pair of electrons on nitrogen within benzene nucleus. Further electron withdrawing if (–NO2) decreases basicity.

29. (b)

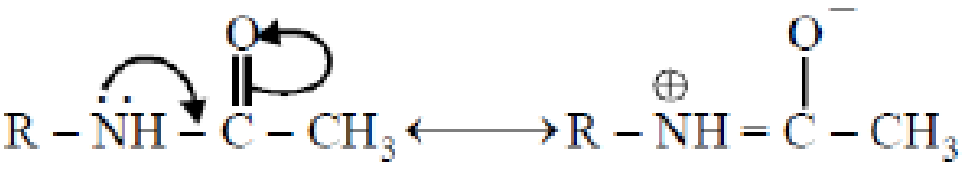
30. (c) Aryl amines produce diazonium salts on treatment with nitrous acid

31. (c) We know that

$$CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3CH_2NC + 3KCl + 3H_2O$$

In this reaction, bad smelling compound ethyl isocyanide (CH_3CH_2NC) is produced. This equation is known as **carbylamine reaction**

32. (a) Acylation occurs in one step only because lone pair of nitrogen is delocalized with acyl group



33. (b)

$$RNH_2 \xrightarrow{HNO_2} ROH + H_2O + N_2\uparrow$$
(A) (B) (C)

34. (c) The compounds containing active H-atoms (H atoms attached to N, O or S) react with CH_3COCl to form acetyl derivatives.

35. (b)

36. (a)

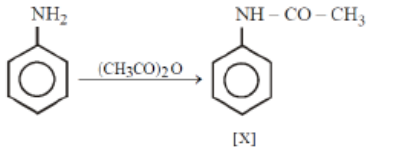
37. (d)

38. (a) Hinsberg's method is based on the use of benzene sulphonyl chloride.

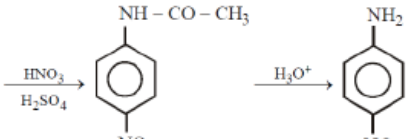
39. (d) In case of substituted aniline, electron releasing groups like –OCH\, $-CH_3$ increase basic strength whereas electron withdrawing groups like $-NO_2$, $-SO_3H$, –COOH,–X decrease it.

40. (a)
$$HNO_3 + 2H_2SO_4 \rightleftharpoons 2HSO_4^- + NO_2^+ + H_3O^+$$

41. (b)



[X]

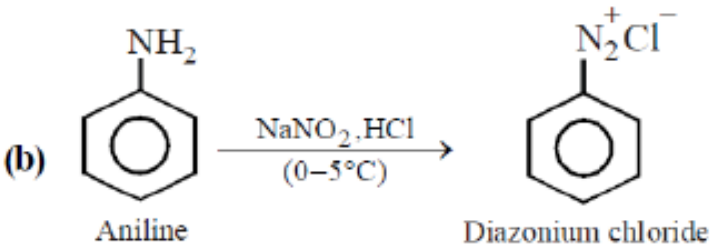


[Y] [Z]

42. (b)

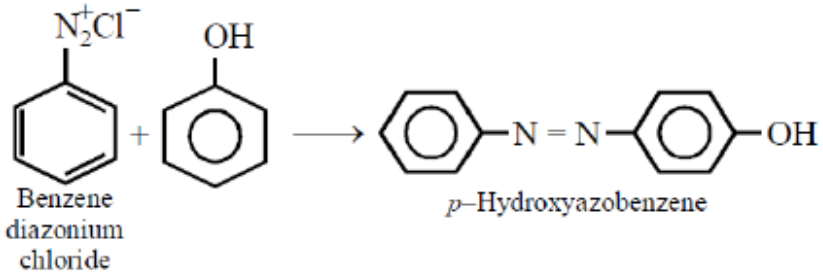
43. (d) Benzene ring becomes less reactive towards electrophile because + R effect of NH2 is greater than -NH-$COCH_3$

44. (b)



45. (a)

46. (a) Azo dye is prepared by diazo coupling reaction of phenol with diazonium salt.

