UNIT 9: CO-ORDINATION COMPOUNDS

The compounds which contain dative bonds between metal atom and surrounding species is called co-ordination compounds .

The branch of inorganic chemistry which deals with hte study of preparation properties of coordination compound is called co-ordination chemistry.

$K_4[Fe(CN)_6]$, $[CuNH_3)_4]SO_4$

POINTS TO REMEMBER:

1. **Coordination compounds**

Coordination compounds are compounds in which a central metal atom or ion is linked to a number of ions or neutral molecules by coordinate bonds or which contain complex ions. Examples- $K_4[Fe(CN)_6]$; $[Cu(NH_3)_4]SO_4$; $Ni(CO)_4$

2.**ThemainpostulatesofWerner'stheoryofcoordinationcompounds**

i) In coordination compounds metals show two types of linkages or valencies- Primary and Secondary.

ii) The primary valencies are ionisable and are satisfied by negative ions.

iii) The secondary valencies are non- ionisable and are satisfied by neutral molecules or negative ions. The secondary valence is equal to the C.N and is fixed for a metal.

iv) The ions or groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination nos.

3.Difference between a double salt and a complex

Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However, double salts such as carnallite, $KCl.MgCl_2.6H_2O$, Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, potash alum, $KAl(SO_4)_2.12H_2O$, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as $[Fe(CN)^6]^{4-}$ of $K4[Fe(CN)_6]$, do not dissociate into Fe^{2+} and CN^- ions.

IMPOTANT TERMINOLOGY

(i) Coordination entity: It constitutes the central metal ion or atom bonded to a fixed number of ions or molecules represented within a square bracket.

(ii) Central atom/ ion: In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion.

iii) **Ligands**: The neutral or negative ions bound to the central metal or

ion in the coordination entity. These donate a pair/s of electrons to the central metal atom /ion. Ligands may be classified as-

a) **Monodentate/Unidentate**: Ligands bound to the central metal atom/ion through a single donor atom. Ex- Cl^- ; H_2O ; NH_3 ; NO_2^-.

b) **Didentate**: Ligates through two donor atoms. Ex- $C_2O_4^{\ 2-}$ (ox); $H_2NCH_2CH_2NH_2$(en)

c) **Polydentate**: which ligates through two or more donor atoms present in a single ligand. Ex- $(EDTA)^{4-}$

d) **Chelating ligands**: Di- or polydentate ligands that uses two or more donor atoms to bind to a single metal ion to form ring- like complexes. (Ox); (edta)

e) **Ambidentate ligand**: A ligand that can ligate through two different atoms, one at a time. Ex-NO_2^- ; SCN^-

v) **Coordination number**: The no. of ligand donor atoms to which the metal is directly bonded through sigma bonds only. It is commonly 4 or 6.

vi) **Counter ions**: The ionisable groups written outside the square bracket. Ex- K+ in $K_4[Fe(CN)_6]$ OR $3Cl^-$ in $[Co(NH_3)_6]Cl_3$

vii) **Coordination Polyhedron**: The spatial arrangement of the ligand atoms which are directly attached to the central metal atom/ion. They are commonly Octahedral, Square-planar or Tetrahedral

Oxidation number: The charge that the central atom would carry if all the ligands are removed along with their pairs of electrons shared with the central atom. It is represented in parenthesis.

viii) **Homoleptic complexes**: Complexes in which a metal is bonded to only one kind of donor groups. Ex- $[Co(NH_3)_6]^{3+}$

ix) **Heteroleptic complexes**: Complexes in which a metal is bonded to more than one kind of donor groups. Ex- $[Co(NH_3)_4 Cl_2]^+$

5. NAMING OF MONONUCLEAR COORDINATION COMPOUNDS

The principle of additive nomenclature is followed while naming the coordination compounds. The following rules are used-

i The cation is named first in both positively and negatively charged coordination entities.

ii The ligands are named in an alphabetical order before the name of the central atom/ion

iii The name of the anionic ligands end in –o, those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO. these are placed within enclosing marks .

iv When the prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, bis, tris , tetrakis are used, the ligand to which they refer being placed in parenthesis.

v Oxidation state of the metal in cation, anion, or neutral coordination entity is indicated by roman numeral in parenthesis.

vi If the complex ion is a cation , the metal is same as the element.

vii The neutral complex molecule is named similar to that of the complex cation.

6.NAMES OF SOME COMMON LIGANDS

NEGATIVE LIGANDS		CHARGE	NEUTRAL LIGANDS		CHARGE
CN-	Cyano	-1	NH_3	Ammine	0
Cl-	Chlorido	-1	H_2O	Aqua/aquo	0
Br-	Bromido	-1	NO	Nitrosyl	0
F-	Fluoride	-1	CO	Carbonyl	0
SO_4^{2-}	Sulphato	-2	PH_3	Phosphine	0
$C_2O_4^{2-}$	Oxalato	-4	CH_2-NH_2 CH_2NH_2	(1,2-Ethane diamine)	0
NH_2^-	Amido	-1	POSITIVE LIGANDS		
NH^{2-}	Imido	-2	NH_2-$NH3^+$	Hydrazinium	+1
ONO^-	Nitrito-O	-1	NO^+	Nitrosonium	+1
NO_2^-	Nitro	-1	NO_2^+	Nitronium	+1
NO_3^-	Nitrato	-1			
SCN^-	Thiocyanato	-1			
NCS^-	Isothiocyanato	-1			
$CH_2(NH_2)COO^-$	Glycinato	-1			
-OH	Hydroxo	-1			

7. ISOMERISM IN COORDINATION COMPOUNDS

Two or more substances having the same molecular formula but different spatial arrangements are called isomers and the phenomenon is called isomerism. Coordination compounds show two main types of isomerism-

A) Structural Isomerism B) Stereoisomerism

STRUCTURAL ISOMERISM:- It arises due to the difference in structures of coordination compounds. It is further subdivided into the following types-

1) **Ionisation isomerism :** This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionization isomers $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.

2) **Hydrate or solvate isomerism**: This form of isomerism is known as ‗hydrate isomerism' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

3) **Linkage Isomerism**: Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS^-, which may bind through the nitrogen to give M–NCS or through sulphur to give M–SCN.

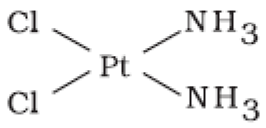
4) **Coordination isomerism:** It arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex .
Example $[Co(NH_3)_6][Cr(CN)_6]$ & $[Cr(NH_3)_6][Co(CN)_6]$

STEREOISOMERISM: Stereo isomers have the same chemical formula and chemical bonds but they have different spatial arrangement. They are of two kinds

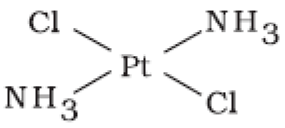
A. Geometrical isomerism

B. Optical isomerism

GEOMETRICAL ISOMERISM- This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6. In a square planar complex of formula $[MX_2L_2]$ (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer [MABXL]-Where A,B,X,L are unidentates Two cis- and one trans- isomers are possible.



cis



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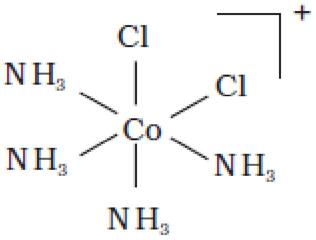

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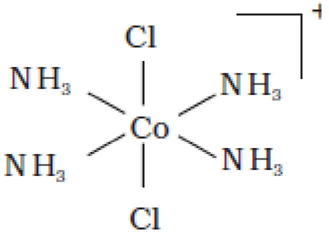
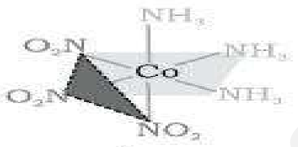
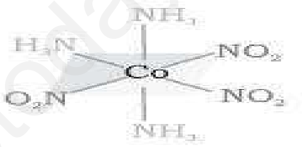


trans

Another type of geometrical isomerism occurs in octahedral coordination entities of the type [Ma_3b_3] like [$Co(NH_3)_3(NO_2)_3$]. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer.

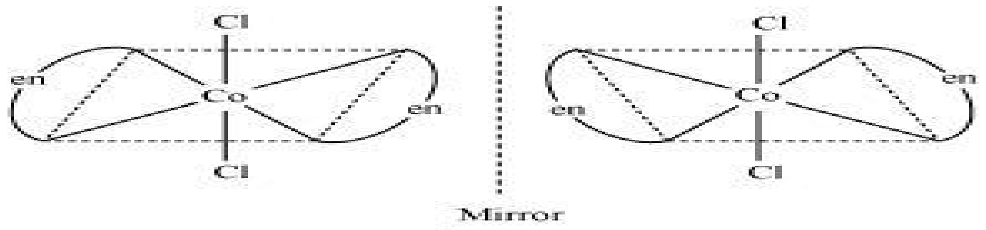


fac–

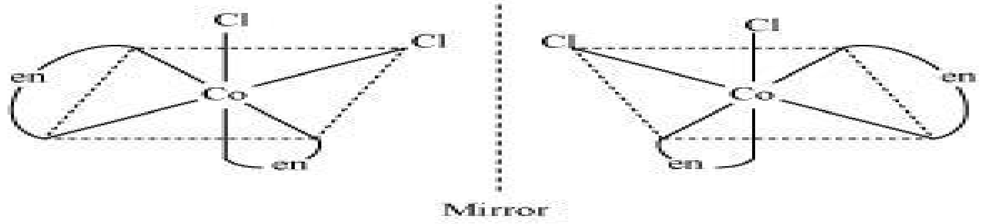


mer–

b) **OPTICAL ISOMERISM:** Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral. The two forms are called dextro (d) and laevo (l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, l to the left). Optical isomerism is common in octahedral complexes involving didentate ligands. In a coordination entity of the type [$CoCl_2(en)_2$]$^{2+}$, only the cis-isomer shows optical activity



Trans $[CoCl_2(en)_2]^+$ isomer-optically inactive
(Superimposable mirror images)



Cis $[CoCl_2(en)_2]^+$ isomer-optically active
(Non-superimposable mirror images)

TYPES OF HYBRIDISATION

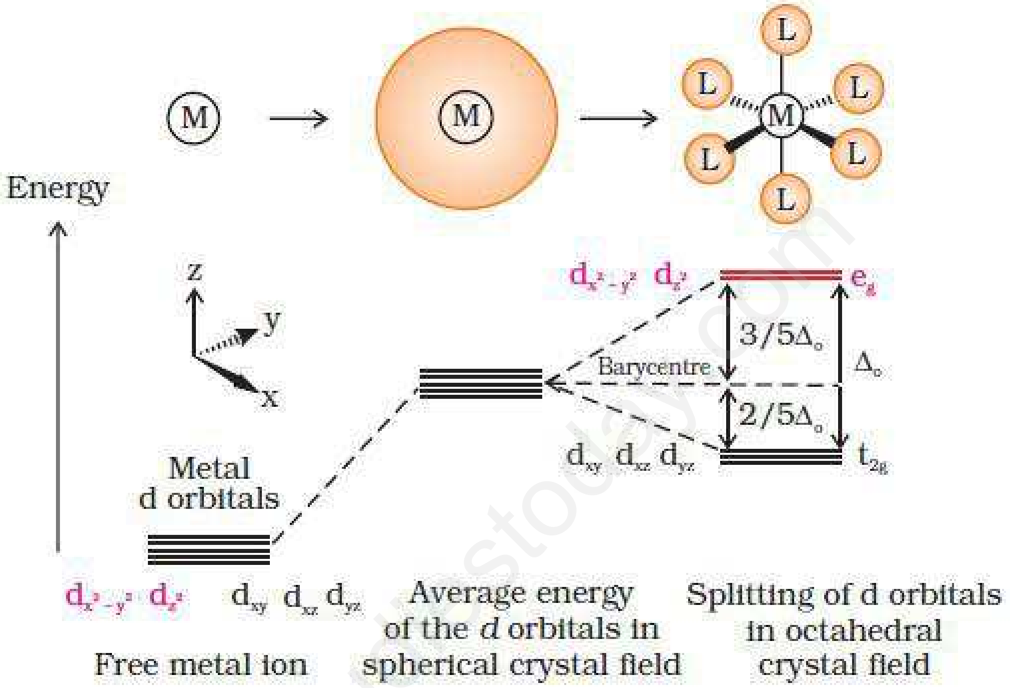
Coordination number	Type of hybridisation	Acquired geometry
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

8.CRYSTAL FIELD THEORY:

1. The metal-ligand bond is ionic arising purely from electrostatic interactions between the metal ion and the ligand.
2. Ligands are treated as point charges or dipoles in case of anions and neutral molecules.
3. In an isolated gaseous metal atom or ion the five d-orbitals are degenerate.
4. Degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal /ion.
5. In a complex the negative field becomes asymmetrical and results in splitting of the

d-orbitals.

A) **CRYSTAL FIELD SPLLITING IN OCTAHEDRAL COORDINATION ENTITIES**



| *d orbital splitting in an octahedral crystal field* |

1. For d^4 ions, two possible patterns of electron distribution arise:
(i) If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the

configuration $t^3{}_{2g}\, e^1{}_g$. Ligands for which $\Delta_o < P$ are known as weak

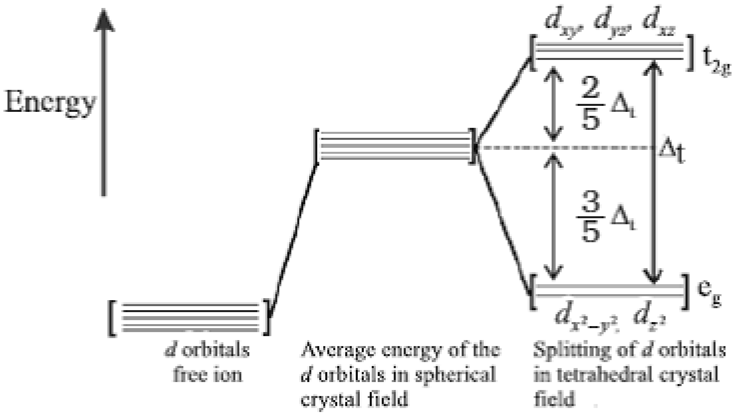
field ligands and form high spin complexes.

(ii) If $\Delta o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t^4{}_{2g}\, e^0{}_g$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.

B) **CRYSTAL FIELD SPLLITING IN TETRAHEDRAL COORDINATION ENTITIES**

1. The four surrounding ligands approach the central metal atom/ion along the planes between the axes.
2. The t_{2g} orbitals are raised in energy (2/5) $_t$.
3. The two e_g orbitals are lowered in energy (3/5) $_t$
4. The splitting is smaller as compared to octahedral field splitting, $_t$=(4/9) $_{0.}$

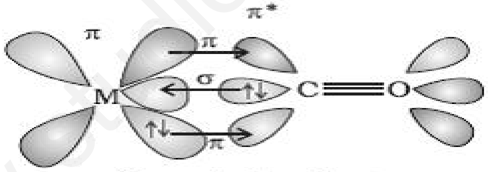
5. Pairing of electrons is rare and thus complexes have generally high spin configurations.



BONDING IN METAL CARBONYLS

The metal-carbon bond in metal carbonyls possess both σ and π character. The M–C σ bond

is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M–C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π^* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal .



