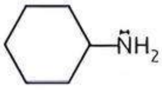
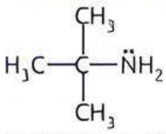
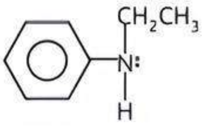
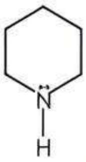
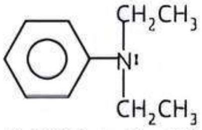
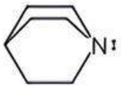
9

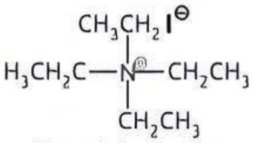
Amines

Fastrack Revision

- **Amines:** Amines are organic derivatives of ammonia with one or more alkyl or aryl groups bonded to the nitrogen atom.
- **Classification of Amines**
  - Amines are classified as **primary** (1°), **secondary** (2°) or **tertiary** (3°),corresponding to one, two or three alkyl or aryl groups bonded to nitrogen.

Types	Examples
Primary (1°) $R-NH_2$	 Cyclohexylamine (1°)  Tert-Butylamine (1°)
Secondary (2°) R_2NH	 N-Ethylaniline (2°)  Piperidine (2°)
Tertiary (3°) R_3N	 N, N-Diethylaniline (3°)  Quinuclidine (3°)

  - Quaternary ammonium salts have four alkyl or aryl bonds to a nitrogen atom. The nitrogen atom bears a positive charge, just as it does in simple ammonium salts such as ammonium chloride.

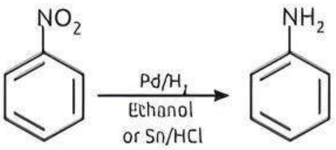


Tetraethylammonium iodide (Quaternary ammonium salt)

- **Methods of Preparation of Amines**
  - **Reduction of Nitro Compounds:**

$$R-NO_2 \xrightarrow[\text{Reduction}]{} R-NH_2 + 2H_2O$$

Reduction can take place by Sn/HCl, Ni/H_2, Zn/NaOH, Pd/H_2.



The reduction of nitroalkane or nitrobenzene in neutral medium gives hydroxyl amines.

  - **Ammonolysis of Alkyl Halides:**

$$\ddot{N}H_3 + R-X \longrightarrow \underset{\text{Substituted ammonium salt}}{R-\overset{+}{N}H_3X^-}$$

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

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

Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt. However, primary amine is obtained as a major product by taking large excess of NH_3.

Order of reactivity of halides with amines is RI > RBr > RCl.

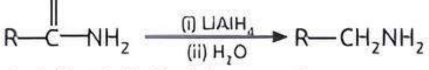
  - **Reduction of Nitriles or Cyanides:**

$$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{Ni/H_2} R-CH_2NH_2$$

  - **Schmidt Reaction:**

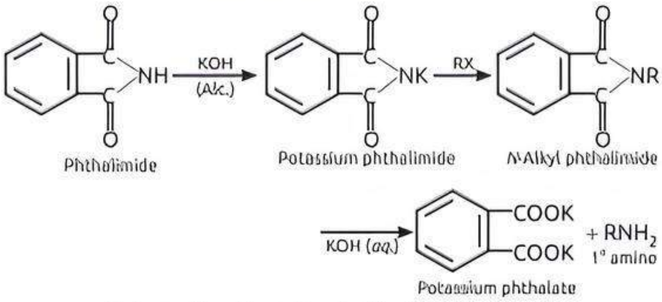
$$RCOOH + \underset{\text{Hydrazoic acid}}{N_3H} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Alkylamine}}{R-NH_2} + N_2 + CO_2$$

  - **Reduction of Amides:**



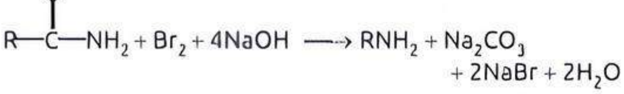
$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} R-CH_2NH_2$$

  - **Gabriel's Phthalimide Reaction:**



This method is not suitable for 1° arylamine.

  - **Hoffmann Bromamide Degradation Reaction:**



$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

- **Physical Properties of Amines**
  - The lower aliphatic amines are gases with fishy smell.
  - Primary amines with three or more carbon atoms are liquid and higher members are all solids.
  - Lower aliphatic amines are water soluble because they can form hydrogen bonds with water molecules, however the solubility decreases with increase in hydrophobic alkyl group.

- The order of boiling points is:
  primary > secondary > tertiary.

Basic Strength of Amines

- Amines act as Lewis bases due to the presence of lone pair of electrons on the nitrogen atom.
- More the K_b (dissociation constant of base), higher is the basicity of amines and lesser the pK_b, higher is the basicity of amines.
- Aliphatic amines (CH_3NH_2) are stronger bases than NH_3 due to the electron releasing +I effect of the alkyl group.
- Among aliphatic methyl amines, the order of basic strength in aqueous solution is as follows:

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

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

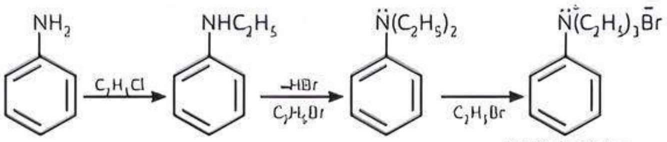
- Aromatic amines are weaker bases than aliphatic amines and NH_3, due to the fact that the electron pair on the nitrogen atom is involved in resonance with the π-electron pairs of the ring.
- Electron releasing groups (*e.g.*, —CH_3, —OCH_3, —NH_2 etc.) increase the basic strength of aromatic amines while electron withdrawing groups (like —NO_2, —X, —CN etc.) tend to decrease the same.

Chemical Properties of Amines

- **Alkylation:**

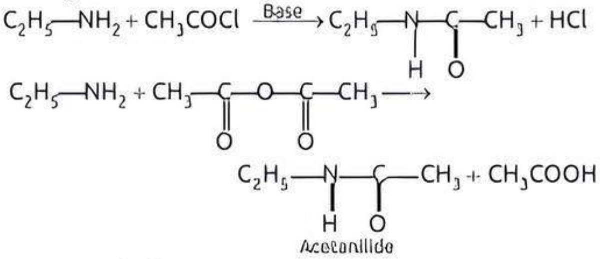
$$\begin{tikzcd} C_2H_5NH_2 + C_2H_5Br \arrow[r, "-HBr"] & (C_2H_5)_2NH \arrow[r, "C_2H_5Br", "-HBr"'] & (C_2H_5)_3\ddot{N} \arrow[d, "C_2H_5Br"] \\ & & (C_2H_5)_4\overset{+}{N}Br^- \end{tikzcd}$$

Aromatic amines also undergo alkylation as given below:



Triethylanilinium bromide

- **Acylation:**



$$C_2H_5—NH_2 + CH_3COCl \xrightarrow{Base} C_2H_5—\underset{H}{\underset{|}{N}}—\underset{O}{\underset{\|}{C}}—CH_3 + HCl$$

$$C_2H_5—NH_2 + CH_3—\underset{O}{\underset{\|}{C}}—O—\underset{O}{\underset{\|}{C}}—CH_3 \longrightarrow \underset{\text{Acetanilide}}{C_2H_5—\underset{H}{\underset{|}{N}}—\underset{O}{\underset{\|}{C}}—CH_3} + CH_3COOH$$

- **Benzoylation:**

$$CH_3NH_2 + C_6H_5COCl \xrightarrow{Pyridine} CH_3NHCOC_6H_5 + HCl$$

Benzoylation of aniline is known as Schotten-Baumann reaction.

- **Carbylamine reaction** (only by 1° amines):

$$RNH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} \underset{\substack{\text{Isocyanide} \\ \text{(A bad smelling compound)}}}{R—N \overset{\rightarrow}{\equiv} C} + 3KCl + 3H_2O$$

MIC or methyl isocyanate gas ($CH_3—N{=}C{=}O$) was responsible for Bhopal gas tragedy in December 1984.

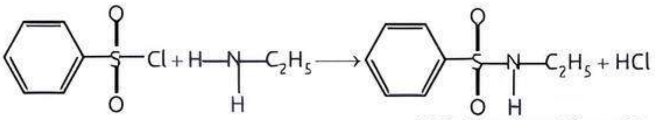
Reaction with Nitrous Acid:

$$RNH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [RN_2^+Cl^-] \xrightarrow{H_2O} ROH + N_2 + HCl$$

Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.

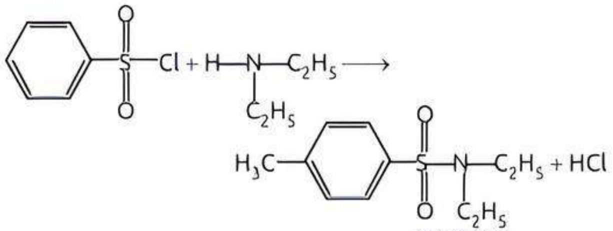
$$\underset{\text{Aniline}}{C_6H_5—NH_2} \xrightarrow[273–278\ K]{NaNO_2 + 2HCl} \underset{\substack{\text{Benzenediazonium} \\ \text{chloride}}}{C_6H_5N_2^+Cl^-} + NaCl + 2H_2C$$

Reaction with Aryl Sulphonyl chloride (Hinsberg Reagent): The reaction of benzenesulphonyl chloride with primary amine yields *N*-ethyl benzenesulphonyl amide.



N-Ethylbenzenesulphonamide
(Soluble in alkali)

The reaction of benzenesulphonyl chloride with secondary amine yields *N*, *N*-diethylbenzenesulphonamide.



N,*N*-Diethyl
benzenesulphonamide
(Insoluble in alkali)

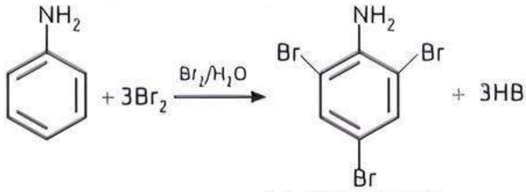
Tertiary amines does not react with benzenesulphonyl chloride.

Reaction with Aldehydes: Schiff base is obtained.