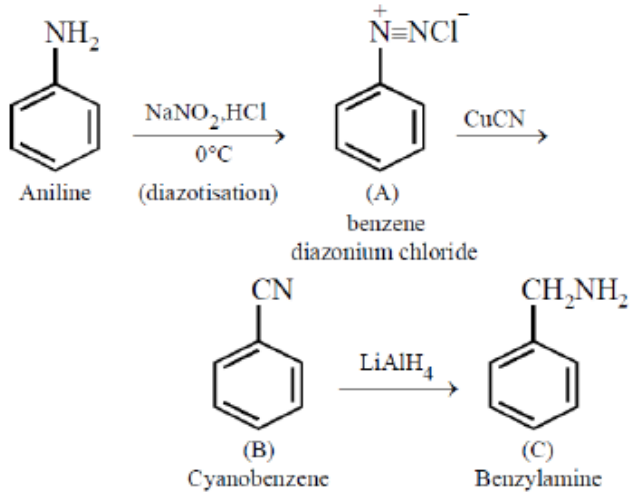


Benzene diazonium chloride

p–Hydroxyazobenzene

(–N=N–) group is called azo – group.

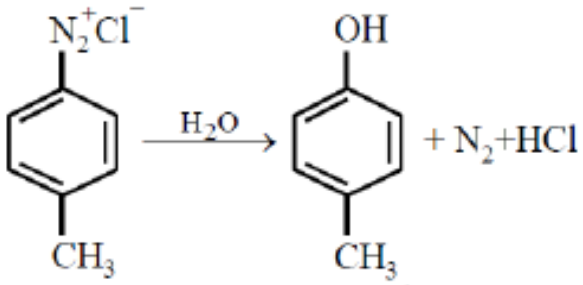
47. (d)



Aniline (diazotisation) (A) benzene diazonium chloride

(B) Cyanobenzene (C) Benzylamine

48. (b)



p-Cresol

49. (c) Primary aromatic amines react with nitrous acid to yield arene diazonium salts.

$$ArNH_2 + NaNO_2 + 2HX \xrightarrow{\text{cold}}$$

1° Aromatic amine

$$Ar{-}N{=}N^+X^- + NaX + 2H_2O$$

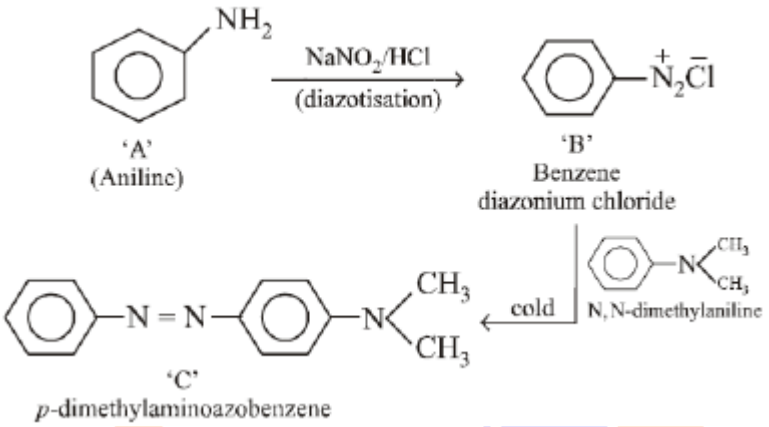
Arene diazonium salt

The diazonium group can be replaced by fluorine by treating the diazonium salt with fluoroboric acid (HBF_4). The precipitated diazonium fluoroborate is isolated, dried and heated until decomposition occurs to yield the aryl fluoride. This reaction is known as **Balz-Schiemann reaction.**