Synergic bonding

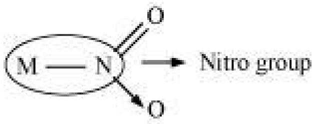
SOLVED QUESTIONS

1 MARK QUESTIONS

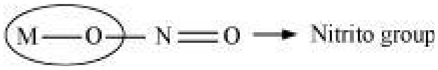
1. What are ambidentate ligands? Give two examples for each.

ANS. Ambidentate ligands are ligands that can attach themselves to the central metal atom through two different atoms. For example:

(a)

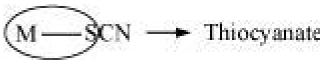


(The donor atom is N)

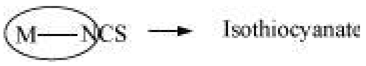


(The donor atom is oxygen)

(b)



(The donor atom is S)



(The donor atom is N)

Q2. Using IUPAC norms write the formula for the following: Tetrahydroxozincate(II)
ANS. $[Zn(OH)_4]^{2-}$

Q3. Using IUPAC norms write the formula for the following: Hexaamminecobalt(III) sulphate
ANS. $[Co(NH_3)_6]_2\ (SO_4)_3$

Q4. Using IUPAC norms write the formula for the following: Pentaamminenitrito-O-cobalt(III)
ANS. $[Co(ONO)\ (NH_3)_5]^{2+}$

Q5. Using IUPAC norms write the systematic name of the following: [Co(NH3)6]Cl3

ANS. Hexaamminecobalt(III) chloride

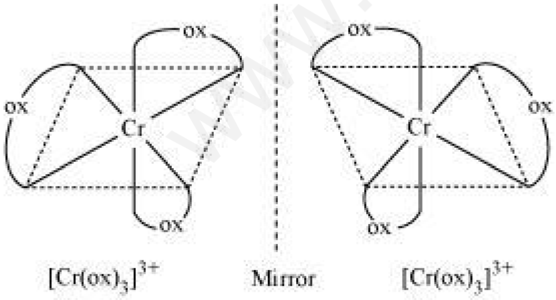
Q6. Using IUPAC norms write the systematic name of the following: [Pt(NH3)2Cl(NH2CH3)]Cl

ANS. Diamminechlorido(methylamine) platinum(II) chloride

Q7. Using IUPAC norms write the systematic name of the following: $[Co(en)_3]^{3+}$

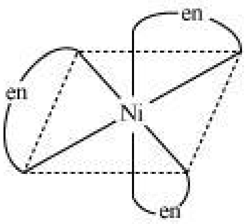
ANS. Tris(ethane-1, 2-diammine) cobalt(III) ion

Q8. Draw the structures of optical isomers of: $c[Cr(C_2O_4)_3]^{3-}$



ANS . $[Cr(ox)_3]^{3+}$ (dextro) $[Cr(ox)_3]^{3+}$ (Laevo)

Q9. What is meant by the chelate effect? Give an example.
ANS. When a ligand attaches to the metal ion in a manner that forms a ring, then the metal-ligand association is found to be more stable.



2 / 3 MARK QUESTIONS

Q1. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

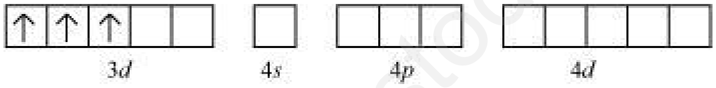
ANS. A spectrochemical series is the arrangement of common ligands in the increasing order of their crystal-field splitting energy (CFSE) values.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3 < F^- < OH^- < C_2O_4^{2-} \sim H_2O < NCS^- \sim H^- < CN^- < NH_3 < en \sim SO_3^{2-} < NO_2^- < phen < CO$

Q2. $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?

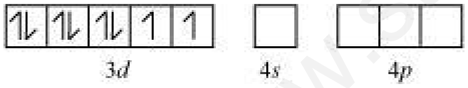
ANS. Cr is in the +3 oxidation state i.e., d^3 configuration. Also, NH_3 is a weak field ligand that does not cause the pairing of the electrons in the 3d orbital.

Cr^{3+} :

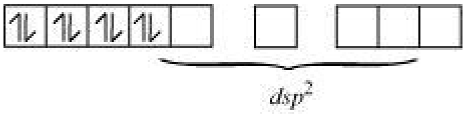


Therefore, it undergoes d^2sp^3 hybridization and the electrons in the 3d orbitals remain unpaired. Hence, it is paramagnetic in nature.
In $[Ni(CN)_4]^{2-}$, Ni exists in the +2 oxidation state i.e., d^8 configuration.

Ni^{2+}:



CN^- is a strong field ligand. It causes the pairing of the 3d orbital electrons. Then, Ni^{2+} undergoes dsp^2 hybridization.



Q3. A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

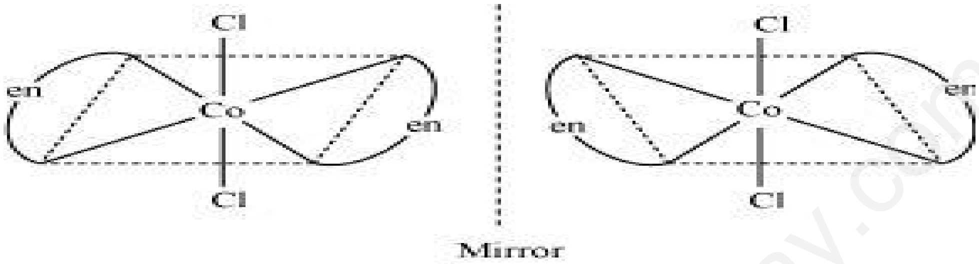
ANS. In $[Ni(H_2O)_6]^{2+}$, $H_2\ddot{O}$ is a weak field ligand. Therefore, there are unpaired electrons in Ni^{2+}. In this complex, the d electrons from the lower energy level can be excited to the higher energy level i.e., the possibility of d−d transition is present. Hence, $Ni(H_2O)_6]^{2+}$ is coloured.

In $[Ni(CN)_4]^{2-}$, the electrons are all paired as CN^- is a strong field ligand. Therefore, d-d transition is not possible in $[Ni(CN)_4]^{2-}$. Hence, it is colourless. As there are no unpaired electrons, it is diamagnetic.

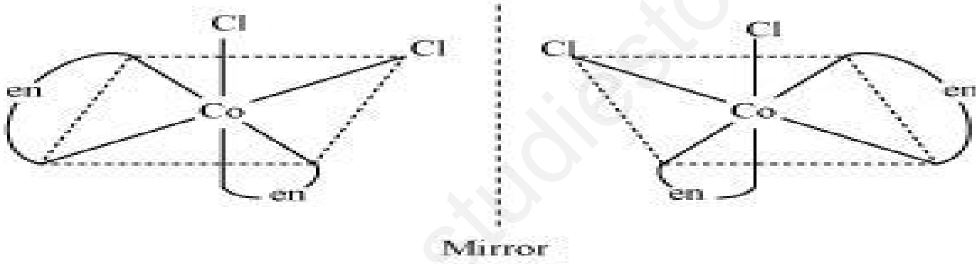
Q2. Draw all the isomers (geometrical and optical) of:

(i) $[CoCl_2(en)_2]^+$
(ii) $[Co(NH_3)Cl(en)_2]^{2+}$
(iii) $[Co(NH_3)_2Cl_2(en)]^+$

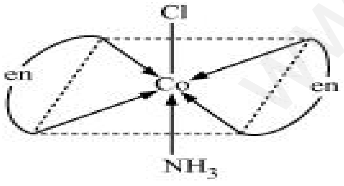
<u>**ANS.**</u> **(i)** $[CoCl_2(en)_2]^+$



Trans $[CoCl_2(en)_2]^+$ isomer-optically inactive
(Superimposable mirror images)



Cis $[CoCl_2(en)_2]^+$ isomer-optically active
(Non-superimposable mirror images)



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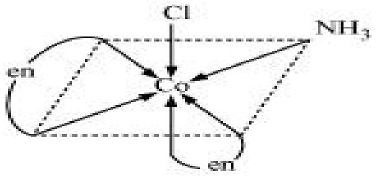
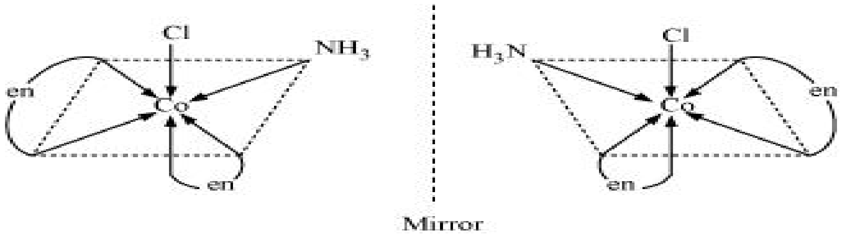


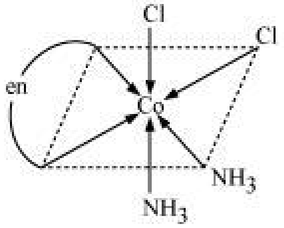
Cis

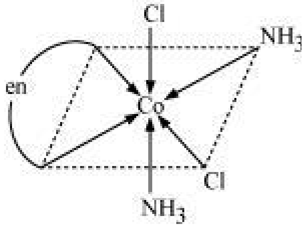


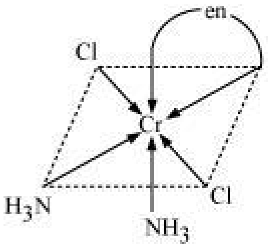
In total, three isomers are possible.

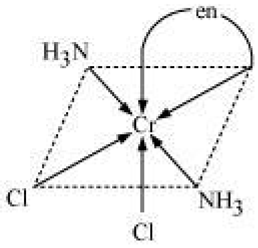
Trans-isomers are optically inactive.

Cis-isomers are optically active.





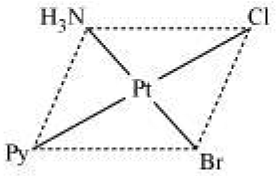


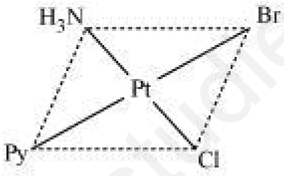


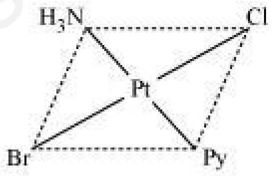
(iii) $[Co(NH_3)_2Cl_2(en)]^+$

Q3. Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?

<u>**ANS.**</u> $[Pt(NH_3)(Br)(Cl)(py)$







From the above isomers, none will exhibit optical isomers. Tetrahedral complexes rarely show optical isomerization. They do so only in the presence of unsymmetrical chelating agents.

Q4. What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

<u>**ANS.**</u> The stability of a complex in a solution refers to the degree of association between the two species involved in a state of equilibrium. Stability can be expressed quantitatively in terms of stability constant or formation constant.

$$M + 3L \longleftrightarrow ML_3$$

$$\text{Stability constant, } \beta = \frac{[ML_3]}{[M]\,[L]^3}$$

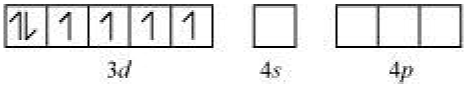
For this reaction, the greater the value of the stability constant, the greater is the proportion of ML_3 in the solution.

5 MARKS QUESTIONS

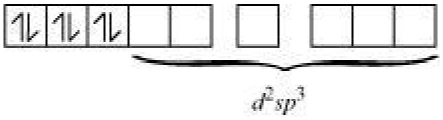
Q1. (a) Discuss the nature of bonding in the following coordination entities on the basisof valence bond theory:

(i) $[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$ (iii) $[Co(C_2O_4)3]^{3-}$ (iv) $[CoF_6]^{3-}$

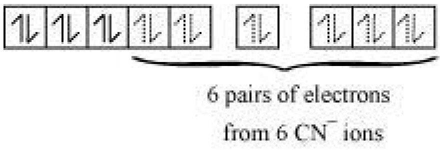
ANS. (i) $[Fe(CN)_6]^{4-}$In the above coordination complex, iron exists in the +II oxidation state.Fe^{2+} : Electronic configuration is $3d^6$ Orbitals of Fe^{2+} ion:



As CN^- is a strong field ligand, it causes the pairing of the unpaired 3d electrons.Since there are six ligands around the central metal ion, the most feasible hybridization is d^2sp^3. d^2sp^3 hybridized orbitals of Fe^{2+} are:



6 electron pairs from CN^- ions occupy the six hybrid d^2sp^3orbitals.Then,



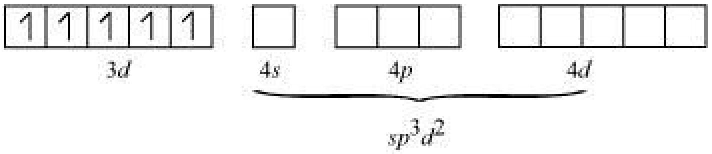
Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons).

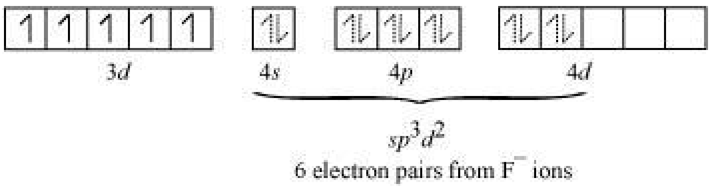
(ii) $[FeF_6]^{3-}$

In this complex, the oxidation state of Fe is +3.

Orbitals of Fe^{+3} ion:

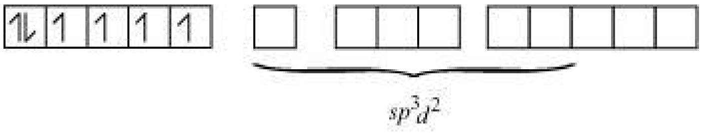
There are 6 F^- ions. Thus, it will undergo d^2sp^3 or sp^3d^2 hybridization. As F^- is a weak field ligand, it does not cause the pairing of the electrons in the 3d orbital. Hence, the most feasible hybridization is sp^3d^2.sp^3d^2 hybridized orbitals of Fe are:



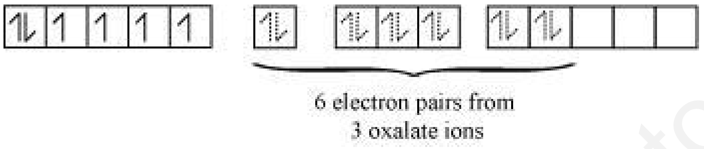


Hence, the geometry of the complex is found to be octahedral.

(iii) $[Co(C_2O_4)_3]^{3-}$
Cobalt exists in the +3 oxidation state in the given complex.Orbitals of Co^{3+} ion:Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the 3d orbital electrons. As there are 6 ligands, hybridization has to be either sp^3d^2 or d^2sp^3 hybridization.sp^3d^2 hybridization of Co^{3+}:



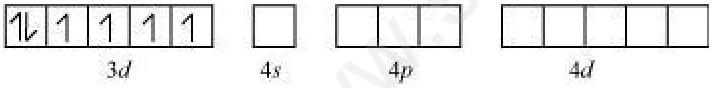
The 6 electron pairs from the 3 oxalate ions (oxalate anion is a bidentate ligand) occupy these sp^3d^2 orbitals.