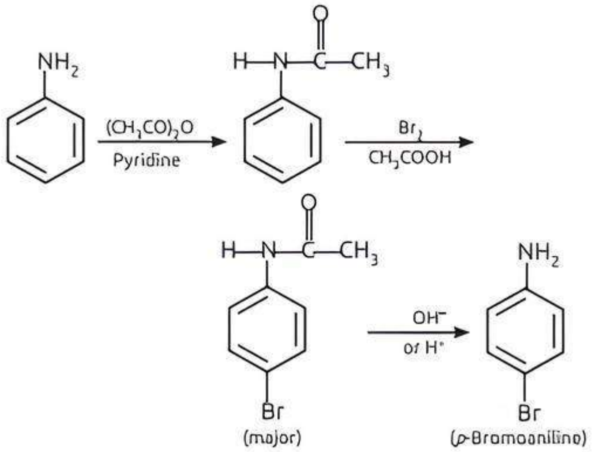
$$C_6H_5NH_2 + \underset{\text{Benzaldehyde}}{OHCC_6H_5} \xrightarrow[\Delta, -H_2O]{ZnCl_2} \underset{\substack{\text{Benzylidene aniline} \\ \text{(Schiff base)}}}{C_6H_5N{=}CHC_6H_5}$$

Electrophilic Substitution Reactions: Aniline is *ortho* and *para* directing towards electrophilic substitution reaction due to high electron density at *ortho* and *para* positions.

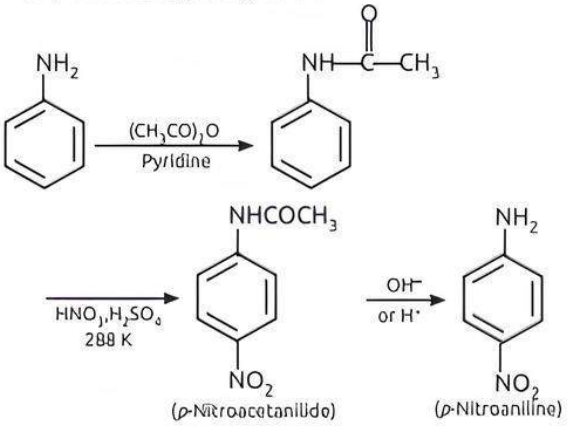
- **Bromination:** Aniline reacts with bromine water at room temperature to give a light yellow precipitate of 2, 4, 6-tribromoaniline.



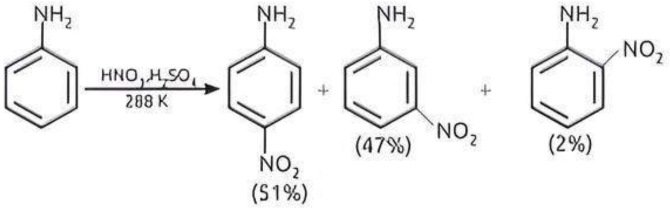
2, 4, 6-Tribromoaniline
(Light yellow ppt.)



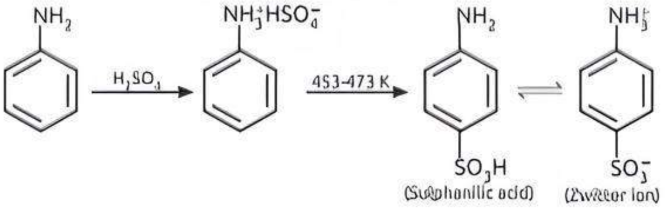
- **Nitration:** Direct nitration of aniline is not possible as it is susceptible to oxidation, thus amino group is first protected by acetylation.



In strongly acidic medium, aniline is protonated as anilinium ion which is meta directing so it gives meta product also.



- **Sulphonation:** On sulphonation, aniline gives sulphanilic acid as the major product.



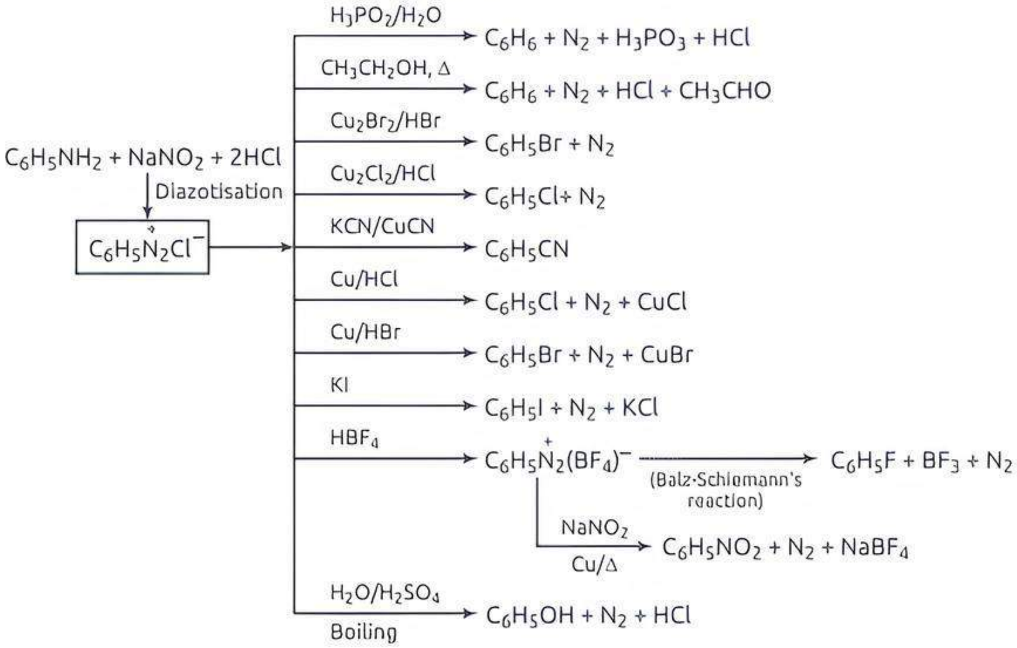
- Aniline does not undergo Friedel-Crafts reaction due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence, behaves like a strong deactivating group for further chemical reaction.

- **Oxidation:** Use of different oxidising agents gives different products.

Oxidising agent	Product
Acidified $KMnO_4$ (or $Na_2Cr_2O_7$ + $CuSO_4$ + dil. acid)	Aniline black (a dye)
Chromic acid ($Na_2Cr_2O_7$ + conc. H_2SO_4)	*p*-Benzoquinone
Caro's acid (H_2SO_5)	Nitrobenzene and nitrosobenzene
Conc. nitric acid	Decomposes

- **Identification of Primary, Secondary and Tertiary Amines**
  - **Sulphonylation-Hinsberg Test**
    - It involves treatment with benzenesulphonyl chloride (Hinsberg reagent) or *p*-toluenesulphonyl chloride.
    - The reaction is used to separate the amine mixture.
    - 1° and 2° amine, due to the presence of active hydrogen, react and give corresponding sulphonamide while 3° amine does not react.
    - 1° amine product, *N*-alkylbenzenesulphonamide is soluble in KOH forming a water-soluble salt.
  - **Nitrous Acid Test**
    - 1° amine on reaction with HNO_2 gives usually an alcohol. The reaction involves the formation of diazonium salt as an intermediate.
    - 2° amine gives nitrosoamine which is a yellow oily liquid.
    - 3° amine dissolves in cold HNO_2 to form an unstable salt which on heating decomposes to give nitrosoamine and an alcohol.
  - **Treatment with $CS_2/HgCl_2$**
    - 1° amine on warming with CS_2 produces dithiocarbamic acid, which is decomposed by mercuric chloride to alkyl isothiocyanate. It is called as **Hoffmann's Mustard Oil Reaction.**
    - Although 2° amine gives dithiocarbamic acid but is not decomposed by mercuric chloride.
    - 3° amine don't react with CS_2.
  - **Carbylamine Reaction**
    - 1° amine on treatment with chloroform and alcoholic KOH gives out unpleasant or pungent vapours of alkyl carbylamine (isocyanide). The reaction is known as a test for 1° amine.
  - **Aromatic Diazonium Salts**
    - Aromatic diazonium salts are prepared by adding a cold aqueous solution of $NaNO_2$ in the presence of HCl at 273-278K. This reaction is called diazotisation.
    - Aromatic diazonium salts are much more stable than aliphatic diazonium salts due to the dispersal of positive charge on benzene ring.

- **Preparation and Chemical Reactions of Benzene Diazonium Chloride**



Practice Exercise

Multiple Choice Questions

Q 1. Which one of the following is formed by Gabriel phthalimide reaction?

a. Primary aromatic amine
b. Primary aliphatic amine
c. Secondary amine
d. Tertiary amine

Q 2. Acetamide reacts with $LiAlH_4$ to give:

a. ethanol b. acetic acid
c. formic acid d. ethyl amine

Q 3. The reagent used to prepare amine from amide is:

a. Br_2/KOH b. $NaOH/CaO$
c. $HCl/ZnCl_2$ d. $K_2Cr_2O_7/H_2SO_4$

Q 4. Which of the following is least basic?

a. NH_3 b. $C_6H_5NH_2$
c. $(C_6H_5)_2NH$ d. $(C_6H_5)_3N$

Q 5. In which of the following solvents, the $C_4H_9NH_3^+X^-$ is soluble? *(CBSE SQP 2023-24)*

a. Ether b. Acetone
c. Water d. Bromine water

Q 6. CH_3CONH_2 on reaction with NaOH and Br_2 in alcoholic medium gives: *(CBSE 2023)*

a. CH_3COONa b. CH_3NH_2
c. CH_3CH_2Br d. $CH_3CH_2NH_2$

Q 7. Which of the following statements is not correct for amines?

a. Most alkyl amines are more basic than ammonia solution.
b. pK_b value of ethylamine is lower than benzylamine.
c. CH_3NH_2 on reaction with nitrous acid releases NO_2 gas.
d. Hinsberg's reagent reacts with secondary amines to form sulphonamides.