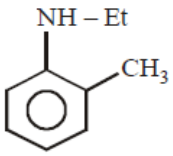
$$Ar{-}N_2^+X^- \xrightarrow{HBF_4} Ar{-}N_2^+BF_4^-\downarrow \xrightarrow{\text{heat}}$$

$$Ar{-}F + BF_3 + N_2$$

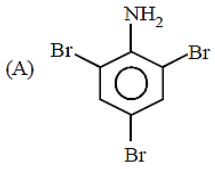
50. (a)
51. (b)
52. (d) The reaction can be completed as follows:

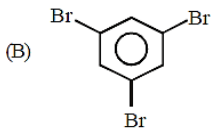


TOPIC WISE PRACTICE QUESTIONS - SOLUTIONS



1. 4) 2° amine will not form diazonium salt.
2. 2)





3. 1)
4. 2)
5. 3)

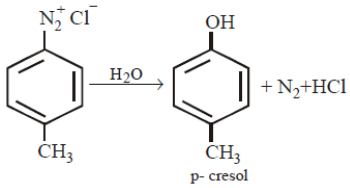
$$\underset{\text{Benzene diazoniumchloride}}{C_6H_5N_2Cl} \xrightarrow[\text{or Cu+HCl}]{CuCl/HCl} \underset{\text{Chloro benzene}}{C_6H_5Cl} + N_2$$

The above reaction is known as Sandmeyer's reaction.

6. (2) The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. Due to the presence of unshared pair of electrons, the angle C–N–E, (where E is C or H) is less than 109.5°.
7. 4)

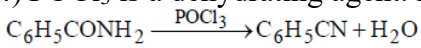
$$\underset{\text{alkyl isocyanide}}{R-N\equiv C} \xrightarrow{4[H]} \underset{\text{secondary amine}}{RNH-CH_3}$$

8. 4) 2° amines are more basic than 1° amines due to the +I effect of alkyl groups attached to 2° amines $H_3CNHCH_3 > CH_3NH_2$
9. (2) N-methyl methanamine $(CH_3)_2NH$ is a secondary amine whereas all other are examples of primary amine. Secondary amines are more basic than either primary or tertiary amines because their conjugate acids possess the best combination of alkyl and hydrogen substituents to permit stabilization both by electron release from alkyl group and by solvation due to hydrogen bonding.
10. 4)
11. 2)

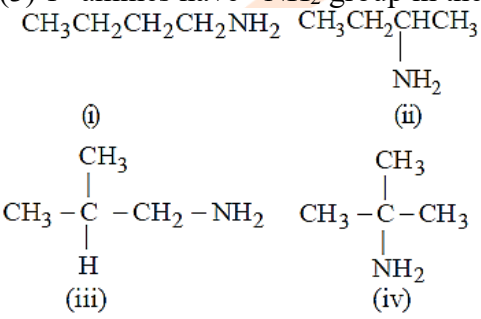


p- cresol

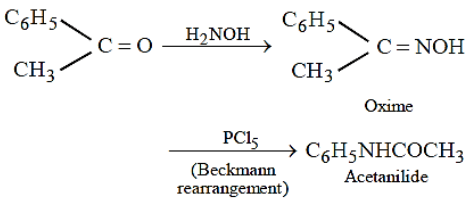
12. 4) $POCl_3$ is a dehydrating agent. Hence



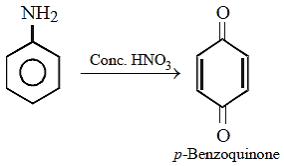
13. 3)
14. (4) Aniline is separated from mixture by steam distillation because it is volatile at the temperature of steam and is immiscible with water.
15. (3) 1° amines have $–NH_2$ group in their structure; 4 primary amines are possible for $C_4H_{11}N$.