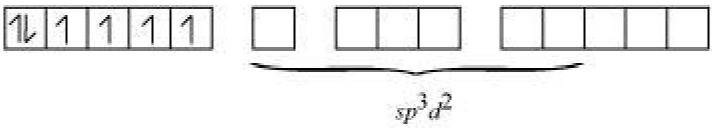
Hence, the geometry of the complex is found to be octahedral.

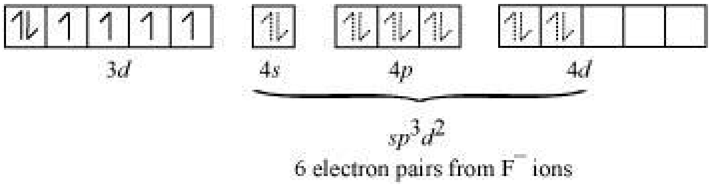
(iv) $[CoF_6]^{3-}$Cobalt exists in the +3 oxidation state.

Orbitals of Co^{3+} ion:



Again, fluoride ion is a weak field ligand. It cannot cause the pairing of the 3d electrons. As a result, the Co^{3+} ion will undergo sp^3d^2 hybridization.sp^3d^2 hybridized orbitals of Co^{3+} ion are:





Hence, the geometry of the complex is octahedral and paramagnetic.

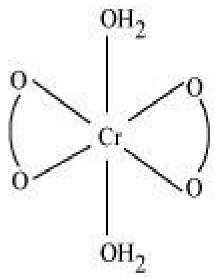
Q3. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:

(i) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$ (ii) $[Co(NH_3)_5Cl]Cl_2$ **ANS.** **(i)** Potassium diaquadioxalatochromate (III) trihydrate.

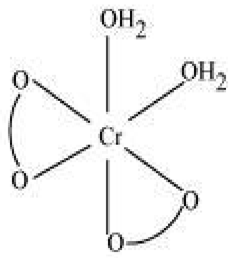
Oxidation state of chromium = 3 Electronic configuration: $3d^3$: t_{2g}^3

Coordination number = 6 Shape: octahedral

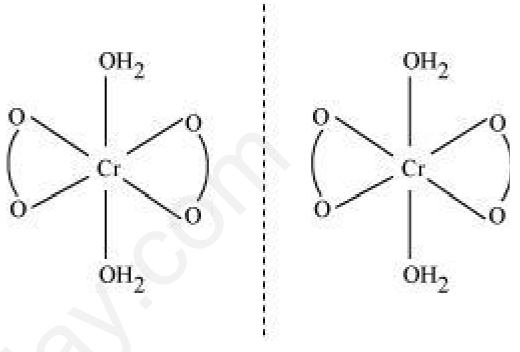
Stereochemistry:



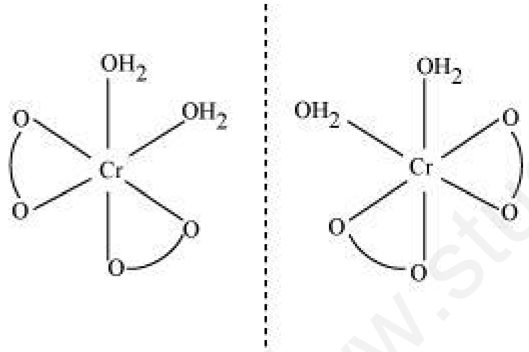
Trans



Cis



Trans is optically inactive



Cis is optically active

Magnetic moment, μ $= \sqrt{n(n+2)}$

$$= \sqrt{3(3+2)}$$

$$= \sqrt{15}$$

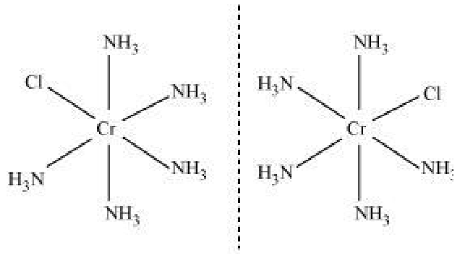
~ 4BM

(ii) $[Co(NH_3)_5Cl]Cl_2$

IUPAC name: Pentaamminechloridocobalt(III) chloride
Oxidation state of Co = +3
Coordination number = 6
Shape: octahedral.

Electronic configuration: d^6: t_{2g}^6.

Stereochemistry:



2 isomers

Magnetic Moment = 0

LEVEL 1

1.Why do tetrahedral complex not show geometrical isomerism?

2. Why does the colour changes on heating $[Ti(H_2O)_6]^{3+}$.

3. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

4. What happens when potassium ferrocyanide solution is added to a ferric salt solution?

LEVEL 2

5. A coordination compound has a formula ($CoCl_3$. $4NH_3$). It does not liberate NH_3but precipitates chloride ion as AgCl. Give the IUPAC name of the complex and write its structural formula.

6. Write the correct formula for the following co-ordination compounds. $CrCl_3$. $6H_2O$ (Violet, with 3 Chloride ions/ Unit formula) $CrCl_3$. $6H_2O$ (Light green colour with 2 Chloride ions/ unit formula)

7. Give the electronic configuration of the d-orbitals of Ti in $[Ti(H_2O)_6]^{3+}$ ion in anoctahedral crystal field.

8. Co(II) is stable in aqueous solution but in the presence of strong ligands and air, it can get oxidized to Co(III). (Atomic Number of cobalt is 27). Explain.

9. Give a chemical test to distinguish between $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5Br]SO_4Br$. Name the type of isomerism exhibited by these compounds.

10. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is that no precipitate of copper sulphate is obtained when H_2S (g) is passed through this solution?

LEVEL 3

11. Aqueous copper sulphate solution (blue in colour) gives a green precipitate with aqueous potassium fluoride, a bright green solution with aqueous potassium chloride. Explain these experimental results.

12. A metal complex having the composition $Cr(NH)_4Cl_2Br$ has been isolated in two forms, A and B. The form A reacts with $AgNO_3$ solution to give a white precipitate readily soluble in dilute aqueous ammonia whereas B give a pale yellow precipitate soluble in concentrated ammonia solution. Write the formulae of A and B and write their IUPAC names.

13. Explain the following

i. All octahedral complexes of Ni^{2+}must be outer orbital complexes. ii.

NH_4^+ ion does not form any complex.

iii. $(SCN)^{-1}$ ion is involved in linkage isomerism in co-ordination compounds.

14. A metal ion Mn^+ having d^4 valence electronic configuration combines with three didentate ligands to form complexes. Assuming $\Delta_o > P$ Draw the diagram showing d orbital splitting during this complex formation. Write the electronic configuration of the valence electrons of the metal Mn^+ ion in terms of t_{2g} and e_g. What type of the hybridization will Mn^+ ion have? Name the type of isomerism exhibited by this complex.

15. The coordination no. of Ni^{2+} is 4.

$NiCl_2 + KCN(excess) \rightarrow A$(a cyano complex)

A + Conc HCl(excess) → B (a chloro complex)

i) Write IUPAC name of A and B

ii) Predict the magnetic nature of A and B

iii) Write hybridization of Ni in A and B

16. Explain the following
i. $Cu(OH)_2$ is soluble in ammonium hydroxide but not in sodium hydroxide solution. ii.

EDTA is used to cure lead poisoning

iii. Blue coloured solution of $[CoCl_4]^{2-}$ changes to pink on reaction with $HgCl_2$.

1 MARK QUESTIONS

Q1. Write the formula for the following coordination compound:
Tetraamineaquachloridocobalt(III) chloride

Q2. Write the IUPAC name of the following coordination compound:

$[CoCl_2(en)_2]Cl$

Q3. Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?

Q4. Out of the following two coordination entities which is chiral (optically active)?

(a) *cis*-$[CrCl_2(ox)_2]^{3-}$ (b) *trans*-$[CrCl_2(ox)_2]^{3-}$

Q5. The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion?

Q6. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

2 MARKS QUESTIONS

Q1. Draw structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$

Q2. Indicate the type of isomerism exhibited by the following complex and draw the structures for these isomers:

$[Co(en)_3]Cl_3$

Q3. Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionization isomers.

Q4. Calculate the overall complex dissociation equilibrium constant for the $[Cu(NH_3)_4]^{2+}$ ion, given that β_4 for this complex is 2.1×10^{13}.

Q5. What is meant by unidentate ligand? Give two examples.

Q6. What is meant by didentate ligand? Give two examples.

Q7. What is meant by ambidentate ligands? Give two examples.

Q8. Draw the structures of optical isomers of:

$[Cr(C_2O_4)_3]^{3-}$

Q9. Discuss the nature of bonding in metal carbonyls.

Q10. What is meant by the *chelate effect*? Give an example.

Q11. Draw the structures of:

(i) $Ni(CO)_4$ (ii) $Fe(CO)_5$

3 MARKS QUESTIONS

Q1. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(i)$[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$ (iii) $[Co(C_2O_4)_3]^{3-}$

Also predict their magnetic behaviour.

Q2. What is crystal field splitting energy? Draw figure to show the splitting of *d* orbitals in an octahedral crystal field. How does the magnitude of Δ_o decide the actual configuration of *d* orbitals in a coordination entity?

Q3. Discuss briefly giving an example in each case the role of coordination compounds in:

(i) biological systems (iii) analytical chemistry

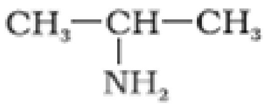
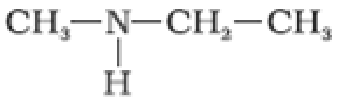
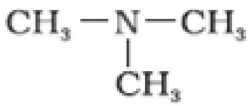
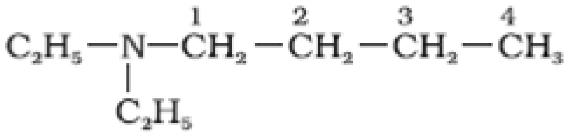
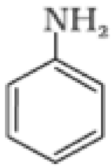
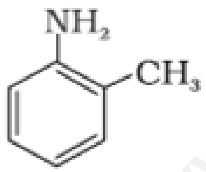
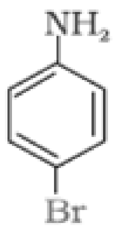
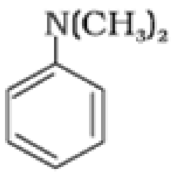
(ii) medicinal chemistry .

UNIT 13:
AMINES

2.	Amines	1. Ammonolysis of alkylholids, Gabriel Phthalimide synthesis, Hoffmann Bromamide Degradation. 2. Basic character of Amines(pK$_b$) and comparisons in gaseous and aqueous phase. 3. Carbylomine Reaction ,Hinsberg's Test. 4. Electrophilic substitution. 5. Diazonium salts –reactions

IUPAC NOMENCLATURE

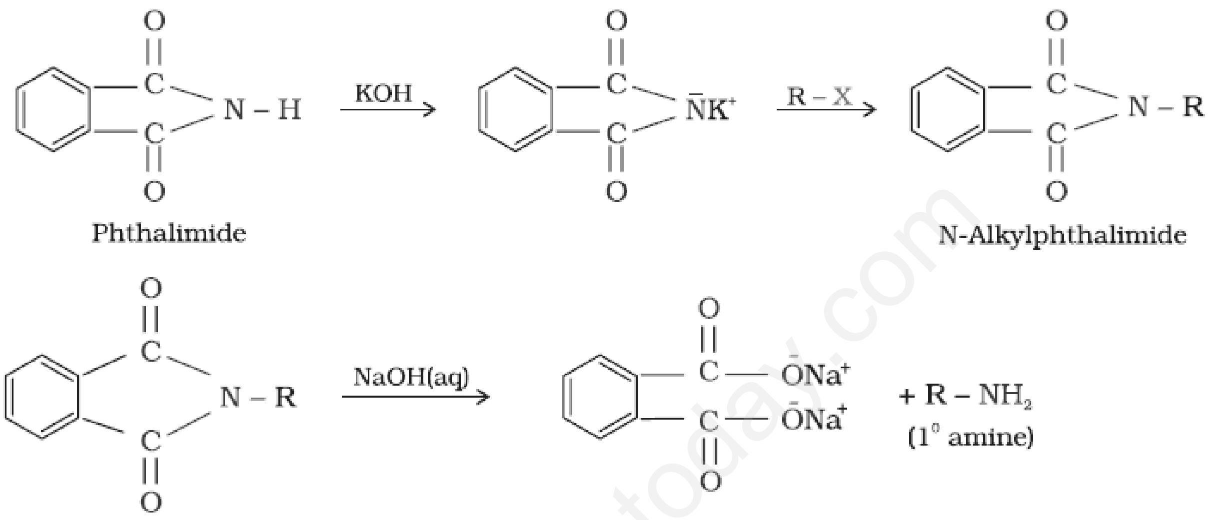
IUPAC NOMENCLATURE

Amine	IUPAC name
$CH_3-CH_2-NH_2$	Ethanamine
$CH_3-CH_2-CH_2-NH_2$	Propan-1-amine
 $CH_3-\underset{\vert\atop NH_2}{CH}-CH_3$	Propan-2-amine
 $CH_3-\underset{\vert\atop H}{N}-CH_2-CH_3$	N-Methylethanamine
 $CH_3-\underset{\vert\atop CH_3}{N}-CH_3$	N,N-Dimethylmethanamine
 $C_2H_5-\underset{\vert\atop C_2H_5}{N}-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$	N,N-Diethylbutan-1-amine
$NH_2-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2$	Prop-2-en-1-amine
$NH_2-(CH_2)_6-NH_2$	Hexane-1,6-diamine
	Aniline or Benzenamine
	2-Aminotoluene
	4-Bromobenzenamine or 4-Bromoaniline
	N,N-Dimethylbenzenamine

NAME REACTIONS

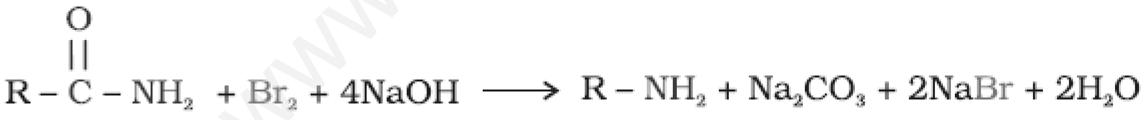
1. Gabriel phthalimide synthesis

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



2. Hoffmann bromamide degradation reaction

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. The amine so formed contains one carbon less than that present in the amide.



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

3. Carbylamine reaction

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

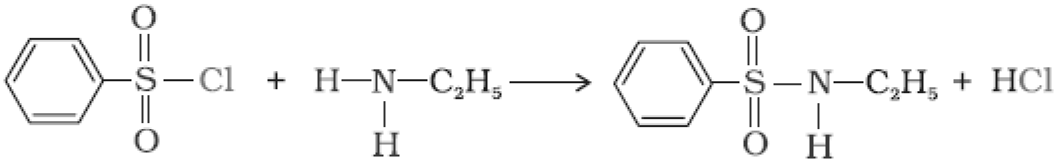
$$R{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R{-}NC + 3KCl + 3H_2O$$

4. Hinsberg Test:

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

(a) The reaction of benzenesulphonyl chloride with primary amine

yields N-ethylbenzenesulphonyl amide.