Q 8. Which of the following amine does not give carbylamine reaction?

a. $CH_3CH_2NH_2$ b. CH_3NH_2
c. $CH_3—NH—CH_3$ d. $C_6H_5NH_2$

Q 9. The reaction between $RNH_2 + CHCl_3 + KOH$ (alc.) is known as:

a. Coupling reaction
b. Carbylamine reaction
c. Hoffmann bromamide reaction
d. Schmidt reaction

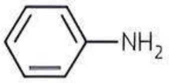
Q 10. The reaction of ammonia with a large excess of methyl chloride will yield mainly: *(CBSE 2023)*

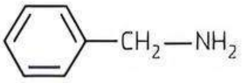
a. methylamine
b. dimethylamine
c. tetramethylammonium chloride
d. trimethylamine

Q 11. The reduction of ethanenitrile with sodium and alcohol gives: *(CBSE 2023)*

a. 1-aminopropane b. 1-aminoethane
c. ethanoic acid d. ethanamide

Q 12. Among the following which has the highest value of pK_b? *(CBSE 2023)*

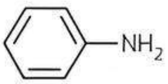
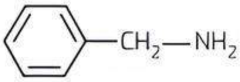
a.


b.


c.


d.


Q 13. **Among the following, which is the strongest base?** *(CBSE 2023)*

a. 
b. 
c. 
d. 

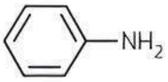
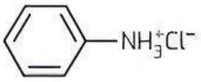
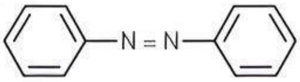
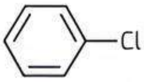
Q 14. **In the nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3, the species which initiate the reaction is ....** *(NCERT EXEMPLAR)*

a. NO_2 b. NO^+ c. NO_2^+ d. NO_2^-

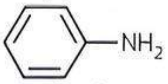
Q 15. **Reduction of nitrobenzene in strongly acidic medium gives the final product as:**

a. aniline b. phenyl hydroxyl amine
c. *p*-aminophenol d. azobenzene

Q 16. **When nitrobenzene is heated with tin and concentrated HCl, the product formed is:** *(CBSE 2023)*

a. 
b. 
c. 
d. 

Q 17. **Which of the following is least basic?** *(CBSE 2023)*

a. $(CH_3)_2NH$ b. NH_3
c.  d. $(CH_3)_3N$

Q 18. **When nitrobenzene is reduced in neutral medium, the product is:**

a. $C_6H_5NH_2$ b. C_6H_5NHOH
c. azobenzene d. *p*-aminophenol

Q 19. **Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride?** *(NCERT EXEMPLAR)*

a. Aniline b. Phenol
c. Anisole d. Nitrobenzene

Q 20. **When benzene diazonium chloride reacts with phenol, it forms a dye. This reaction is called:** *(CBSE 2023)*

a. diazotisation reaction
b. condensation reaction
c. coupling reaction
d. acetylation reaction

Q 21. **Benzene diazonium chloride reacts with phenol in weakly alkaline medium to give:**

a. diphenyl ether b. *p*-hydroxyphenol
c. chlorobenzene d. benzene

Q 22. **Arrange the following in the increasing order of their boiling points:**
A **: Butanamine,** ***B*** **: N, N-Dimethylethanamine,**
C **: N-Ethylethanamine** *(CBSE SQP 2022-23)*

a. $C < B < A$ b. $A < B < C$
c. $A < C < B$ d. $B < C < A$

Q 23. **Out of the following, the strongest base in aqueous solution is:** *(CBSE 2020)*

a. methylamine b. dimethylamine
c. trimethylamine d. aniline

Assertion & Reason Type Questions

Directions (Q. Nos. 24-32): *Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:*

a. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
b. Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
c. Assertion (A) is true but Reason (R) is false.
d. Assertion (A) is false but Reason (R) is true.

Q 24. **Assertion (A):** Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.
Reason (R): Acyl group sterically hinders the approach of further acyl groups.

Q 25. **Assertion (A):** Acetylation of aniline gives a monosubstituted product.
Reason (R): Activating effect of $—NHCOCH_3$ group is more than that of amino group. *(CBSE 2023)*

Q 26. **Assertion (A):** Tertiary amines are more basic than corresponding secondary and primary amines in gaseous state.
Reason (R): Tertiary amines have three alkyl groups which cause +I effect. *(CBSE SQP 2022-23)*

Q 27. **Assertion (A):** Hoffman bromamide reaction is given by primary amines.
Reason (R): Primary amines are more basic than secondary amines.

Q 28. **Assertion (A):** N, N-Diethylbenzene sulphonamide is insoluble in alkali.
Reason (R): Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.

Q 29. **Assertion (A):** $—NH_2$ group is *o*- and *p*-directing in electrophilic substitution reactions.
Reason (R): Aniline cannot undergo Friedel-Crafts reaction. *(CBSE 2023)*

Q 30. **Assertion (A):** Monobromination of aniline can be conveniently done by protecting the amino group by acetylation.
Reason (R): Acetylation decreases the activating effect of the amino group. *(CBSE 2023)*

Q 31. Assertion (A): Aromatic 1° amines can be prepared by Gabriel Phthalimide Synthesis.

Reason (R): Aryl halides do not undergo nucleophilic substitution with anion formed by phthalimide.

Q 32. Assertion (A): $(C_2H_5)_2NH$ is more basic than $(C_2H_5)_3N$ in aqueous solution.

Reason (R): In $(C_2H_5)_2NH$, there is more steric hindrance and +I effect than $(C_2H_5)_3N$. *(CBSE 2023)*

Answers

1. (b) Primary aliphatic amine

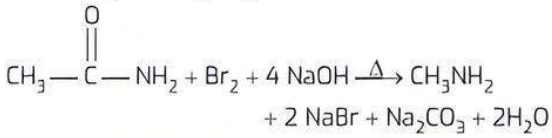
2. (d) ethyl amine

3. (a) Br_2/KOH

4. (d) $(C_6H_5)_3N$

5. (c) Water

6. (b) Reaction of CH_3CONH_2 and Br_2, NaOH in alcoholic medium gives CH_3NH_2.



$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4\,NaOH \xrightarrow{\Delta} CH_3NH_2 + 2\,NaBr + Na_2CO_3 + 2H_2O$$

7. (c) CH_3NH_2 on reaction with nitrous acid releases NO_2 gas

The evolution of nitrogen (N_2) gas takes place when CH_3NH_2 reacts with nitrous acid.

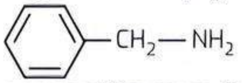
8. (c) $CH_3-NH-CH_3$

9. (b) Carbylamine reaction

10. (c) tetramethylammonium chloride

11. (b) 1-amino ethane

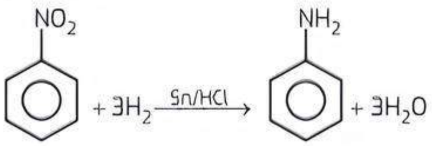
12. (d) Higher is the pK_b value, weaker is the base. Presence of $-NO_2$ group in the ring decreases the basic character as it is an electron withdrawing group. Thus,  will have largest value of pK_b.

13. (c)  is the strongest base among all because the aliphatic amines are more basic than aromatic amines.

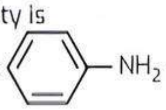
14. (c) NO_2^+

15. (a) aniline

16. (a) The reduction of nitrobenzene with Sn/HCl produces aniline.



17. (b) The +I effect of alkyl groups increases electron density on N atom which further increases the basicity of amines. Hence, the increasing order of basicity is

$NH_3 <$  $< (CH_3)_2\,NH < (CH_3)_3\,N$.

18. (b) C_6H_5NHOH

19. (d) Nitrobenzene

20. (a) Diazotisation reaction

21. (b) *p*-hydroxyphenol

22. (d) $B < C < A$

In primary amine, intermolecular association due to H-bonding is maximum while in tertiary amine, it is minimum. So, N,N-Dimethylethanamine has the least boiling point whereas N-Ethylethanamine has the maximum boiling point.

23. (b) dimethylamine

24. (c) Assertion (A) is true but Reason (R) is false.

25. (c) Acetylation of aniline gives a monosubstituted product Hence assertion is true but reason is false *i.e.*, activating effect of $-NHCOCH_3$ group is less than that of amino group.

26. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).

27. (c) Assertion (A) is true but Reason (R) is false.

28. (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).

29. (b) $-NH_2$ group is *o* and *p*-directing in electrophilic substitution reactions due to excess of electron or negative charge over *o* and *p*-positions because of its various resonating structures.

30. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).

31. (d) Aromatic 1° amines cannot be prepared by Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

32. (a) $(C_2H_5)_2NH$ is more basic than $(C_2H_5)_3N$ in aqueous solution because there is an interplay of the +I effect, solvation effect and steric hindrance of the alkyl group which decides the basic strength of alkyl amines in the aqueous state.

Case Study Based Questions

Case Study 1

Amines constitute one of the most important class of organic compounds. In nature, they occur among vitamins, proteins, alkaloids and hormones. These are the derivatives of ammonia, obtained by the replacement of one, two or three hydrogen atoms by alkyl/aryl groups.

Amines are very reactive due to the difference in electronegativity between nitrogen and hydrogen atoms and due to the presence of unshared pair of electrons over N-atom. The number of hydrogen atoms attached to the N-atom decides the course of reactions of amine, that is why amines differ in many reactions. In aromatic amines like aniline, electron density at *ortho* and *para positions* with respect to NH_2 group is high. Therefore, this group is *ortho* or *para* directing and a powerful activating group.

Read the given passage carefully and give the answer of the following questions:

Q 1. Carbylamine test is done for:

a. detection of NO_2 group

b. confirming the presence of secondary amine

c. confirming the presence of primary amine

d. for confirming the basic nature of $—NH_2$ group

Q 2. Which of the following on reduction with lithium aluminium hydride yields secondary amine?

a. Methyl cyanide b. Nitroethane

c. Methyl isocyanide d. Acetamide

Q 3. Which of the following amines cannot be prepared by Gabriel phthalimide synthesis?

a. Ethylamine b. Isopropyl amine

c. Propylamine d. Ethyl methyl amine

Q 4. The solubility of water for $C_6H_5NH_2$ (I), $(C_2H_5)_2NH$ (II) and $C_2H_5NH_2$ (III) increases in the order:

a. II < III < I b. I < II < III

c. III < II < I d. II < I < III

Answers

1. (d) for confirming the basic nature of $—NH_2$ group
2. (d) Acetamide
3. (c) Propylamine
4. (a) II < III < I

Case Study 2

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl groups. Amines are usually formed from nitro compounds, halides, amides, etc. They exhibit hydrogen bonding which influences their physical properties. Alkyl amines are found to be stronger bases than ammonia. In aromatic amines, electron releasing and withdrawing groups, respectively increase and decrease their basic character. Reactions of amines are governed by availability of the unshared pair of electrons on nitrogen. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. Reactivity of aromatic amines can be controlled by acylation process.