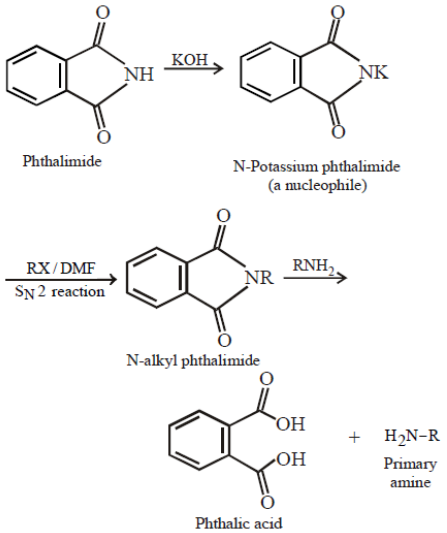
16. 1)



17. 1)
18. 3)



19. 3)



20. 4)
21. 4)

22. 1)

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

24. 3)

$$(CH_3)_4N^+OH^- \xrightarrow{heat} (CH_3)_3N + CH_3OH$$

25. 2)

26. 1)

$$CH_3CH_2Cl \xrightarrow{NaCN} \underset{X}{CH_3CH_2CN} \xrightarrow{Ni/H_2}$$

$$\underset{Y}{CH_3CH_2CH_2NH_2} \xrightarrow{(CH_3CO)_2O} \underset{Z}{CH_3CH_2CH_2NHCOCH_3}$$

27. 3)

28. 1) The reaction is Hoffmann bromamide reaction

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

$$R-NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

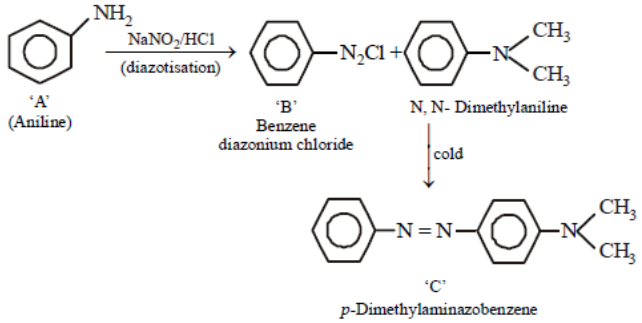
$R-NH_2$ contains one carbon less than $R-\overset{\overset{O}{\|}}{C}-NH_2$

29. (2) Amines possess fishy smell.

30. (1) Excess of HCl is used to convert free aniline to aniline hydrochloride otherwise free aniline would undergo coupling reaction with benzenediazonium chloride.

31. (2)

32. (4) The reaction can be completed as follows:



33. 3)

34. 2) In II, intermolecular H-bonding between similar molecules is possible, while this is not so in I.

35. 4)

$$CH_3COONH_4 \xrightarrow{\Delta} \underset{(X)}{CH_3CONH_2}$$

$$\xrightarrow{\Delta/P_2O_5} \underset{(Y)}{CH_3CN} \xrightarrow{H_3O^+} \underset{(Z)}{CH_3COOH}$$

36. (4) Amines are basic in nature

37. (1) Secondary amine is more basic than primary amine.

38. (4)

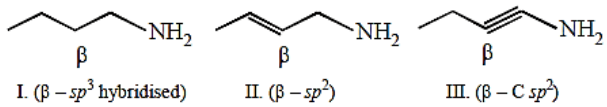
39. (1)

40. (1) Secondary amines are more basic than tertiary amines due to stabilisation of 2° amine by hydrogen bonding with solvent molecule.

41. (3) Aliphatic amines are more basic than aromatic amines. Resonance decreases the basic character due to delocalisation of shared pair of electrons on nitrogen within benzene nucleus. Further electron withdrawing if ($-NO_2$) decreases basicity.

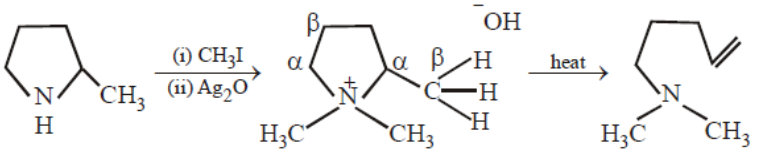
$$RNH_2 \xrightarrow{HNO_2} ROH + H_2O + N_2\uparrow$$
(A) (B) (C)