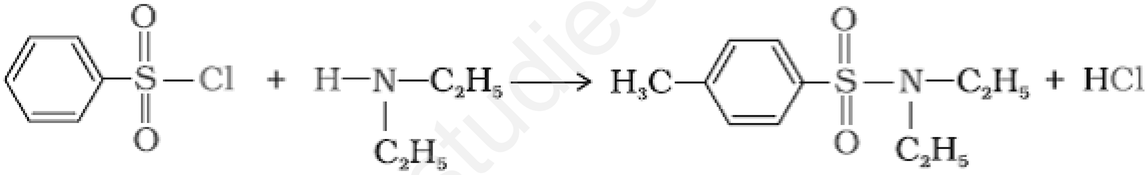


N-Ethylbenzenesulphonamide
(soluble in alkali)

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

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

is formed.



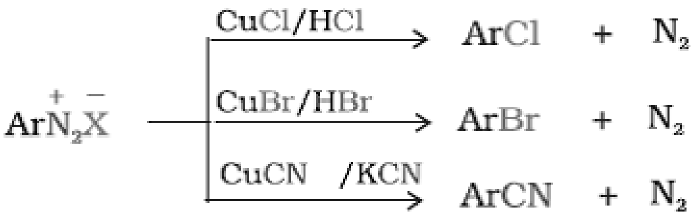
N,N-Diethylbenzenesulphonamide

Since N, N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

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

5. Sandmeyer Reaction

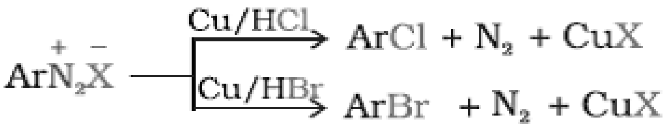
The Cl–, Br– and CN– nucleophiles can easily be introduced in the benzene ring of diazonium salts in the presence of Cu(I) ion.



$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{CuCl/HCl} ArCl + N_2$$
$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{CuBr/HBr} ArBr + N_2$$
$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{CuCN/KCN} ArCN + N_2$$

6. Gatterman Reaction

Chlorine or bromine can be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.

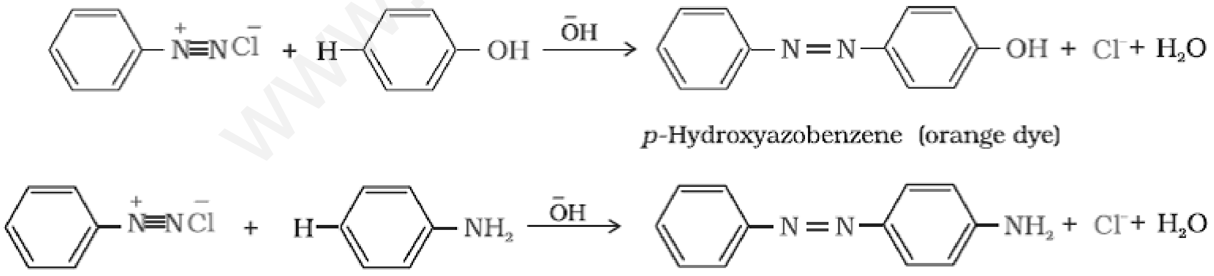


$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$$
$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{Cu/HBr} ArBr + N_2 + CuX$$

7. Coupling reactions

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

Similarly the reaction of diazonium salt with aniline yields p-aminoazobenzene.



p-Hydroxyazobenzene (orange dye)

p-Aminoazobenzene
(yellow dye)

DISTINCTION BETWEEN PAIRS OF COMPOUNDS

Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine
(ii) Secondary and tertiary amines
(iii) Ethylamine and aniline

(iv) Aniline and benzylamine

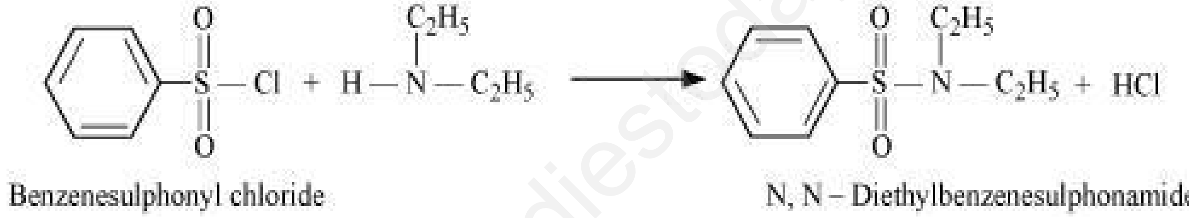
(v) Aniline and N-methylaniline.

ANS. (i) Methylamine and dimethylamine can be distinguished by the carbylamine test. Carbylamine test: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form foul-smelling isocyanides or carbylamines. Methylamine (being an aliphatic primary amine) gives a positive carbylamine test, but dimethylamine does not.

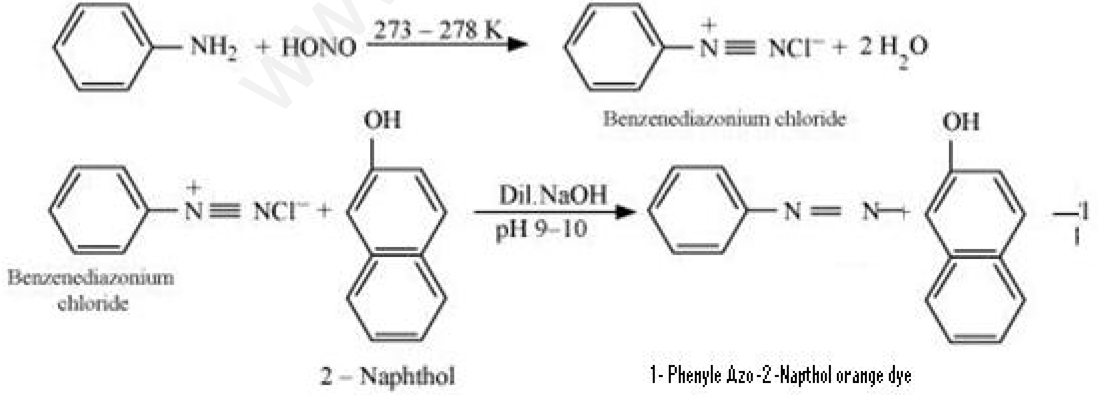
$$\underset{\text{Methylamine}(1^0)}{CH_3-NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\substack{\text{Methyl isocyanide}\\ \text{(foul smell)}}}{CH_3-NC} + 3KCl + 3H_2$$

$$(CH_3)_2NH + CHCl_3 + 3KOH \xrightarrow{\Delta} \text{No reaction}$$

(ii) Secondary and tertiary amines can be distinguished by allowing them to react with Hinsberg's reagent (benzenesulphonyl chloride, $C_6H_5SO_2Cl$).Secondary amines react with Hinsberg's reagent to form a product that is insoluble in an alkali. For example, N, N−diethylamine reacts with Hinsberg's reagent to form N, N−diethylbenzenesulphonamide, which is insoluble in an alkali. Tertiary amines, however, do not react with Hinsberg's reagent.



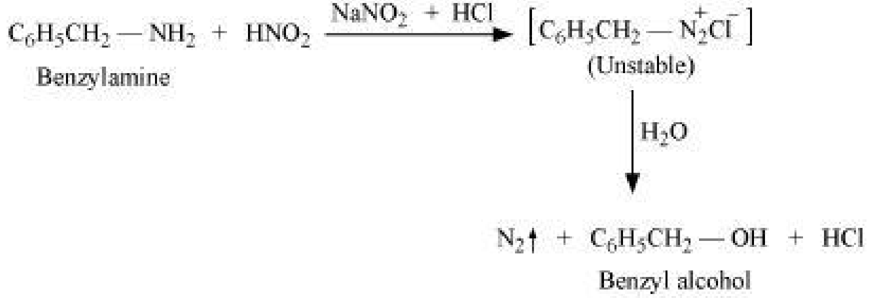
(iii) Ethylamine and aniline can be distinguished using the azo-dye test. A dye is obtained when aromatic amines react with HNO_2 ($NaNO_2$ + dil.HCl) at 0-5°C, followed by a reaction with the alkaline solution of 2-naphthol. The dye is usually yellow, red, or orange in colour. Aliphatic amines give a brisk effervescence due (to the evolution of N_2 gas) under similar conditions.



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

(iv) Aniline and benzylamine can be distinguished by their reactions with the help of nitrous acid, which is prepared in situ from a mineral acid and sodium nitrite.

Benzylamine reacts with nitrous acid to form unstable diazonium salt, which in turn gives alcohol with the evolution of nitrogen gas.



$$\underset{\text{Benzylamine}}{C_6H_5CH_2-NH_2} + HNO_2 \xrightarrow{NaNO_2 + HCl} \underset{\text{(Unstable)}}{[C_6H_5CH_2-\overset{+}{N_2}\overset{-}{Cl}]} \xrightarrow{H_2O} N_2\uparrow + \underset{\text{Benzyl alcohol}}{C_6H_5CH_2-OH} + HCl$$

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

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

$$\underset{\text{Benzylamine}(1^0)}{C_6H_5-NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\substack{\text{Benzyl isocyanide}\\ \text{(foul smell)}}}{C_6H_5-NC} + 3KCl + 3H_2O$$

$$\underset{\text{N-Methylaniline}}{C_6H_5NHCH_3} + CHCl_3 + 3KOH \xrightarrow{\Delta} \text{No reaction}$$

REASONING QUESTIONS

Q1. Account for the following:

(i) pKb of aniline is more than that of methylamine.

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

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

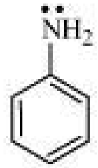
(iv) Although amino group is o– and p– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

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

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

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

ANS. (i) pK_b of aniline is more than that of methylamine:

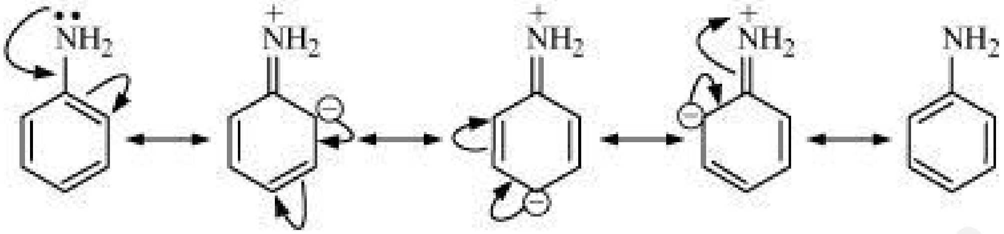


Aniline

$CH_3-\ddot{N}H_2$

Methylamine

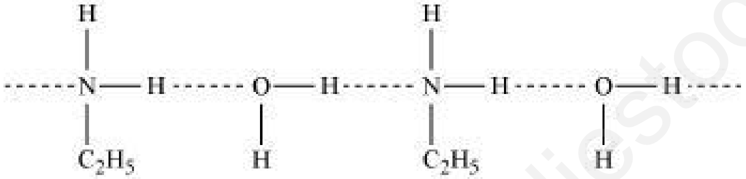
Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.



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

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

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



Ethylamine

But aniline does not undergo H−bonding with water to a very large extent due to the presence of a large hydrophobic $-C_6H_5$ group. Hence, aniline is insoluble in water.

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

$CH_3 \longrightarrow NH_2$ $\qquad H—OH$

Methylamine $\qquad$ Water

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

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

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

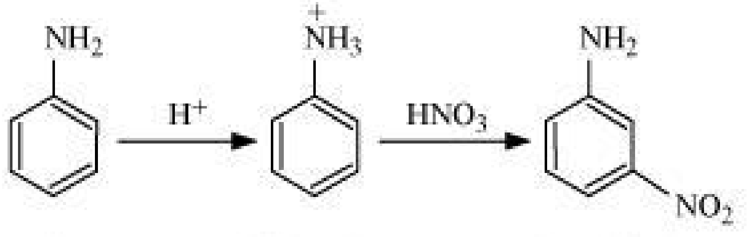
$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

Then, OH^- ion reacts with Fe^{3+} ion to form a precipitate of hydrated ferric oxide.

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

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

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

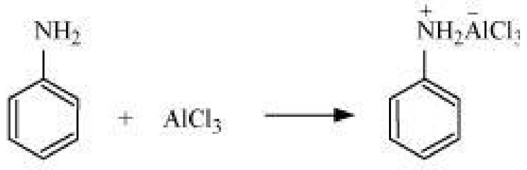


Aniline Anilinium ion *m*-Nitroaniline (47%)

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

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

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

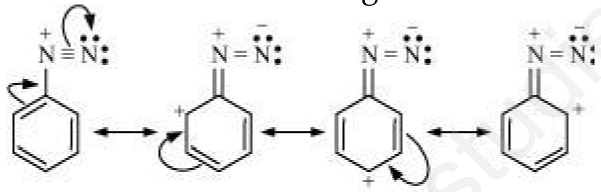


Aniline Salt

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

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

The diazonium ion undergoes resonance as shown below:



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

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

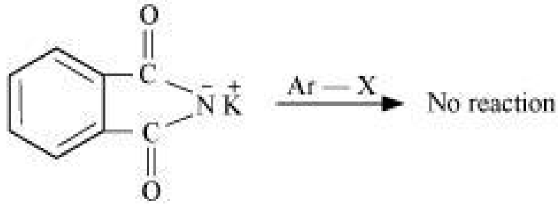
Gabriel phthalimide synthesis results in the formation of 1° amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

Q2. Why cannot aromatic primary amines be prepared by Gabriel phthalimide

synthesis?

ANS. Gabriel phthalimide synthesis is used for the preparation of aliphatic primary amines. It involves nucleophilic substitution (S_N2) of alkyl halides by the anion formed by the phthalimide.

But aryl halides do not undergo nucleophilic substitution with the anion formed by the phthalimide.



Hence, aromatic primary amines cannot be prepared by this process.

Q3. Give plausible explanation for each of the following:

(i) Why are amines less acidic than alcohols of comparable molecular masses?

(ii) Why do primary amines have higher boiling point than tertiary amines?

(iii) Why are aliphatic amines stronger bases than aromatic amines?

ANS. (i) Amines undergo protonation to give amide ion.

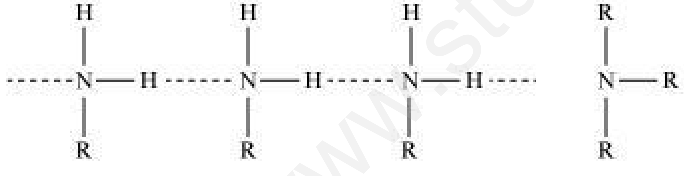
$$R-NH_2 \longrightarrow \underset{\text{Amide ion}}{R-\bar{N}H} + H^+$$

Similarly, alcohol loses a proton to give alkoxide ion.

$$\underset{\text{Alcohol}}{R-OH} \longrightarrow \underset{\text{Alkoxide ion}}{R-\bar{O}} + H^+$$

In an amide ion, the negative charge is on the N-atom whereas in alkoxide ion, the negative charge is on the O-atom. Since O is more electronegative than N, O can accommodate the negative charge more easily than N. As a result, the amide ion is less stable than the alkoxide ion. Hence, amines are less acidic than alcohols of comparable molecular masses.

(ii) In a molecule of tertiary amine, there are no H−atoms whereas in primary amines, two hydrogen atoms are present. Due to the presence of H−atoms, primary amines undergo extensive intermolecular H−bonding.



Primary amine Tertiary amine

As a result, extra energy is required to separate the molecules of primary amines. Hence, primary amines have higher boiling points than tertiary amines.