Read the given passage carefully and give the answer of the following questions:

Q 1. Why does aniline not give Friedel-Crafts reaction?

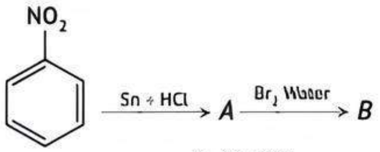
Q 2. Arrange the following in the increasing order of their pK_b values:

$$C_6H_5NH_2, NH_3, C_2H_5NH_2, (CH_3)_3N$$

Q 3. (i) How can you distinguish between $CH_3CH_2NH_2$ and $(CH_3CH_2)_2NH$ by Hinsberg test?

(ii) Write the structures of *A* and *B* in the following reactions:

(a)



$$\text{(b) } CH_3CH_2CONH_2 \xrightarrow{Br_2/\text{alc. KOH}} A \xrightarrow[\text{Pyridine}]{CH_3COCl} B$$

OR

How will you convert the following:

(i) Benzoic acid to aniline

(ii) Aniline to p-bromoaniline

Answers

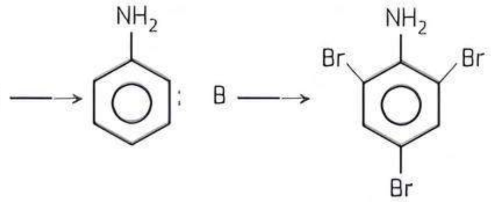
1. Aniline forms salt with the lewis acid catalyst *i.e.*, $AlCl_3$, which is used in Friedel-crafts reaction. Further, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.
2. $C_6H_5NH_2 < NH_3 < C_2H_5NH_2 < (CH_3)_3N$
3. (i) When ethylamine is shaken with benzene sulphonyl chloride (Hinsberg's reagent) and aqueous KOH solution, it gives a clear solution.

$$C_6H_5SO_2Cl + CH_3CH_2NH_2 \longrightarrow C_6H_5SO_2NHCH_2CH_3$$

$$\xrightarrow{KOH} \underset{\text{Potassium salt (Clear solution)}}{[C_6H_5SO_2–N–CH_2CH_3]K} + H_2O$$

While diethylamine is 2° amine, on similar treatment it forms an insoluble substance.

(ii)



$$\text{(b) } A \longrightarrow CH_3CH_2NH_2;\ B \longrightarrow CH_3CH_2NHCOCH_3$$

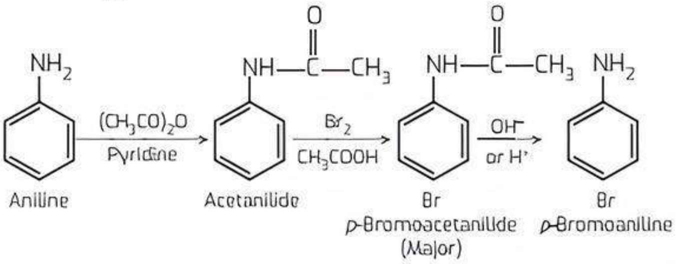
OR

$$\text{(i) } \underset{\text{Benzoic acid}}{C_6H_5COOH} + NaOH \longrightarrow C_6H_5COONa$$

$$\xrightarrow[\text{Dry distillation}]{\text{Sodalime}} C_6H_6$$

$$\xrightarrow[323-333\text{ K}]{\text{conc. }HNO_3/H_2SO_4} C_6H_5NO_2 \xrightarrow[(6H)]{Sn/HCl} \underset{\text{Aniline}}{C_6H_5NH_2}$$

(ii)



Case Study 3

Amines are usually formed from nitro compounds, halides, amides, imides, etc. They exhibit hydrogen bonding which influences their physical properties. In alkyl amines, a combination of electron releasing, steric and hydrogen bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. In aromatic amines, electron releasing and withdrawing groups, respectively increase and decrease their basic character. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. Presence of amino group in aromatic ring enhances reactivity of the aromatic amines. Aryl diazonium salts provide advantageous methods for producing aryl halides, cyanides, phenols and arenes by reductive removal of the diazo group.

Read the given passage carefully and give the answer of the following questions:

Q 1. **Arrange the following in the increasing order of their pK_b values in aqueous solution:**

$C_2H_5NH_2, (C_2H_5)_2NH, (C_2H_5)_3N$

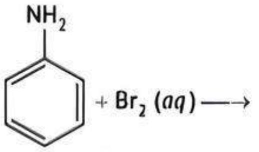
Q 2. **Aniline on nitration gives a substantial amount of *m*-nitroaniline, though amino group is *o/p* directing. Why?**

Q 3. **An aromatic compound '*A*' of molecular formula $C_7H_6O_2$ on treatment with aqueous ammonia and heating forms compound '*B*'. Compound '*B*' on heating with Br_2 and aqueous KOH gives a compound '*C*' of molecular formula C_6H_7N. Write the structures of *A*, *B* and *C*.**

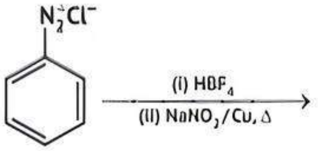
OR

Complete the following reactions giving main products:

(i)



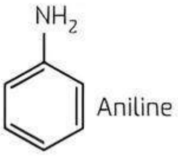
(ii)



(CBSE 2023)

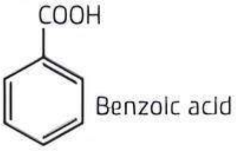
Answers

1. $C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$
2. Nitration is carried out in an acidic medium. In a strongly acidic medium, aniline is protonated to give anilinium ion (which is meta-directing). Hence, it gives a substantial amount of m-nitro aniline on nitration.
3. Compound *C* has the molecular formula C_6H_7N which 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 with the molecular formula, C_6H_7N is aniline i.e., $C_6H_5NH_2$.

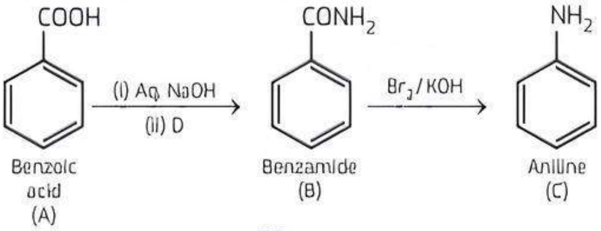


So, the compound *'B'* must be benzamide ($C_6H_5CONH_2$).

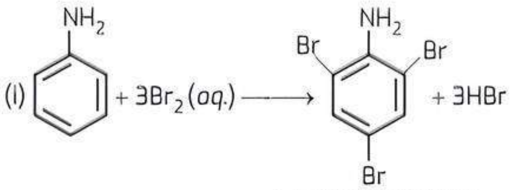
Further, benzamide is formed by heating compound 'A' with aqueous ammonia. Therefore, compound 'A' must be benzoic acid.



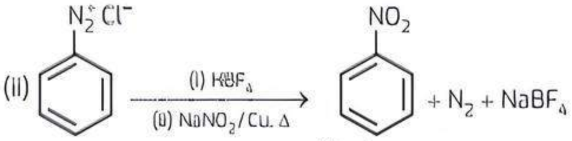
The given reactions are explained as under:



OR



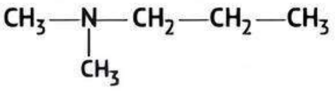
2, 4, 6-Tribromo aniline
(main product)



Nitrobenzene
(main product)

Very Short Answer Type Questions

Q 1. Write the IUPAC name of the following compound:

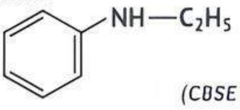


$$CH_3—\underset{\large CH_3}{\underset{|}{N}}—CH_2—CH_2—CH_3$$

(CBSE 2019)

Ans. N, N—dimethyl propanamine.

Q 2. Write the IUPAC name of



(CBSE 2019)

Ans. N—ethylaniline.

Q 3. Write IUPAC name of the following compound:
$(CH_3CH_2)_2NCH_3$ (CBSE 2017)

Ans. N—ethyl, N—methylethanamine.

Q 4. Write IUPAC name of the following compound:
$CH_3NHCH(CH_3)_2$ (CBSE 2017)

Ans. N—methylpropan-2-amine.

Q 5. Write IUPAC name of the following compound:
$(CH_3)_2N—CH_2\ CH_3$ (CBSE 2017)

Ans. N, N—dimethylethanamine.

Q 6. Write chemical equation for the preparation of methyl amine from acetamide.