42. 2)
43. 4)
44. 1) Note the point of difference in the given compounds which here lies at b-carbon. In I, II, III, the β-carbon atoms are sp^3, sp^2 and sp hybridised respectively which in turn cause the difference in their s character. We know that more is the s character of an atom, greater will be its electron-withdrawing nature. Thus sp (50% s character) hybridised carbon is most electron withdrawing, while sp^3 (25% s character) is least electron-withdrawing. Further, we know that presence of an electron-withdrawing group decreases basicity of an amine. Thus



I. (β – sp^3 hybridised) II. (β – sp^2) III. (β – C sp^2)

45. 3) Since the organic amino compound on reaction with nitrous acid at low temperature produces an oily nitrosoamine so the organic amino compound is a secondary aliphatic amine. ***Note :*** This reaction is used as a test for aliphatic amines since no other class of amines liberates N_2 gas on treatment with HNO_2.
46. 1)
47. 2)



48. 4)

$$HCCl_3 \xrightarrow{OH^-} :\bar{C}Cl_3 \xrightarrow{-Cl^-} :CCl_2$$
Dichlorocarbene
(a neutral electron deficient species)

49. 4) Ethyl isocyanide on hydrolysis form primary amines.

$$CH_3CH_2N\equiv C + H_2O \xrightarrow{H^+} CH_3CH_2NH_2 + HCOOH$$

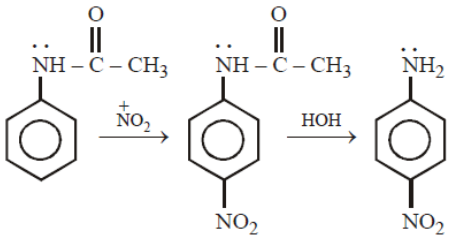
50. 3)

$$CH_3 - C \equiv \ddot{N}: \qquad CH_3 - \ddot{N}H_2$$
sp sp^3

51. (1) Among the given reagents, only $LiAlH_4$ is the reducing agent.
52. (2) Hydrolysis of phenyl isocyanide forms formic acid.
53. (2)
54. (4)
55. 4)

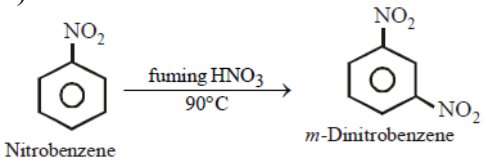
$$CH_3CN \xrightarrow{\text{Reduction}} CH_3 - CH_2 - NH_2 \xrightarrow{HONO} CH_3CH_2OH$$
(A) (B)

56. 2)
57. 1) Nitriles having a -hydrogen atom form alkyl derivatives with RBr in presence of $NaNH_2$ / NH_3 .
58. 3)
59. 2)



60. 4) The reaction involves the conversion of one NO_2 to NH_2 group (reduction) which occurs in presence of NH_4HS.
61. (1) Of the given compounds toluene which contains an electron donating group in the ring will be nitrated easily.

62. 1)



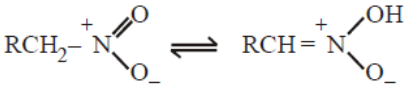
63. 3)

$$C_6H_5NH_2 \xrightarrow[0°C-5°C]{NaNO_2/HCl} \underset{(X)}{C_6H_5N_2^+Cl^-} \xrightarrow[H_2O]{HNO_2} C_6H_5NO_2 + N_2 + HCl$$

(Y)

64. 4)

65. 4) Nitro compounds having α-hydrogen show tautomerism



66. 2)

67. 4) 1° Nitroalkanes on hydrolysis with boiling 85% H_2SO_4 give acids.

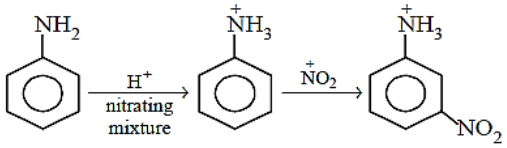
68. 4)

69. 3)

70. 1) Dynamite is a mixture of nitroglycerine and saw dust.