(iii) Due to the −R effect of the benzene ring, the electrons on the N- atom are less available in case of aromatic amines. Therefore, the electrons on the N-atom in aromatic amines cannot be donated easily. This explains why aliphatic amines are stronger bases than aromatic amines.

SOLVED QUESTIONS

1 MARK QUESTIONS

Q1. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$(CH_3)_2CHNH_2$ 1-Methylethanamine (1^0 amine)

Q2. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$CH_3(CH_2)_2NH_2$ Propan-1-amine (1^0 amine)

Q3. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$CH_3NHCH(CH_3)_2$ N−Methyl-2-methylethanamine (2^0 amine)

Q4. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

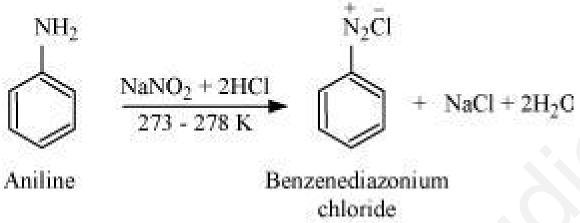
$(CH_3)_3CNH_2$ 2-Methylpropan-2-amine (1^0 amine)

Q5. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$C_6H_5NHCH_3$ N−Methylbenzamine or N-methylaniline (2^0 amine)

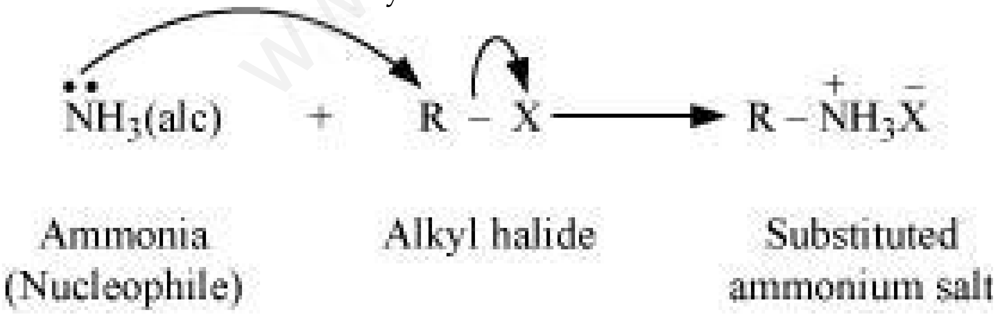
Q6. Write short notes on diazotization

Aromatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at low temperatures (273-278 K) to form diazonium salts. This conversion of aromatic primary amines into diazonium salts is known as diazotization. For example, on treatment with $NaNO_2$ and HCl at 273−278 K, aniline produces benzenediazonium chloride, with NaCl and H_2O as by-products.



Q7. Write short notes on ammonolysis

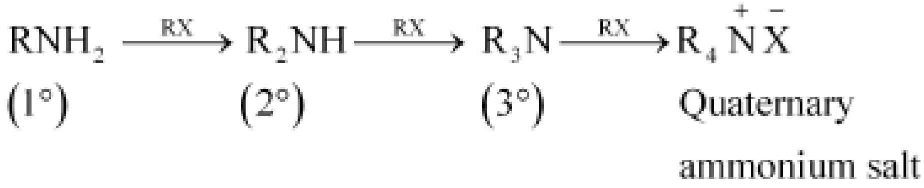
When an alkyl or benzyl halide is allowed to react with an ethanolic solution of ammonia, it undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino (−NH_2) group. This process of cleavage of the carbon-halogen bond is known as ammonolysis.



When this substituted ammonium salt is treated with a strong base such as sodium hydroxide, amine is obtained.

$$R-\overset{+}{N}H_3\overset{-}{X} + NaOH \longrightarrow \underset{\text{Amine}}{R-NH_2} + H_2O + NaX$$

Though primary amine is produced as the major product, this process produces a mixture of primary, secondary and tertiary amines, and also a quaternary ammonium salt



$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} R_4\overset{+}{N}\overset{-}{X}$$

Quaternary ammonium salt

Q8. Write short notes on acetylation.

Acetylation (or ethanoylation) is the process of introducing an acetyl group into a molecule. Aliphatic and aromatic primary and secondary amines undergo acetylation reaction by nucleophilic substitution when treated with acid chlorides, anhydrides or esters. This reaction involves the replacement of the hydrogen atom of $-NH_2$ or $> NH$ group by the acetyl group, which in turn leads to the production of amides. To shift the equilibrium to the right hand side, the HCl formed during the reaction is removed as soon as it is formed. This reaction is carried out in the presence of a base (such as pyridine) which is stronger than the amine.

$$C_2H_5NH_2 + CH_3COCl \xrightarrow{\text{pyridine}} C_2H_5NHCOCH_3 + HCl$$

Q9.Why are amines basic in character?

ANS. Like ammonia, the nitrogen atom in amines RNH_2 is trivalent and bears an unshared pair of electrons. Thus it acts like a Lewis base and donates the pair of electrons to electron-deficient species which further increases due to +I effect of alkyl radical.

Q10. Arrange the following in decreasing order of their basic strength:

$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

The decreasing order of basic strength of the above amines and ammonia

follows the following order:

$(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > C_6H_5NH_2$

<u>SOLVED EXAMPLES</u> (2 Marks)

Q1. Write chemical equations for the following reactions:

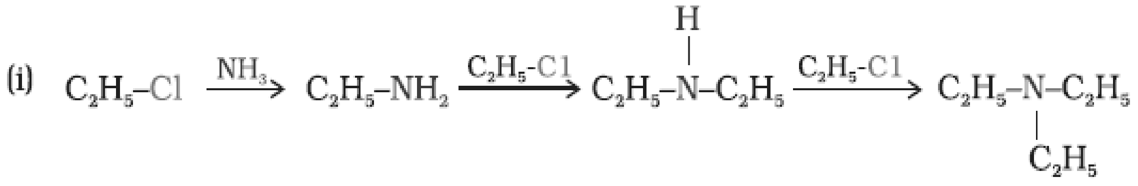
(i) Reaction of ethanolic NH_3 with C_2H_5Cl.

(ii) Ammonolysis of benzyl chloride and reaction of amine so formed

with two moles of CH_3Cl

ANS.

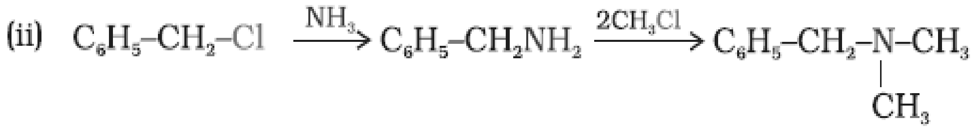
(i)



$$C_2H_5{-}Cl \xrightarrow{NH_3} C_2H_5{-}NH_2 \xrightarrow{C_2H_5\text{-}Cl} C_2H_5{-}\overset{H}{\underset{}{N}}{-}C_2H_5 \xrightarrow{C_2H_5\text{-}Cl} C_2H_5{-}\underset{C_2H_5}{N}{-}C_2H_5$$

Chloroethane Ethanamine N-Ethylethanamine N,N-Diethylethanamine

(ii)



$$C_6H_5{-}CH_2{-}Cl \xrightarrow{NH_3} C_6H_5{-}CH_2NH_2 \xrightarrow{2CH_3Cl} C_6H_5{-}CH_2{-}\underset{CH_3}{N}{-}CH_3$$

Benzylchloride Benzylamine N,N-Dimethylphenylmethanamine

Q2. Write chemical equations for the following conversions:

(i) CH_3 –CH_2 –Cl into CH_3 –CH_2 –CH_2 –NH_2

(ii) C_6H_5–CH_5 –Cl into C_6H_5 –CH_2 –CH_2 –NH_2

(i) $CH_3{-}CH_2{-}Cl \xrightarrow{\text{Ethanolic NaCN}} CH_3{-}CH_2{-}C{\equiv}N \xrightarrow{\text{reduction}} CH_3{-}CH_2{-}CH_2{-}NH_2$

Chloroethane Propanenitrile Propan-1-amine

(ii) $C_6H_5{-}CH_2{-}Cl \xrightarrow{\text{Ethanolic NaCN}} C_6H_5{-}CH_2{-}C{\equiv}N \xrightarrow{H_2/Ni} C_6H_5{-}CH_2{-}CH_2{-}NH_2$

Chlorophenylmethane (Benzyl chloride) Phenylethanenitrile (Benzyl cyanide) 2-Phenylethanamine

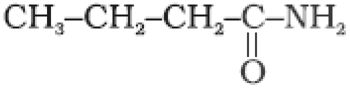
Q3.Write structures and IUPAC names of

(i) the amide which gives propanamine by Hoffmann bromamide

reaction.

(ii) the amine produced by the Hoffmann degradation of benzamide.

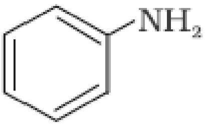
ANS. (i) Propanamine contains three carbons. Hence, the amide molecule must contain four carbon atoms. Structure and IUPAC name of the starting amide with four carbon atoms are given below:



$$CH_3{-}CH_2{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}NH_2$$

(Butanamide)

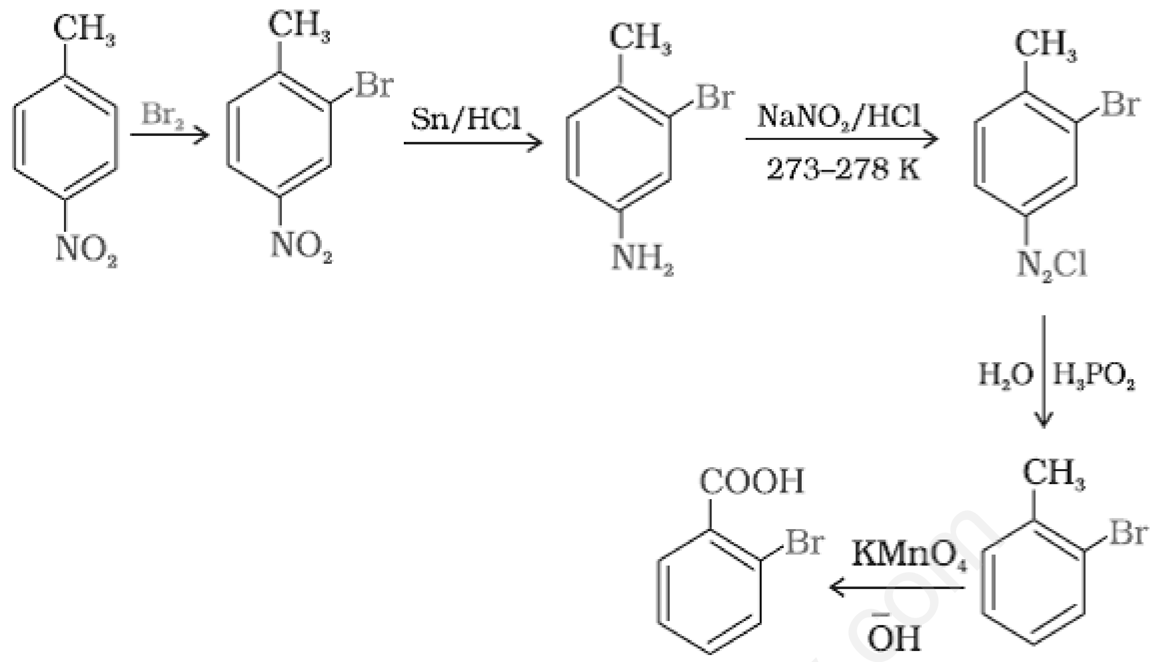
(ii) Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is aromatic primary amine containing six carbon atoms.



(Aniline or benzenamine)

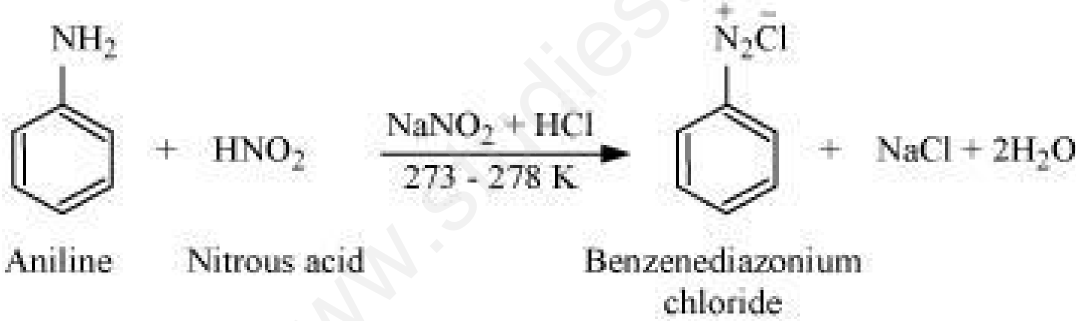
Q4. How will you convert 4-nitrotoluene to 2-bromobenzoic acid?

ANS.

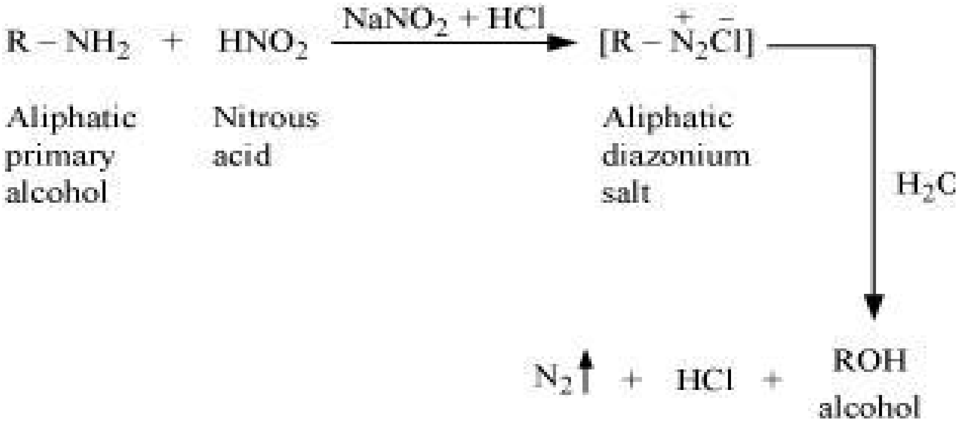


Q5. Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

ANS. (i) Aromatic amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at 273 − 278 K to form stable aromatic diazonium salts i.e., NaCl and H_2O.



(ii) Aliphatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) to form unstable aliphatic diazonium salts, which further produce alcohol and HCl with the evolution of N_2 gas.