Ans.
$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH(as) \xrightarrow{\text{Hoffmann bromamide reaction}} CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

Q 7. Complete the following reaction:

$$RX \xrightarrow{KCN} A \xrightarrow{H} B$$

Ans.
$$\underset{\text{Alkyl halide}}{RX} \xrightarrow[(-KX)]{KCN} \underset{\text{Alkyl cyanide}}{\underset{'A'}{RCN}} \xrightarrow{4H} \underset{\text{Alkyl amine}}{\underset{'B'}{RCH_2NH_2}}$$

Q 8. Identify compounds *(A)* and *(B)* in the following reactions and write the related balanced chemical equation:

$$CH_3CONH_2 \xrightarrow[\Delta]{P_2O_5} (A) \xrightarrow[Sn + HCl]{4[H]} (B)$$

Ans.
$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\Delta\ (-H_2O)]{P_2O_5} \underset{(A)}{\underset{\text{Methyl cyanide}}{CH_3CN}}$$

$$\xrightarrow[Sn + HCl]{4(H)} \underset{(B)}{\underset{\text{Ethylamine}}{CH_3CH_2NH_2}}$$

Q 9. What happens when $R—N \equiv C$ is hydrolysed? (write chemical equation only)

Ans. Primary amine and formic acid are formed.

$$R—N \equiv C + 2H_2O \xrightarrow{H^+} \underset{1^\circ \text{ amine}}{RNH_2} + \underset{\text{Formic acid}}{HCOOH}$$

Q 10. Arrange in the following order:

(i) Arrange in the decreasing order of basicity:
$p\text{-}H_2N—C_6H_4—NH_2$, $m\text{-}H_2N—C_6H_4—NH_2$ and $C_6H_5NH_2$

(ii) Arrange in increasing order of basicity:
CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3\ N$

Ans. (i) $C_6H_5NH_2 < m\text{-}H_2N—C_6H_4—NH_2 < p\text{-}H_2N—C_6H_4—NH_2$

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

Q 11. Complete the following chemical reaction:

(i) $C_2H_5NH_2 + CS_2 + HgCl_2 \xrightarrow{Heat} .... + HgS + HCl$

(ii) $R—NH_2 + CHCl_3 + 3KOH\ (alc.) \xrightarrow{Heat} ...... + KCl + H_2O$

Ans. (i)
$$C_2H_5NH_2 + CS_2 + HgCl_2 \xrightarrow{Heat} \underset{\text{(Hoffmann mustard oil reaction)}}{\underset{\text{Ethyl isothicyanate}}{C_2H_5NCS}} + HgS + HCl$$

(ii)
$$R—NH_2 + CHCl_3 + 3KOH\ (alc.) \xrightarrow{Heat} R—NC + 3KCl + H_2O$$

Q 12. Complete the following chemical reaction:

$$C_2H_5NH_2 \xrightarrow{HNO_2} 'A' \xrightarrow{'B'} CH_3COOC_2H_5$$

Write the names of *A* and *B*.

Ans.
$$C_2H_5NH_2 \xrightarrow{HNO} \underset{'A'}{\underset{\text{Ethanol}}{C_2H_5OH}} \xrightarrow[\text{(in the presence of conc. } H_2SO_4)]{CH_3COOH\ 'B'} CH_3COOC_2H_5$$

'A' ⟶ Ethanol and 'B' ⟶ Acetic acid.

Q 13. Confirm the presence of $—NH_2$ group in the organic compounds with the help of carbylamine test.

Ans. All the organic compounds having $—NH_2$ group give carbylamine reaction. When an organic compound having $—NH_2$ group is heated with chloroform and alcoholic KOH solution, it releases a bad smelling gas, called isocyanide or carbylamine. This reaction is called carbylamine reaction and is used to confirm the presence of $—NH_2$ group in the organic compound.

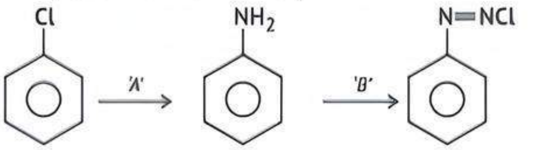
$$CH_3CH_2NH_2 + CHCl_3 + 3KOH\ (alc.) \longrightarrow \underset{\text{Ethyl isocyanide}}{CH_3CH_2NC} + 3KCl + 3H_2O$$

Q 14. Write the reaction of reduction of nitrobenzene in neutral medium.

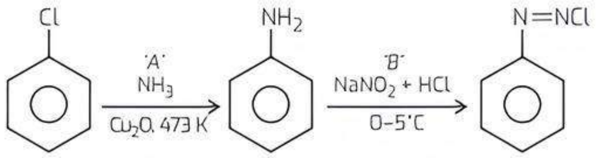
Ans. When nitrobenzene is reduced by zinc and ammonium chloride or calcium chloride *i.e.*, in neutral medium, it forms N-phenyl hydroxylamine.

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 4(H) \xrightarrow[\text{or } Zn + CaCl_2]{Zn + NH_4Cl,\ H_2O} \underset{\text{N-phenylhydroxylamine}}{C_6H_5NHOH}$$

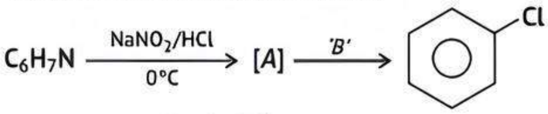
Q 15. Complete the chemical equation:



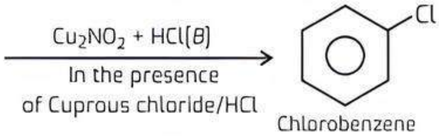
Ans.



Q 16. Identify compounds [*A*] and [*B*] in the following reactions and write their names:



Ans. $\underset{\text{Aniline}\ (C_6H_7N)}{C_6H_5NH_2} \xrightarrow[0^\circ C]{NaNO_2/HCl} \underset{\text{Benzene diazonium chloride}[A]}{C_6H_5\overset{+}{N}\equiv N\overset{-}{Cl}}$



Chlorobenzene

Q 17. How will you convert Ar—NH$_2$ into ArN $\equiv$ C?

Ans. It can be accomplished by warming Ar—NH$_2$ with chloroform and alcoholic KOH. As a result, *t* = ArN $\equiv$ C is formed.

The reaction is known as carbylamine reaction.

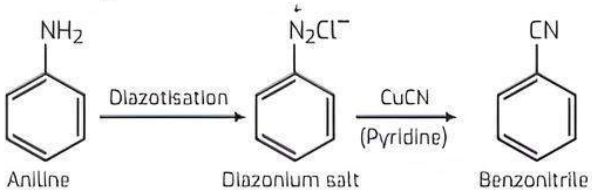
$$ArNH_2 + CHCl_3 + 3\ KOH(alc.) \xrightarrow{(Warm)} \underset{\text{Aryl carbylamine}}{ArN \equiv C} + 3KCl + 3H_2O$$

Q 18. How will you convert nitrobenzene to aniline?

Ans. $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6(H) \xrightarrow[\text{(reduction)}]{Sn/HCl} \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$

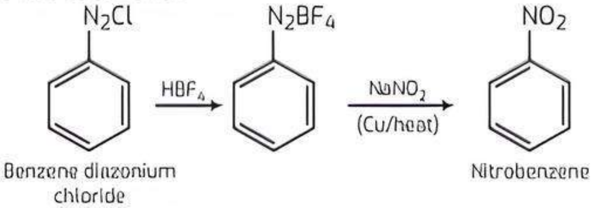
Q 19. How will you convert aniline to benzonitrile?

Ans.



Q 20. How will you convert benzene diazonium chloride to nitrobenzene?

Ans.



Q 21. How will you convert ethanamide to methanamine?

Ans. $\underset{\text{Ethanamide}}{CH_3—\overset{O}{\overset{\|}{C}}—NH_2} + Br_2 + 4KOH \xrightarrow{Heat} \underset{\text{Methanamine}}{CH_3NH_2} + 2KBr + K_2CO_3 + 2H_2O$

Q 22. What happens when nitroethane is boiled with dilute HCl?

Ans. Nitroethane gets hydrolysed to give a mixture of acetic acid and hydroxylamine.

$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} + H_2O \xrightarrow{HCl} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Hydroxylamine}}{NH_2OH}$$

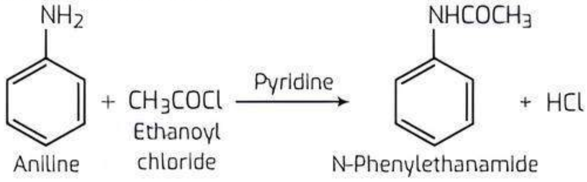
Q 23. What happens when nitrobenzene is treated with Sn/HCl?

Ans. Aniline is formed by reduction of nitrobenzene.

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6(H) \xrightarrow{Sn/HCl} \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$$

Q 24. How will you convert aniline into N-phenylethanamide?

Ans.



Q 25. What are the products of exhaustive ammonolysis of an alkyl halide? *(CBSE 2019)*

Ans. Mixture of amines (RNH$_2$, R$_2$NH, R$_3$N) including quaternary ammonium salts $(R_4\overset{+}{N}\overset{-}{X})$ are the products of exhaustive ammonolysis of an alkyl halide.

Short Answer Type-I Questions

Q 1. What are amines? Give one example of each primary, secondary and tertiary amines and write their general names.

Ans. **Amines:** Alkyl or aryl derivatives of ammonia are called amines. These are derived by substituting hydrogen atoms from ammonia by alkyl (R—) or aryl (Ar—) groups.

$$\underset{\text{Ammonia}}{NH_3} \xrightarrow[-HX]{RX} \underset{\text{Primary amine}}{RNH_2} \xrightarrow[-HX]{RX} \underset{\text{Secondary amine}}{R_2NH} \xrightarrow[-HX]{RX} \underset{\text{Tertiary amine}}{R_3N}$$

Thus, in primary amines alkyl or aryl group is attached with —NH$_2$ groups, *e.g.*, CH$_3$—NH$_2$ (methyl amine). In case of secondary amines, a group is present in between two alkyl or aryl groups. *e.g.*, CH$_3$—NH—CH$_3$ or (CH$_3$)$_2$NH, (dimethyl amine). In case of tertiary amines, three alkyl or aryl groups are attached with group *e.g.*, (CH$_3$)$_3$N or $CH_3—\underset{\underset{CH_3}{|}}{N}—CH_3$

(trimethylamine)

Thus, amines are of three types: Primary amines, secondary amines and tertiary amines.

Q 2. How will you obtain? (Give only chemical equations)

(i) Methyl amine from acetamide.

(ii) Ethyl amine from propionic acid.

(i) $\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH(aq) \xrightarrow[-K_2CO_3,\ -2H_2O]{-2KBr,} \underset{\text{Methylamine}}{CH_3NH_2}$

(ii) $\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow{NH_3} CH_3CH_2COONH_4 \xrightarrow[-H_2O]{\Delta}$

$$CH_3CH_2CONH_2 \xrightarrow[-2KBr,\ -H_2O,\ -K_2CO_3]{Br_2 + 4KOH(aq)} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

Q 3. Ethylamine exhibits basic nature, why ? Explain.