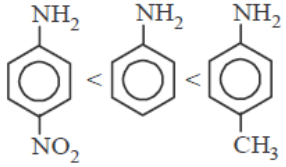
NEET PREVIOUS YEARS QUESTIONS-EXPLANATIONS

1. 3)



2. 3) $-NO_2$ group has strong – R effect and $-CH_3$ shows + R effect.

$\therefore$ order of basic strength is

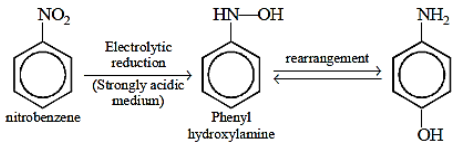


3. 1)

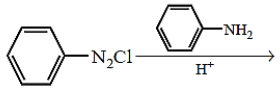
$$CH_3-\underset{\text{acetamide}}{\overset{O}{\overset{\|}{C}}}-NH_2 + Br_2 + 4NaOH \xrightarrow{\Delta} \underset{\text{methanamine}}{CH_3-NH_2} + 2NaBr + Na_2CO_3 + 3H_2O$$

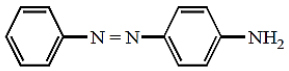
4. (1) Arylamines are generally less basic than alkylamines due to following factors
(1) Due to resonance in aromatic amines.
(2) Lower stability of anilinium ion

5. 4)



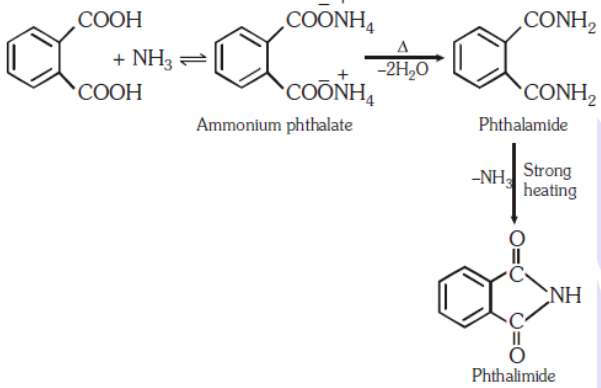
6. 4)



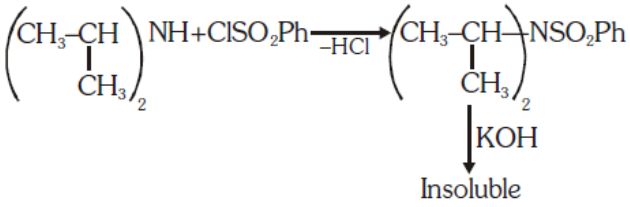


7. 1)The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows :
$(C_2H_5)_2$ NH > $(C_2H_5)_3N$ > $C_2H_5NH_2$ >NH_3
$(CH3)_2NH$ > CH_3NH_2 > $(CH_3)_3N$ > NH_3

8. 2)

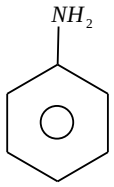


9. 1)



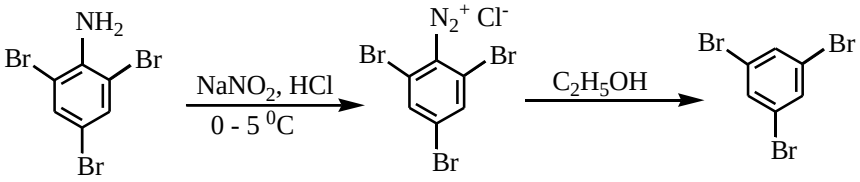
10. 1)

11. 2) primary amines will give carbylamine test



12. 2) Primary amines with benzene sulphonyl chloride form sulphonamides. The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to presence of strong electron withdrawing sulphonyl group. Hence it is soluble in alkali.

13. 1)



14. Statement – I is correct, statement – II is wrong as diazonium salts are stable at ice coral conditions

15.