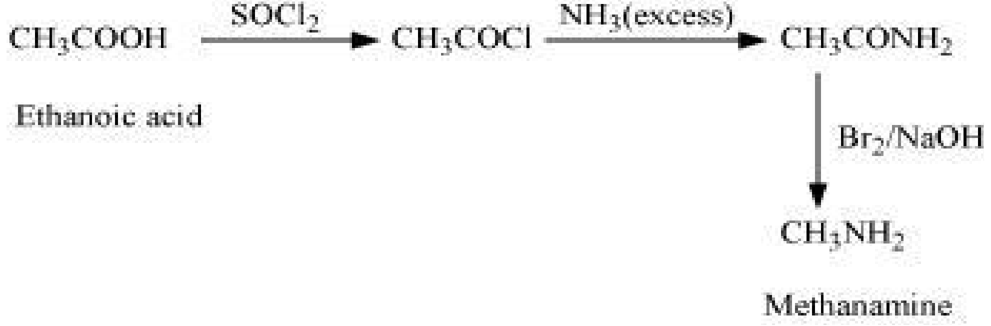


Q6. How will you convert:

(i) Ethanoic acid into methanamine

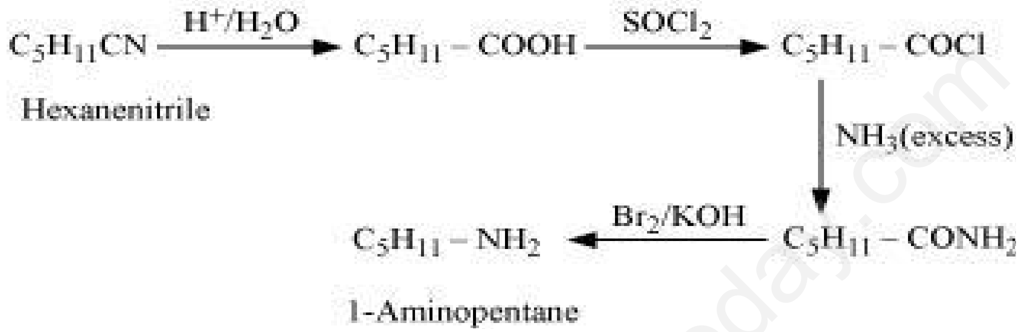
(ii) Hexanenitrile into 1-aminopentane

ANS. (i)



$$\begin{tikzcd}
CH_3COOH \arrow[r, "SOCl_2"] & CH_3COCl \arrow[r, "NH_3(excess)"] & CH_3CONH_2 \arrow[d, "Br_2/NaOH"] \\
& & CH_3NH_2
\end{tikzcd}$$

(ii)



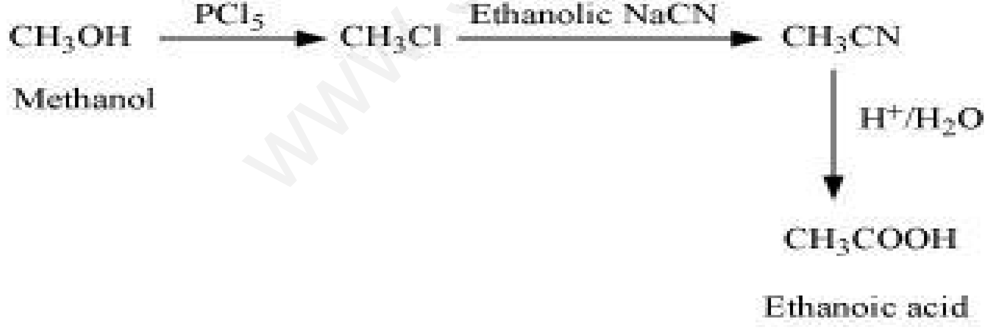
$$\begin{tikzcd}
C_5H_{11}CN \arrow[r, "H^+/H_2O"] & C_5H_{11}-COOH \arrow[r, "SOCl_2"] & C_5H_{11}-COCl \arrow[d, "NH_3(excess)"] \\
& C_5H_{11}-NH_2 & C_5H_{11}-CONH_2 \arrow[l, "Br_2/KOH"']
\end{tikzcd}$$

Q7. How will you convert:

(i) Methanol to ethanoic acid

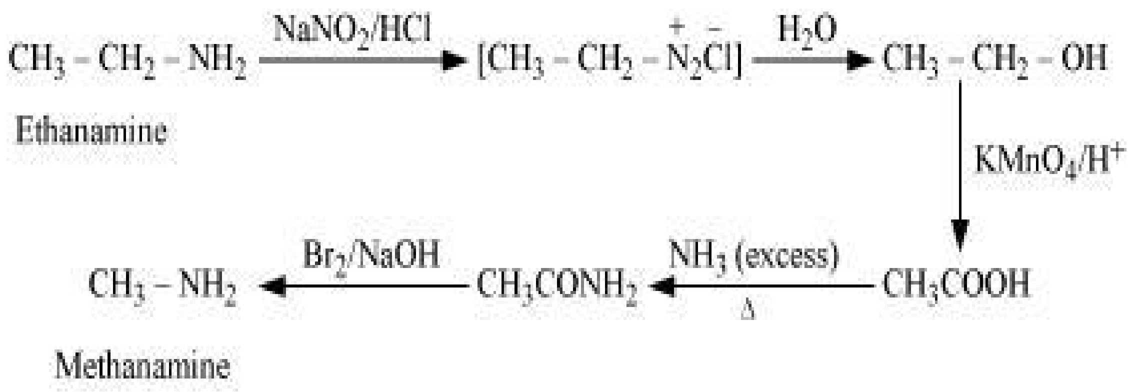
(ii) Ethanamine into methanamine

ANS. (i)



$$\begin{tikzcd}
CH_3OH \arrow[r, "PCl_5"] & CH_3Cl \arrow[r, "Ethanolic\ NaCN"] & CH_3CN \arrow[d, "H^+/H_2O"] \\
& & CH_3COOH
\end{tikzcd}$$

(ii)

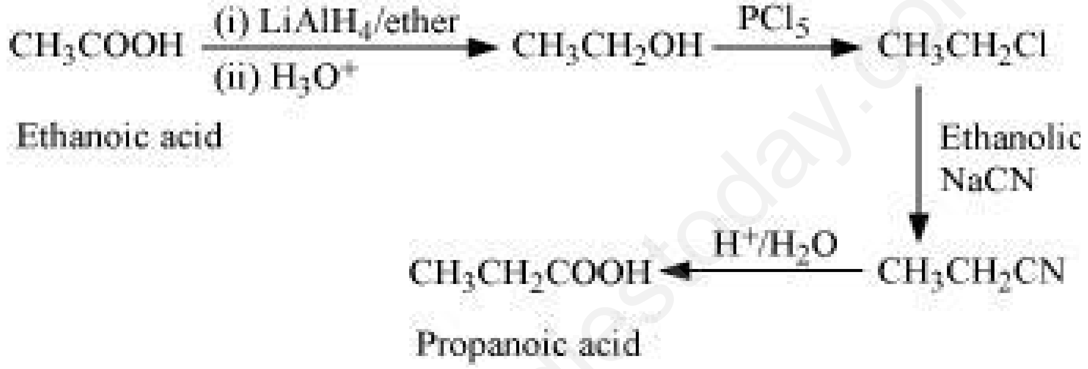


Q8. How will you convert

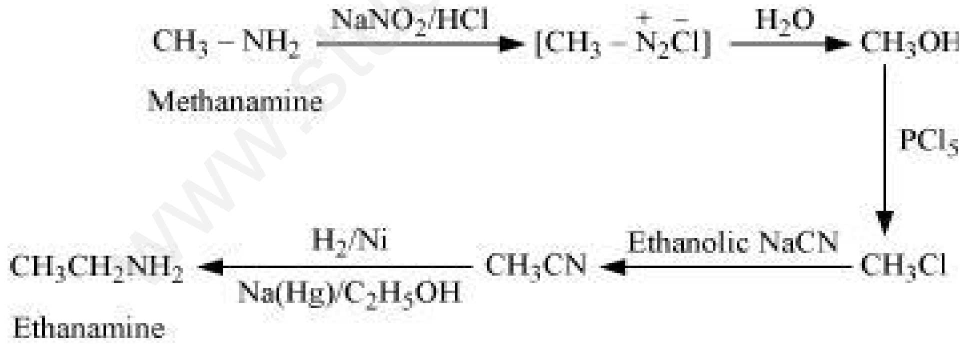
(i) Ethanoic acid into propanoic acid

(ii) Methanamine into ethanamine

<u>ANS.</u> (i)



(ii)

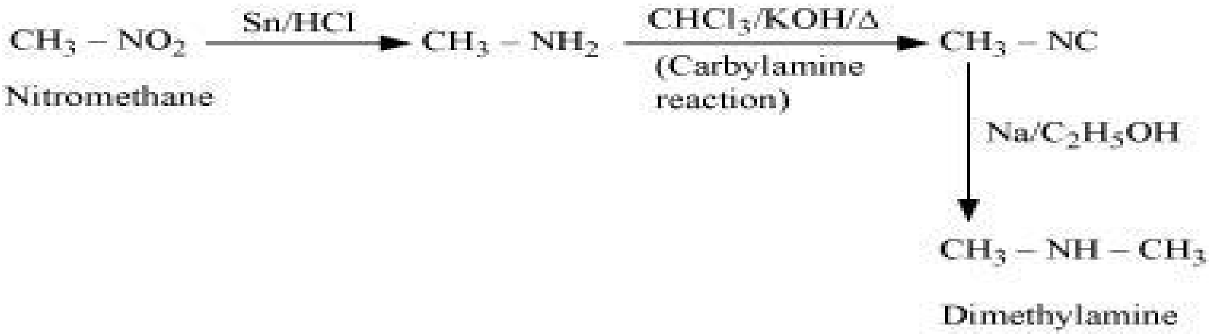


Q9. How will you convert

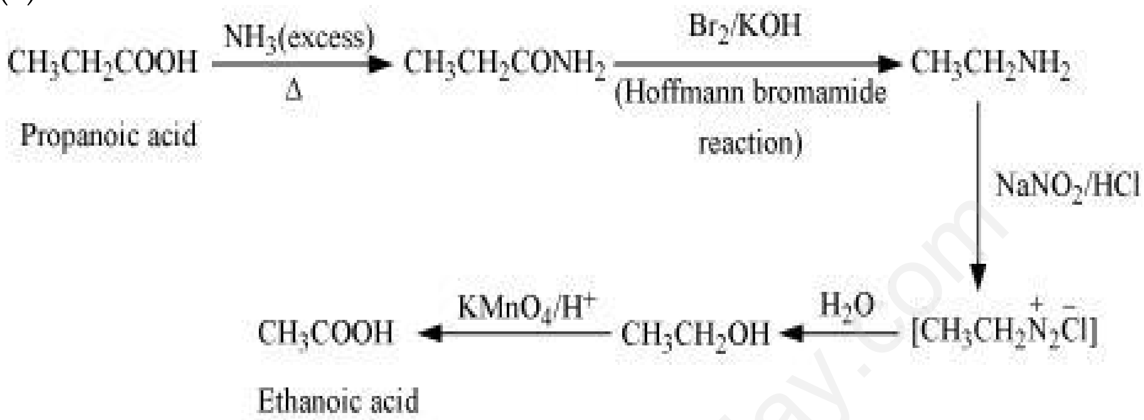
(i) Nitromethane into dimethylamine

(ii) Propanoic acid into ethanoic acid?

(i)

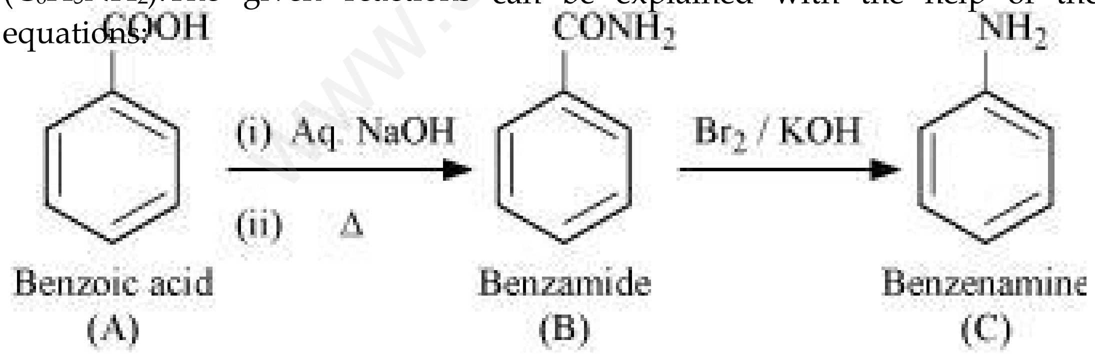


(ii)



Q10. An aromatic compound ‗A‘ on treatment with aqueous ammonia and heating forms compound ‗B‘ which on heating with Br_2 and KOH forms a compound ‗C‘ of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

ANS. It is given that compound ‗C‘ having the molecular formula, C_6H_7N is formed by heating compound ‗B‘ with Br_2 and KOH. This is a Hoffmann bromamide degradation reaction. Therefore, compound ‗B‘ is an amide and compound ‗C‘ is an amine. The only amine having the molecular formula, C_6H_7N is aniline, $(C_6H_5NH_2)$.The given reactions can be explained with the help of the following equations:



3 MARKS QUESTIONS

Q1. Arrange the following:

(i) In decreasing order of the pKb values:
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

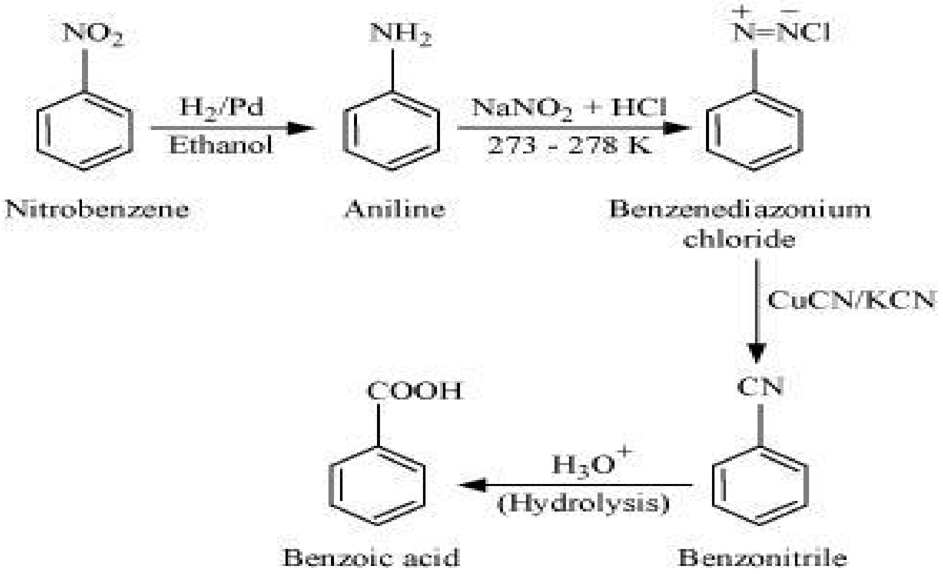
(ii) In increasing order of basic strength:

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

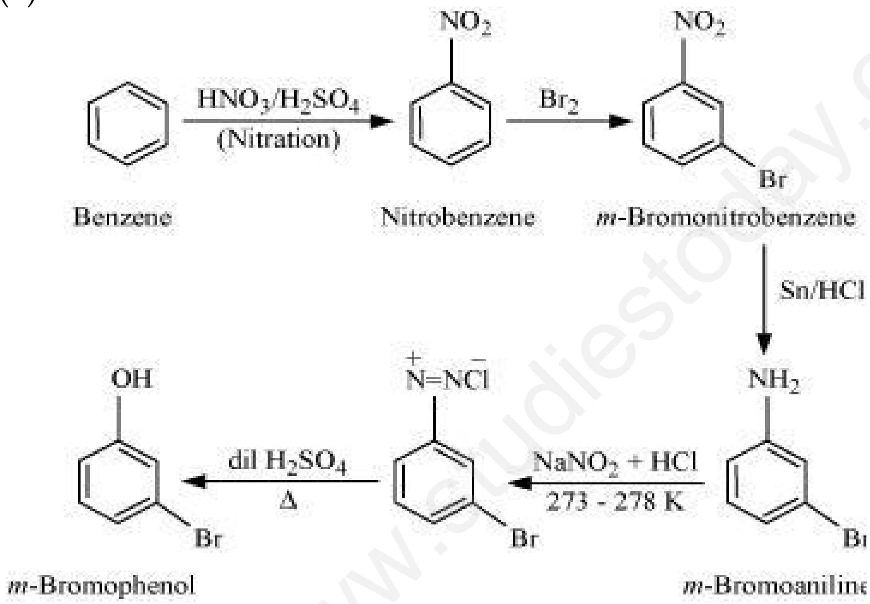
(iii) In increasing order of basic strength:

Aniline, p-nitroaniline and p-toluidine

ANS. (i) The order of increasing basicity of the given compounds is as follows:
$C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$
We know that the higher the basic strength, the lower is the pK_b values.
$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$
(ii)The increasing order of the basic strengths of the given compounds is as follows:
$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$
(iii) The increasing order of the basic strengths of the given compounds is :
p-Nitroaniline < Aniline < p-Toluidine
Q2. Arrange the following
(i) In decreasing order of basic strength in gas phase:
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3
(ii) In increasing order of boiling point:
C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$
(iii) In increasing order of solubility in water:
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.
ANS. (i) The given compounds can be arranged in the decreasing order of their basic strengths in the gas phase as follows:
$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
(ii) The given compounds can be arranged in the increasing order of their boiling points as follows:
$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$
(iii) The more extensive the H−bonding, the higher is the solubility. $C_2H_5NH_2$ contains two H-atoms whereas $(C_2H_5)_2NH$ contains only one H-atom. Thus, $C_2H_5NH_2$ undergoes more extensive H−bonding than $(C_2H_5)_2NH$. Hence, the solubility in water of $C_2H_5NH_2$ is more than that of $(C_2H_5)_2NH$.
Q3. Accomplish the following conversions:
(i) Nitrobenzene to benzoic acid
(ii) Benzene to m-bromophenol
(iii) Benzoic acid to aniline
ANS. (i)



(ii)



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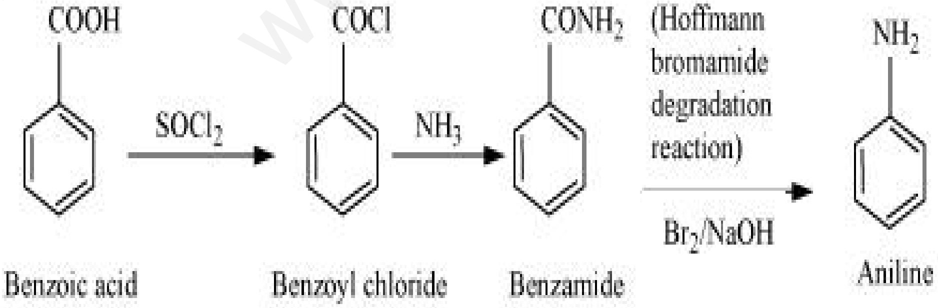


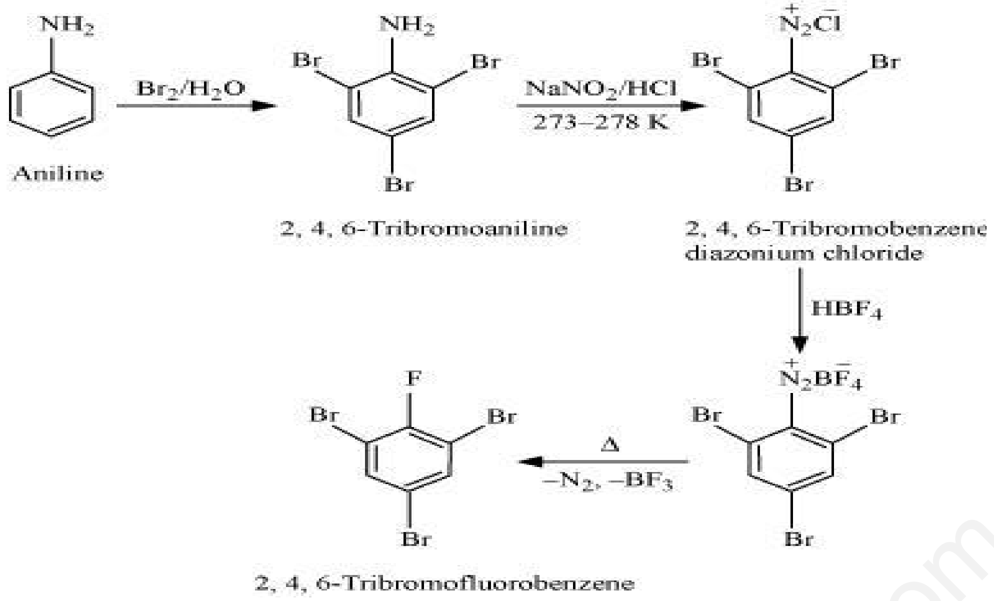
Q4. Accomplish the following conversions:

(i) Aniline to 2,4,6-tribromofluorobenzene

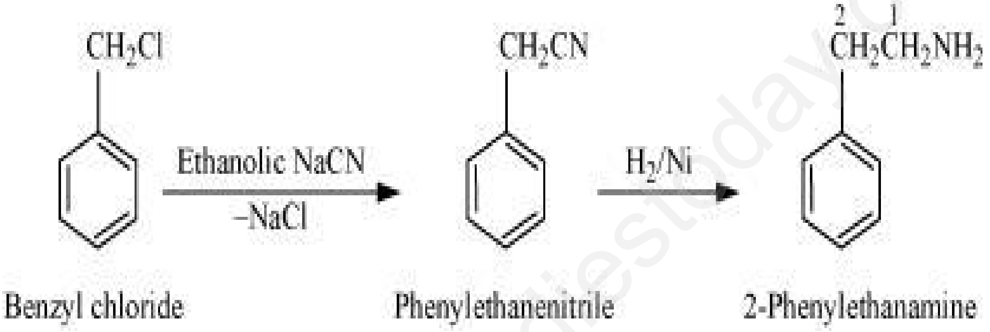
(ii) Benzyl chloride to 2-phenylethanamine

(iii) Chlorobenzene to p-chloroaniline

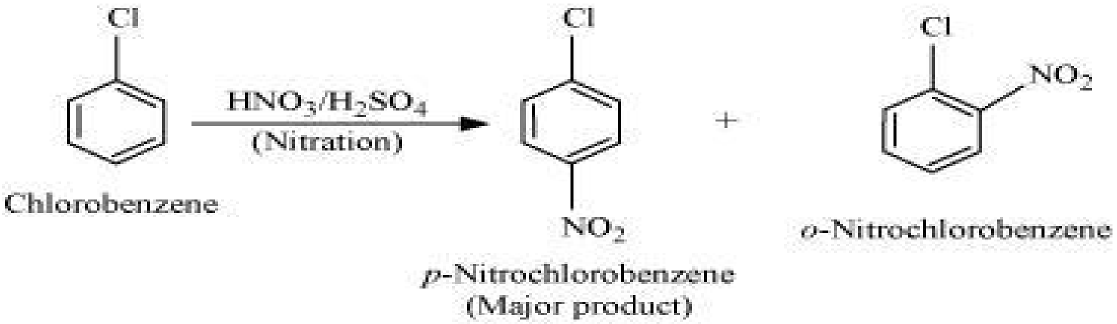
ANS. (i)

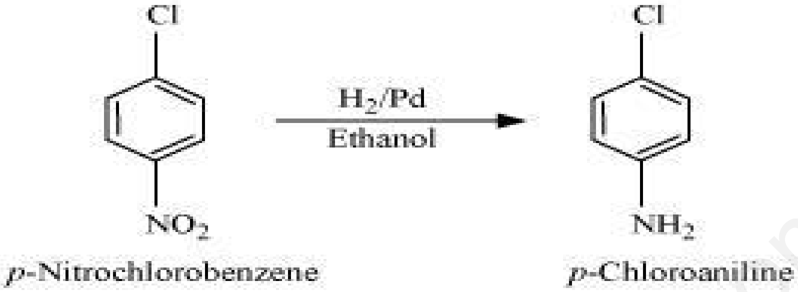

NH$_2$
Aniline
Br$_2$/H$_2$O
NH$_2$
Br
Br
Br
2, 4, 6-Tribromoaniline
NaNO$_2$/HCl
273–278 K
$\overset{+}{N}_2\overset{-}{Cl}$
Br
Br
Br
2, 4, 6-Tribromobenzene diazonium chloride
HBF$_4$
$\overset{+}{N}_2\overset{-}{BF_4}$
Br
Br
Br
Δ
–N$_2$, –BF$_3$
F
Br
Br
Br
2, 4, 6-Tribromofluorobenzene

(ii)


CH$_2$Cl
Benzyl chloride
Ethanolic NaCN
–NaCl
CH$_2$CN
Phenylethanenitrile
H$_2$/Ni
2 1
CH$_2$CH$_2$NH$_2$
2-Phenylethanamine

(iii)





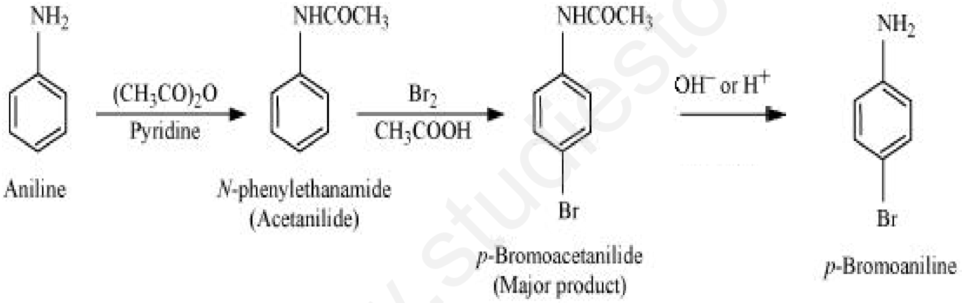
Q5. Accomplish the following conversions:

(i) Aniline to p-bromoaniline

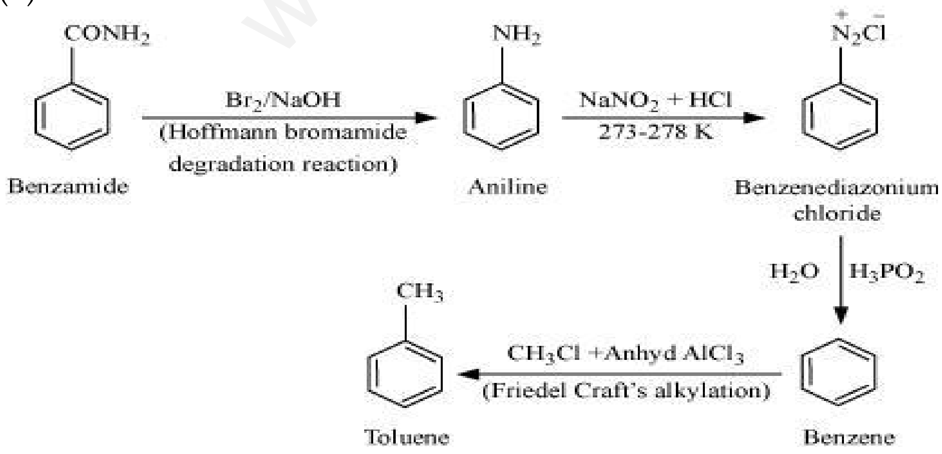
(ii) Benzamide to toluene

(iii) Aniline to benzyl alcohol.

ANS. (i)



(ii)



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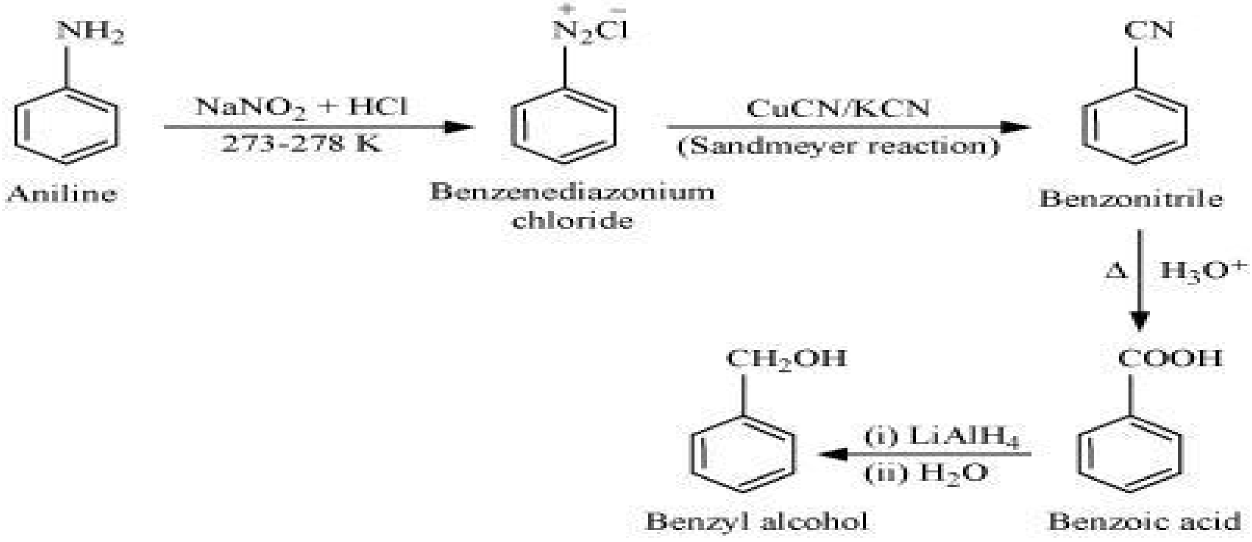


5 MARKS QUESTIONS

Q1. Give the structures of A, B and C in the following reactions:

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH, Br_2} C$

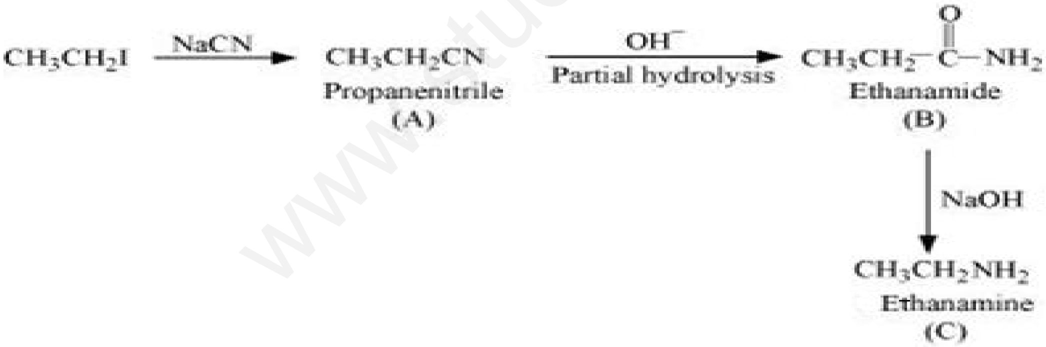
(ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^0 C]{HNO_2} C$