Ans. Ethylamine is an ethyl derivative of ammonia, which acts as a Lewis base due to the presence of lone pair of electrons on nitrogen atom. This lone pair combines with a proton to form bond. Similarly, in ethyl amine +*I* effect of alkyl (ethyl) group, increases the electron density at *N* atom. Thus, the tendency of *N* atom of ethyl amine to give its lone pair is more, hence it exhibits basic character and is more basic than ammonia.

$$:NH_3 + H^+ \longrightarrow \overset{+}{N}H_4$$

$$R—\ddot{N}H_2 + H^+ \longrightarrow R—\overset{+}{N}H_3$$

Q 4. Arrange the following in increasing order of their basic strength:

(i) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$

(ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_6H_5NH_2$

Ans. (i) $C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

(ii) $C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$

Q 5. Write two tests of aniline.

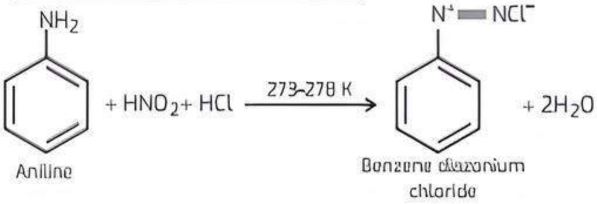
Ans. Tests for Aniline:

(i) Aniline is cooled and to it cold aqueous solution of $NaNO_2$ and dilute HCl is added. When naphthol is added to this solution, orange colour dye is formed.

(ii) On adding bromine water to aniline, pale yellow precipitate is formed.

Q 6. Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid. *(NCERT EXERCISE)*

Ans. Aromatic primary amines react with HNO_2 at 273-278 K to give aromatic diazonium salt.



Aliphatic primary amines react with HNO_2 at 273-278 K to form aliphatic diazonium salt, which being unstable at low temperature, readily decomposes to give a mixture of alkyl chloride, alkane and alcohol, among which alcohol (in general) is in excess.

$$\underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + NaNO_2 + HCl \xrightarrow{273-278\ K}$$

$$\underset{\substack{\text{Ethane diazonium chloride}\\\text{(unstable)}}}{(CH_3CH_2—\overset{+}{N}\equiv N)Cl^-} \xrightarrow{H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH} + N_2\uparrow + HCl$$

Q 7. Explain briefly:

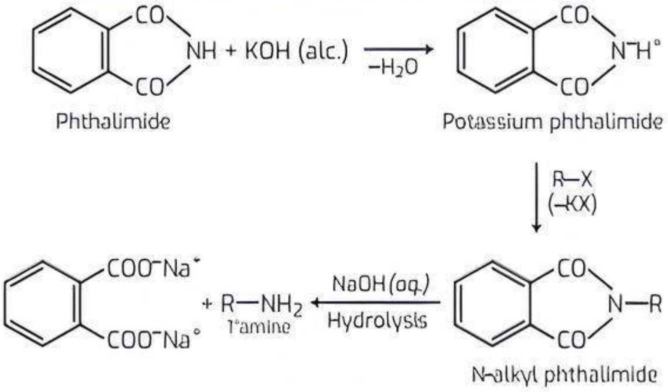
(i) Carbylamine reaction

(ii) Gabriel phthalimide synthesis *(CBSE 2023)*

Ans. (i) Carbylamine reaction: When an organic compound having —NH_2 group is heated with chloroform and alcoholic KOH solution, it releases a bad smelling gas called isocyanide or carbylamine. This reaction is called carbylamine reaction and it is used to confirm the presence of —NH_2 group in the organic compound.

$$CH_3CH_2NH_2 + CHCl_3 + 3KOH\ (alc.) \longrightarrow \underset{\text{Ethyl isocyanide}}{CH_3CH_2NC} + 3KCl + 3H_2O$$

(ii) Gabriel phthalimide synthesis: When a phthalimide is treated with alcoholic KOH, it forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis forms corresponding primary amines as:



Primary amines are produced through this method without the traces of secondary or tertiary amines. So, this method is preferred for the synthesis of primary amines.

Q 8. How do you prepare chlorobenzene by preparing benzene diazonium chloride from aniline? Explain by giving all the chemical reactions.

Ans. Benzene diazonium chloride is prepared by the diazotisation of aniline by $NaNO_2$ and HCl at 0-5° C. Its chemical reaction is as follows:

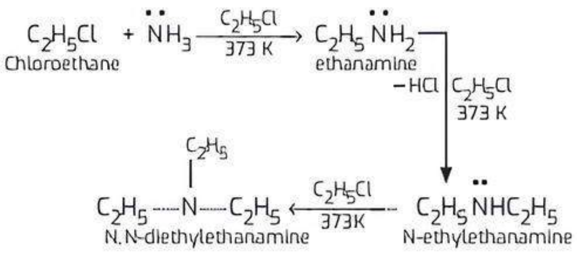
$$\underset{\text{Aniline}}{C_6H_5NH_2} + NaNO_2 + 2HCl \xrightarrow{0\ to\ 5^\circ C} \underset{\text{Benzene diazonium chloride}}{C_6H_5N_2Cl} + NaCl + 2H_2O$$

This benzene diazonium chloride is converted into chlorobenzene by Sandmeyer's reaction in the presence of Cu_2Cl_2 with HCl. The chemical equation of the above reaction is as follows:

$$C_6H_5N_2Cl + HCl \xrightarrow[\Delta]{Cu_2Cl_2} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + N_2\uparrow + HCl$$

Q 9. Write chemical equation for the formation of N, N-diethylethanamine from chloroethane.

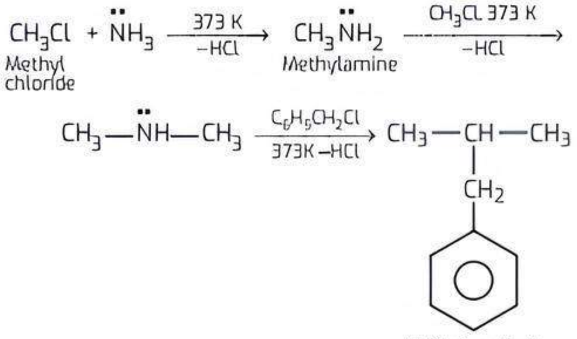
Ans.



$$\underset{\text{Chloroethane}}{C_2H_5Cl} + \ddot{N}H_3 \xrightarrow[373\,K]{C_2H_5Cl} \underset{\text{ethanamine}}{C_2H_5\ddot{N}H_2} \xrightarrow[373\,K]{C_2H_5Cl,\ -HCl} \underset{\text{N-ethylethanamine}}{C_2H_5\ddot{N}HC_2H_5} \xrightarrow[373K]{C_2H_5Cl} \underset{\text{N, N-diethylethanamine}}{(C_2H_5)_3N}$$

Q 10. Write chemical equation for the formation of N, N-dimethylphenylmethanamine from methyl chloride.

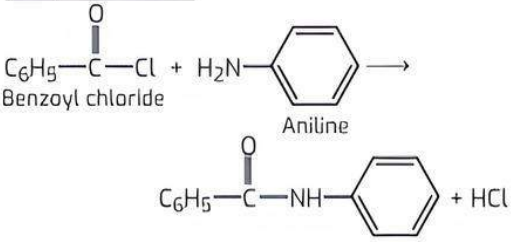
Ans.



N, N-dimethyl-phenylmethanamine

Q 11. Write the chemical reaction of aniline with benzoyl chloride and write the name of the product obtained. *(NCERT INTEXT)*

Ans. Aniline will undergo benzoylation to form benzoyl derivative. The reaction will take place in the presence of aqueous alkali.



N-phenylbenzamide (Benzanilide)

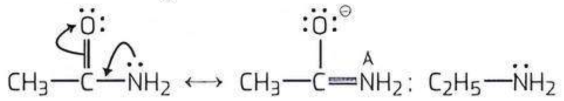
Q 12. Why are alkylamines stronger bases than arylamine?

Ans. Alkylamines $(R-\ddot{N}H_2)$ are stronger bases than arylamines $(C_6H_5-\ddot{N}H_2)$ because in the latter, the basic strength is considerably reduced due to conjugation as well as −I effect of phenyl group. Actually the electron pair on the N atom of $-NH_2$ group is involved in conjugation with the π–electron pairs of the ring. Therefore, the basic character of arylamines is reduced.

Q 13. Why is acetamide a weaker base than ethylamine?

Ans. Acetamide is a weaker base than ethylamine because of the presence of electron withdrawing carbonyl group in acetamide. It reduces the electron density on the nitrogen atom considerably thereby reducing the basic strength.

However, no such group is present in ethylamine and it is a stronger base than acetamide.



Q 14. Complete and name the following reaction:

(i) $RNH_2 + CHCl_3 + 3KOH \longrightarrow$

(ii) $RCONH_2 + Br_2 + 4NAOH \longrightarrow$

Ans. (i) $$RNH_2 + CHCl_3 + 3KOH\ (alc.) \xrightarrow{(Warm)} \underset{\text{Alkyl isocyanide}}{RN \equiv C} + 3KCl + 3H_2O$$

The reaction is known as **carbylamine reaction.**

(ii) $$\underset{\text{Acid amide}}{RCONH_2} + Br_2 + 4NaOH\ (alc.) \xrightarrow{Heat} \underset{\text{Primary amine}}{RNH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

The reaction is known as **Hoffmann's bromamide reaction**.

Q 15. How will you convert an isocyanide to a secondary amine?

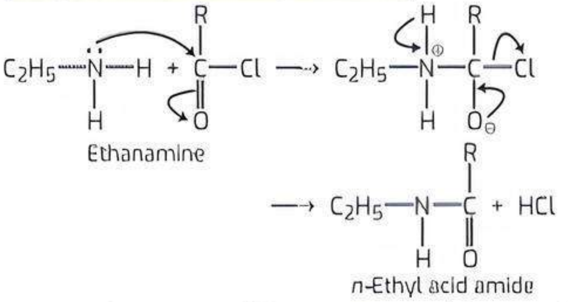
Ans. It can be done by carrying out the reduction of alkyl isocyanide with a reducing agent like $LiAlH_4$.

$$\underset{\text{Alkyl isocyanide}}{R-N \equiv C} \xrightarrow[\text{(Reduction)}]{LiAlH_4} \underset{\text{Secondary amine}}{R-NH-CH_3}$$

$$\underset{\text{Methyl isocyanide}}{CH_3-N \equiv C} \xrightarrow[\text{(Reduction)}]{LiAlH_4} \underset{\text{Dimethylamine}}{CH_3-NH-CH_3}$$

Q 16. Give the mechanism of acylation of ethanamine and write the IUPAC name of the product formed.

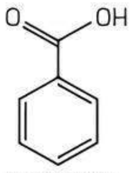
Ans. Mechanism of acylation of ethanamine is nucleophilic in nature. The amine donates the electron pair on the nitrogen atom for nucleophilic attack.



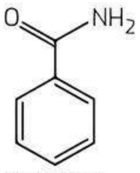
Q 17. An aromatic compound (*A*) on treatment with ammonia followed by heating forms compound (*B*) which on heating with Br_2 and KOH forms a compound (*C*) having molecular formula C_6H_7N. Give the structures of *A*, *B* and *C* and write the reactions involved.

Ans. The chemical formula C_6H_7N for the compound (*C*) is for aniline. The compound (*B*) which gives aniline on reacting with Br_2 and KOH (Hoffmann Bromamide reaction) is benzamide. The compound (*A*) is benzoic acid and forms (*B*) on heating with ammonia.

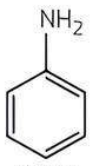
The structures of A, B and C are—



Benzoic acid
(A)



Benzamide
(B)

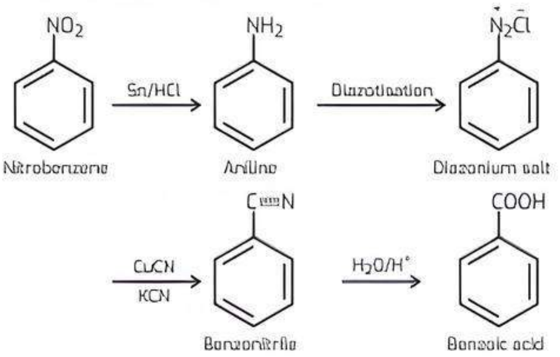


Aniline
(C)

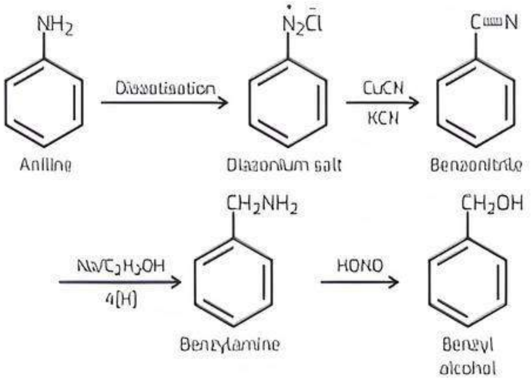
and the reaction involved is as under—

Q 18. How will you convert: (i) Nitrobenzene to benzoic acid (ii) Aniline to benzyl alcohol.

Ans. (i)



(ii)



Q 19. Give reasons for the following:

(i) *o*-toluidine is less basic than aniline.

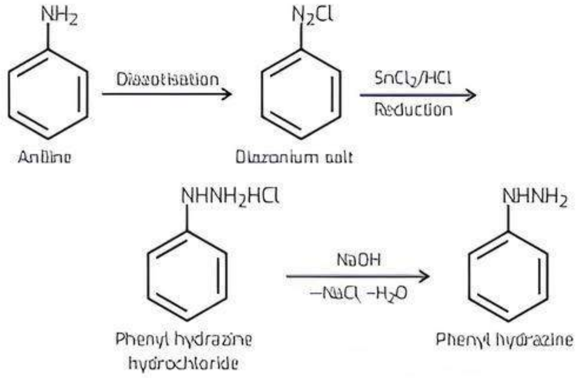
(ii) Tertiary amines do not undergo acylation reaction.

Ans. (i) In *o*-toluidine, the presence of electron releasing CH_3 group at the *ortho* position in the ring increases the electron density on the nitrogen atom of $—NH_2$ group in aniline. As a result, *o*-toluidine is expected to be more basic than aniline. However, it is less basic. The K_b value for aniline is 4.2×10^{-10} while that of *o*-toluidine is 3×10^{-10}. This is probably due to *o*-effect of the CH_3 group present at the ortho position in the ring. However, exact explanation is not clear.

(ii) Tertiary amines (R_3N) do not have replaceable hydrogen atom. Therefore, they do not undergo acylation reaction with either acid chlorides or acid anhydrides.

Q 20. How will you convert aniline to phenyl hydrazine?

Ans.



Short Answer Type-II Questions

Q 1. Arrange the following:

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

(ii) In increasing order of basic strength:
$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(iii) In increasing order of basic strength:
(a) Aniline, *p*-nitroaniline and *p*-toluidine.
(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$

(iv) In decreasing order of basic strength in gaseous phase:
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(v) In increasing order of boiling point:
C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

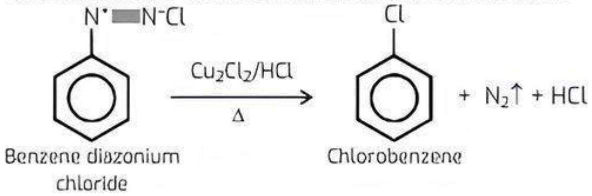
(vi) In increasing order of solubility in water:
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$ *(NCERT EXERCISE)*

Ans. (i) $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$
(ii) $(C_2H_5)_2NH > CH_3NH_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2$
(iii) (a) *p*-nitroaniline > aniline < *p*-toluidine
(b) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$
(iv) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
(v) $(CH_3)_2NH < C_2H_5\ NH_2 < C_2H_5OH$
(vi) $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

Q 2. What is diazonium salt? Write the chemical reaction of preparation of chlorobenzene from benzene diazonium chloride.

Ans. **Diazonium salt** is the most reactive derivative of aromatic primary amines. Their general formula is $ArN_2^+ X$ (*i.e.*, $Ar\overset{+}{N}\equiv NCl^-$) where Ar is an aryl group and $X^- = Cl^-, Br^-, I^-, HSO_4^-, BF_4^-$ etc. In these salts $-\overset{+}{N}\equiv N$ group is called **diazonium group**. If this group is attached with a hydrocarbon, it is named by adding suffix diazonium followed by the name of anion present. *e.g.*, $C_6H_5N_2Cl$ is named as benzene diazonium chloride.

Chlorobenzene from benzene diazonium chloride:



Q 3. How will you convert (Give only chemical equation):

(i) Propanamide to ethylamine

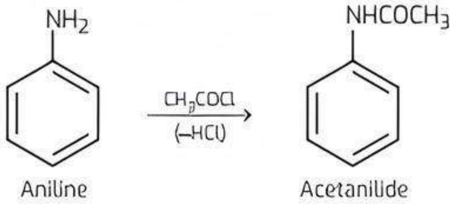
(ii) Ethyl amine to methane

(iii) Aniline to acetanilide.

Ans. (i) $\underset{\text{Propanamide}}{CH_3CH_2CONH_2} \xrightarrow[\substack{(-2KBr, \\ -K_2CO_3, \\ -2H_2O}]{Br_2 + 4KOH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$

(ii) $\underset{\text{Ethylamine}}{C_2H_5NH_2} + \underset{\substack{\text{Grignard} \\ \text{reagent}}}{CH_3MgX} \longrightarrow \underset{\text{Methane}}{CH_4} + C_2H_5NHMgX$

(iii)



Q 4. Complete the following reactions *i.e.*, identify *A*, *B*, *C*, *D*, *E* and *X*.

(i) $C_6H_5CONH_2 \xrightarrow{Br_2/KOH} A \xrightarrow[0\text{-}5°C]{NaNO_2/HCl} B$

$\xrightarrow{steam} C \xrightarrow[conc.\ HNO_3]{conc. H_2SO_4} D$

(ii) $A \xrightarrow{HNO_2} C_2H_5OH \xrightarrow{[O]} B$, identify A and B.

Write their formula and name.

(iii) $CH_3CN \xrightarrow{A} CH_3COOH$, identify A.

(iv) $C_6H_5CONH_2 \xrightarrow{P_2O_5} A \xrightarrow[H^+]{H_2O} B$

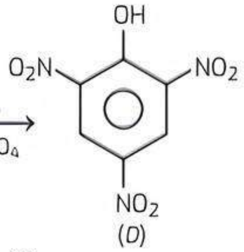
(v) $C_6H_5NO_2 \xrightarrow{Fe/HCl} C \xrightarrow{NaNO_2 + conc.\ HCl}$

$D \xrightarrow{H_2O/H^+} E$

(vi) $C_6H_5NH_2 \xrightarrow{NaNO_2 + HCl} A \xrightarrow{CuCN/KCN} B$

Ans. (i) $C_6H_5CONH_2 \xrightarrow[\substack{(-2KBr, \\ -2H_2O, \\ -K_2CO_3)}]{Br_2/KOH} \underset{(A)}{C_6H_5NH_2} \xrightarrow[0°C]{NaNO_2/HCl} \underset{(B)}{C_6H_5N_2Cl}$

$\xrightarrow[-N_2, -HCl]{H_2O\ (Steam)} \underset{(C)}{C_6H_5OH} \xrightarrow[\substack{\text{and conc. } H_2SO_4 \\ (-3\ H_2O)}]{\text{conc. } 3HNO_3}$



(D)

(ii) $\underset{\substack{(A) \\ \text{Ethyl amine}}}{C_2H_5NH_2} \xrightarrow{HNO_2} C_2H_5OH \xrightarrow[(Ag)]{(O)} \underset{\substack{(B) \\ \text{Acetaldehyde}}}{CH_3CHO}$

(iii) $CH_3CN \xrightarrow[(A)]{2H_2O/H^+} CH_3COOH$ (A dilute mineral acid)

(iv) $C_6H_5CONH_2 \xrightarrow{P_2O_5} \underset{(A)}{C_6H_5CN} \xrightarrow{H_2O/H^+} \underset{(B)}{C_6H_5COOH}$

(v) $C_6H_5NO_2 \xrightarrow{Fe/HCl} \underset{(C)}{C_6H_5NH_2} \xrightarrow[0\text{-}5°C]{NaNO_2 + conc.\ HCl}$