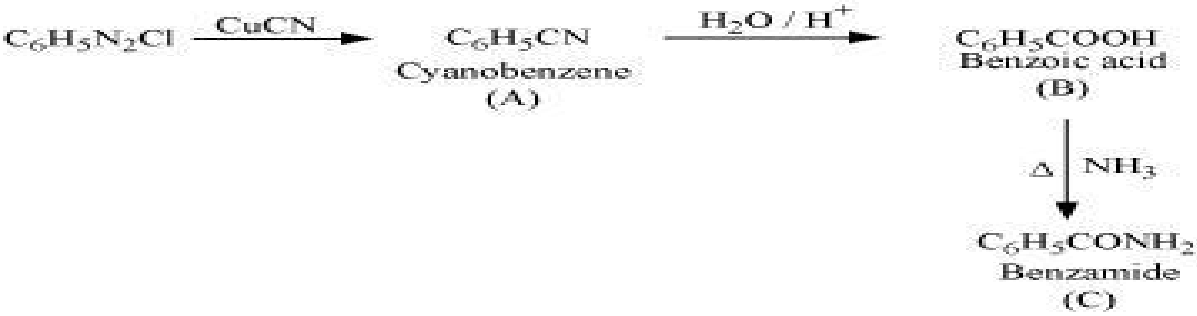
(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

(v) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

ANS. (i)

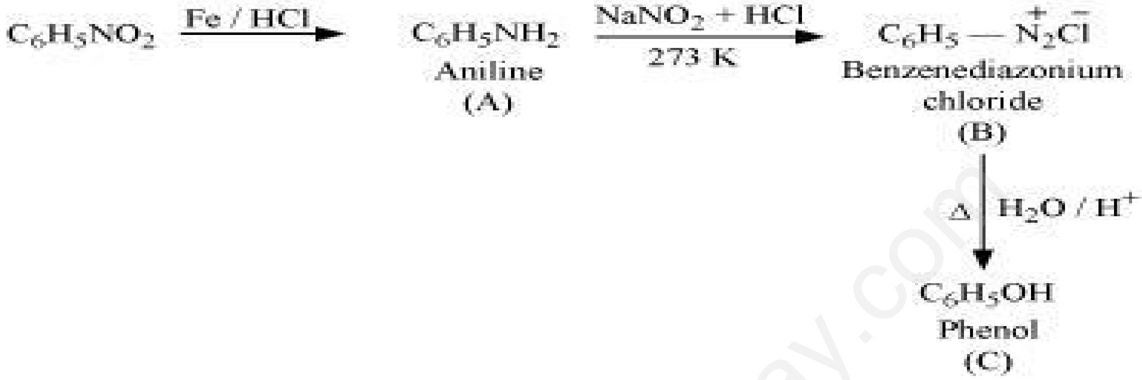


(ii)

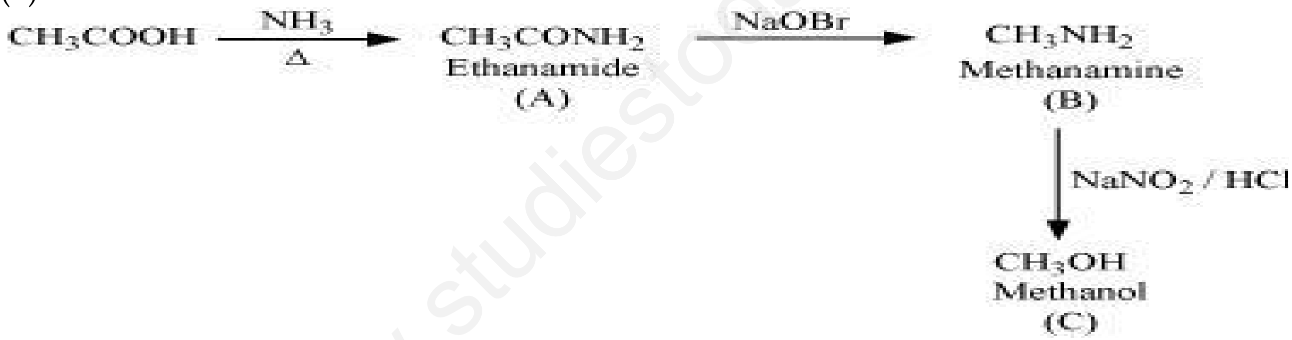


(iii)

(iv)



(v)



Q2. Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + alc.KOH \rightarrow$

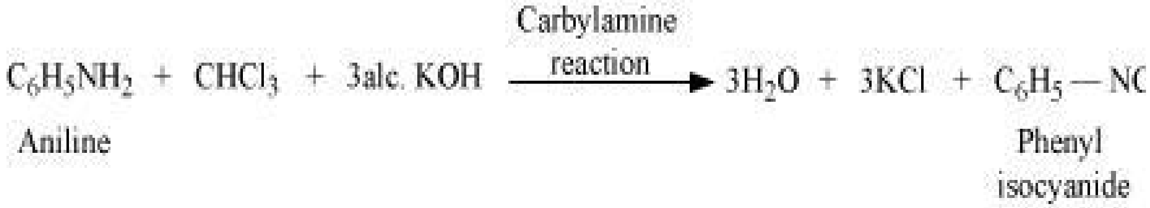
(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(iii) $C_6H_5NH_2 + H_2SO_4(conc.) \rightarrow$

(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(v) $C_6H_5NH_2 + Br_2(aq) \rightarrow$

<u>ANS.</u> (i)



$$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + 3alc.\ KOH \xrightarrow[\text{reaction}]{\text{Carbylamine}} 3H_2O + 3KCl + \underset{\text{Phenyl isocyanide}}{C_6H_5-NC}$$

(ii)

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} + H_3PO_2 + H_2O \rightarrow \underset{\text{Benzene}}{C_6H_6} + N_2 + H_3PO_3 + HCl$$

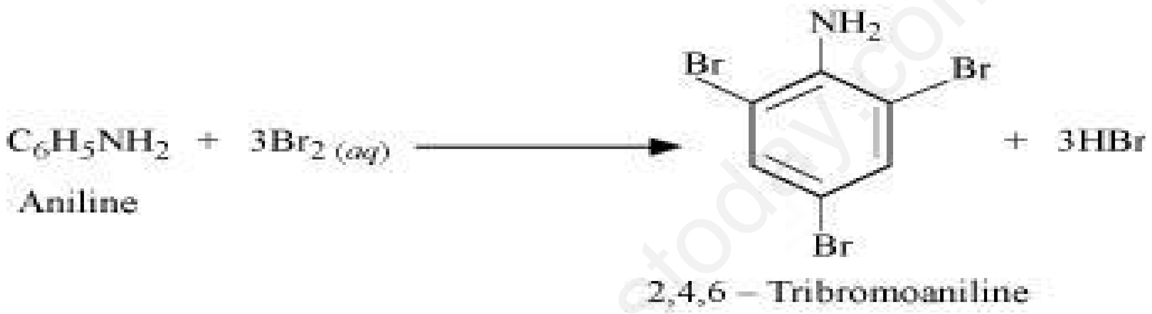
(iii)

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \text{conc.}H_2SO_4 \rightarrow \underset{\text{Anilinium hydrogen sulphate}}{C_6H_5\overset{+}{N}H_3HS\overset{-}{O}_4}$$

(iv)

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} + \underset{\text{Ethanol}}{C_2H_5OH} \rightarrow \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethanal}}{CH_3CHO} + N_2 + HCl$$

(v)



Assignments

Level 1

1. Write IUPAC Name of $C_6H_5N(CH_3)_3Br$?
2. Which reaction is used for preparation of pure aliphatic & aralkyl primary amine ?
3. Name one reagent used for the separation of primary, secondary & tertiary amine ?
4. What amine salts are used for determing their molecular masses ?
5. What is the directive influence of amino group in arylamines?
6. Why are benzene diazonium salts soluble in water ?
7. Which is more basic: CH_3NH_2 & $(CH_3)_3N$?
8. Which is more acidic, aniline or ammonia ?
9. Write the IUPAC name of $C_6H_5NHCH_3$?
10. Mention two uses of sulphanilic acid?

Level 2

1. What for are quaternary ammonium salts widely used ?
2. What product is formed when aniline is first diazotized and then treated with Phenol in alkaline medium ?

3. How is phenyl hydrazine prepared from aniline ?
4. What is the IUPAC name of a tertiary amine containing one methyl, one ethyl And one n-propyl group ?

5. Explain why silver chloride is soluble in aqueous solution of methylamine ?
6. Write the IUPAC name of $C_6H_5N(CH_3)_3$ Br ?
7. Primary amines have higher boiling points then tertiary amines why ?

8. Why is it necessary to maintain the temperature between 273 K & 278 K during diazotization?
9. Arrange the following in order of decreasing basic strength : Ethyl amine, Ammonia, Triethylamine ?
10. Why aniline is acetylated first to prepare mono bromo derivative?

LEVEL 3

1. Arrange the following in decreasing order of their basic strength.

   $C_6H_5NH_2$, C2H5NH2, $(C_2H_5)_2NH$, NH_3

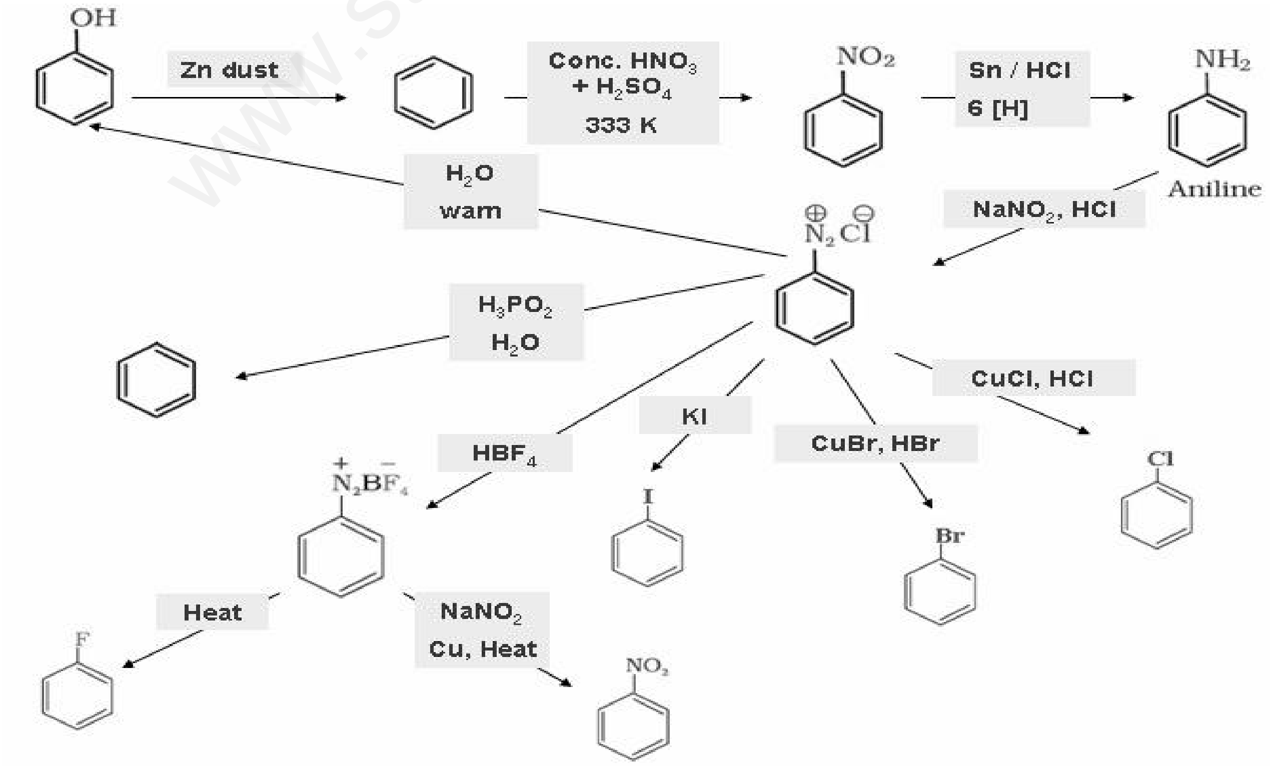
2. Write chemical equation for the conversion

   CH_3-CH_2-Cl into CH_3 –CH_2-CH_3-NH_2

3. Write the equation involved in Carbylamines reactions?

4. How will you distinguish the following pairs? (i) Methanamine and N-methyl methane amine (ii) Aniline and ethyl amine

5. Write chemical sections involved in following name reactions. (i) Hoffmann Bromoamide reaction. (ii) Diazotisation reaction.



COMMON ERRORS

Basic character of amines in aqueous and in gaseous state, p_{ka} and p_{kb} values

1 MARK QUESTIONS

Q1. Arrange the following in decreasing order of their basic strength: $C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

Q2. Arrange the following in decreasing order of the p*Kb* values: $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

Q3. p*Kb* of aniline is more than that of methylamine. Why?

Q4. Ethylamine is soluble in water whereas aniline is not. Give reason.

Q5. Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide. Why?

Q6. Although amino group is *o*– and *p*– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of
m-nitroaniline. Give reason.

Q7. Aniline does not undergo Friedel-Crafts reaction. Why?

Q8. Diazonium salts of aromatic amines are more stable than those of aliphatic amines. Why?

Q9. Gabriel phthalimide synthesis is preferred for synthesising primary amines. Give reason

Q10. Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

Q11. Why do primary amines have higher boiling point than tertiary amines?

Q12. Why are aliphatic amines stronger bases than aromatic amines?

Q13. Direct nitration of aniline is not carried out. Give reason.

Q14. The presence of base is needed in the ammonolysis of alkyl halides. Why?

2 MARKS QUESTIONS

Q1. Write structures and IUPAC names of

(i) the amide which gives propanamine by Hoffmann bromamide reaction.

(ii) the amine produced by the Hoffmann degradation of benzamide.

Q2. Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine (ii) Ethylamine and aniline

Q3. Write short notes on the following:
(i) Carbylamine reaction (ii) Diazotisation
Q4. Explain the following with the help of an example.
(i) Hofmann's bromamide reaction (ii) Coupling reaction
Q5. Explain the following with the help of an example.
(i) Ammonolysis (ii) Gabriel phthalimide synthesis
Q6. How can you convert an amide into an amine having one carbon less than the starting compound? Name the reaction.
Q7. Give a chemical test to distinguish between:
(a) $C_6H_5NH_2$ & CH_3NH_2
(b) CH_3NHCH_3 & $(CH_3)_3N$
Q8. Give the IUPAC names of:
(a) $(CH_3)_2CHNH_2$
(b) $(CH_3CH_2)_2NCH_3$
Q9. Write the structures of:
(a) 3-Bromobenzenamine
(b) 3-Chlorobutanamide

3 MARKS QUESTIONS

Q1. How will you convert
(i) Benzene into aniline (ii) Benzene into N, N-dimethylaniline
(iii) Aniline to Sulphanilic acid

Q2. An aromatic compound 'A' on treatment with aqueous ammonia and heatingforms compound 'B' which on heating with Br_2 and KOH forms a compound 'C'of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

Q3. How will you carry out the following conversions (Write Chemical equations and reaction conditions):
(a) Aniline to Phenol
(b)Acetamide to Ethylamine
(c) Aniline to *p*-nitroaniline