$\underset{(D)}{C_6H_5N_2Cl} \xrightarrow{H_2O/H^+} \underset{(E)}{C_6H_5OH}$

(vi) $C_6H_5NH_2 \xrightarrow[0\text{-}5°C]{NaNO_2 + HCl} \underset{(A)}{C_6H_5N_2Cl}$

$\xrightarrow{CuCN/KCN} \underset{(B)}{C_6H_5CN}$

Q 5. How will you convert:

(i) Ethanoic acid to methanamine

(ii) Hexanenitrile into 1-aminopentane

(iii) Methanol into ethanoic acid

(iv) Ethanamine into methanamine

(v) Ethanoic acid into propanoic acid

(vi) Methanamine to ethanamine

Ans. (i) Conversion of ethanoic acid into methanamine:

$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{SOCl_2} \underset{\text{Ethanoyl chloride}}{CH_3COCl} \xrightarrow{NH_3\ (excess)}$

$\underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[\substack{\text{Hoffmann bromamide} \\ \text{reaction}}]{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$

(ii) Conversion of hexanenitrile into 1-aminopentane:

$\underset{\text{Hexanenitrile}}{CH_3(CH_2)_4CN} \xrightarrow[\substack{\text{Partial} \\ \text{hydrolysis}}]{H_3O^+} \underset{\text{Hexanoic acid}}{CH_3(CH_2)_4COOH} \xrightarrow{SOCl_2}$

$\underset{\text{Hexanoyl chloride}}{CH_3(CH_2)_4COCl} \xrightarrow{NH_3\ (excess)} \underset{\text{Hexanamide}}{CH_3(CH_2)_4CONH_2}$

$\xrightarrow[\substack{\text{Hoffmann bromamide} \\ \text{reaction}}]{Br_2/KOH} \underset{\text{1-aminopentane}}{CH_3(CH_2)_4NH_2}$

(iii) Conversion of methanol into ethanoic acid:

$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{(P/Cl_2)} \underset{\text{Chloromethane}}{CH_3Cl} \xrightarrow{KCN\ (alc.)}$

$\underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow[\text{(Hydrolysis)}]{H_3O^+} \underset{\text{Ethanoic acid}}{CH_3COOH}$

(iv) Conversion of ethanamine into methanamine:

$\underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow[-N_2, -H_2O]{HONO} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{(Oxidation)}]{K_2Cr_2O_7/H_2SO_4}$

$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[\text{(Oxidation)}]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Ethanoic acid}}{CH_3COOH}$

$$\xrightarrow{NH_3} \underset{\text{Ammonium acetate}}{CH_3COONH_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}$$

$$\xrightarrow[\text{Hofmann bromamide reaction}]{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(v) Conversion of ethanoic acid into propanoic acid:

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\text{Reduction}]{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{or } PI_3]{P/I_2} \underset{\text{Iodomethane}}{CH_3CH_2I}$$

$$\xrightarrow[KI]{KCN} \underset{\text{Propanenitrile (ethyl cyanide)}}{CH_3CH_2CN} \xrightarrow[\text{Hydrolysis}]{H\ /H\ O} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

(vi) Conversion of methanamine into ethanamine:

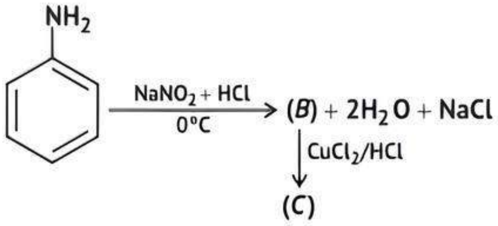
$$\underset{\text{Methanamine}}{CH_3NH_2} \xrightarrow[-N_2,\ H_2O]{HONO} \underset{\text{Methanol}}{CH_3CH_2OH} \xrightarrow[\text{or } PI_3]{P/I_2}$$

$$\underset{\text{Iodomethane}}{CH_3I} \xrightarrow[-KI]{KCN} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow[\text{Reduction}]{Na/C_2H_5OH} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$$

Q 6. Identify *A*, *B* and *C* in the following equations:

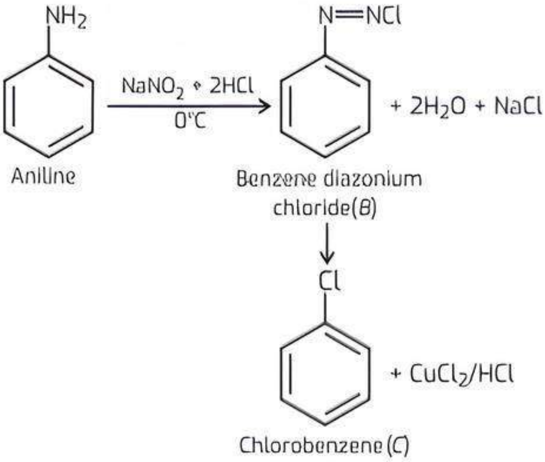
(i) $C_6H_5NO_2 \xrightarrow[6[H]]{Sn/HCl} (A) + H_2O$

(ii)



Ans. (i) $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow[Sn/HCl]{6[H]} \underset{\text{Aniline }(A)}{C_6H_5NH_2} + 2H_2O$

(ii)



Q 7. Give reasons for any three of the following observations:

(i) Aniline is acetylated before nitration reaction.

(ii) pK_b of aniline is lower than the *m*-nitroaniline.

(iii) Primary amine on treatment with benzenesulphonyl chloride forms a product which is soluble in NaOH however secondary amine gives product which is insoluble in NaOH.

(iv) Aniline does not react with methyl chloride in the presence of anhydrous $AlCl_3$ catalyst.

(CBSE SQP 2022-23)

Ans. (i) Aniline is acetylated before nitration reaction in order to avoid formation of tarry oxidation products and protecting the amino group, so that *p*-nitro derivative can be obtained as major product.

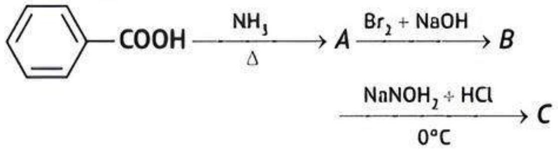
(ii) pK_b of aniline is lower than m-nitro aniline. The basic strength of aniline is more than m-nitroaniline and pK_b value is inversely proportional to basic strength. Presence of electron withdrawing group on *m*-nitro aniline decreases the basic strength thereby raising its pK_b.

(iii) Due to the presence of acidic hydrogen in the product *n*-alkylbenzenesulphonamide formed by the treatment of primary amines with benzene sulphonyl chloride. It is soluble in NaOH but the product formed by secondary amine is insoluble in NaOH due to the absence of acidic hydrogen.

(iv) Aniline does not react with methyl chloride in the presence of $AlCl_3$ catalyst, because aniline is a base and $AlCl_3$ is Lewis acid which lead to the formation of salt.

Q 8. Write the structures of *A*, *B* and *C* in the following reactions:

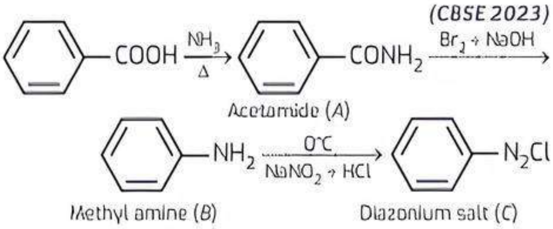
(i)



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

(CBSE 2023)

Ans. (i)



(ii) $CH_3CH_2Br \xrightarrow{KCN} \underset{\text{Ethyl cyanide }(A)}{CH_3CH_2CN} \xrightarrow{LiAlH_4} \underset{\text{Propanamine }(B)}{CH_3CH_2CH_2NH_2}$

$$\xrightarrow[HNO_2/0°C]{} \underset{\text{Propanol }(C)}{CH_3CH_2CH_2OH}$$

Q 9. Account for the following:

(i) Aniline cannot be prepared by the ammonolysis of chlorobenzene under normal conditions.

(ii) N-ethylethanamine boils at 329.3K and butanamine boils at 350.8K, although both are isomeric in nature.

(iii) Acylation of aniline is carried out in the presence of pyridine. *(CBSE SQP 2022 Term-2)*

Ans. (i) In case of chlorobenzene, the C—Cl bond is quite difficult to break as it acquires a partial double bond character due to conjugation. So under the normal conditions, ammonolysis of chlorobenzene does not yield aniline.

(ii) Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and hydrogen of another molecule. Due to the presence of three hydrogen atoms, the intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it. Thus, butanamine boils at 350.8 K while N-ethylethanamine boils at 329.3 K.

(iii) During the acylation of aniline, stronger base pyridine is added. This is done in order to remove the HCl so formed during the reaction and to shift the equilibrium to the right hand side.

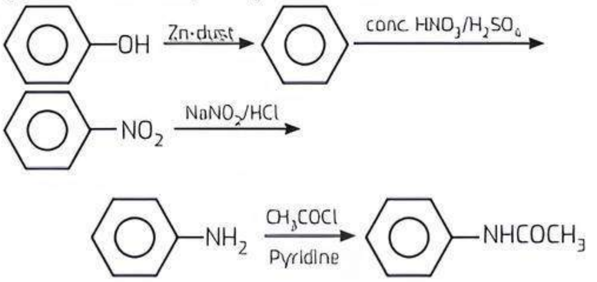
Q 10. Convert the following:

(i) Phenol to N-phenylethanamide.

(ii) Chloroethane to methanamine.

(iii) Propanenitrile to ethanol. *(CBSE SQP 2022 Term-2)*

Ans. (i) Phenol to N-phenylethanamide:



(ii) Chloroethane to methanamine:

$$C_2H_5Cl \xrightarrow{aq.\ NaOH} C_2H_5OH \xrightarrow{KMnO_4} CH_3COOH \xrightarrow{NH_3/heat} CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2$$

(iii) Propanenitrile to ethanol:

$$CH_3CH_2CN \xrightarrow{H_3O^+} CH_3CH_2CONH_2 \xrightarrow{Br_2/KOH} CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow{PCC} CH_3CHO$$

Q 11. What happens when reactions:

(i) N-ethylethanamine reacts with benzenesulphonyl chloride.

(ii) Benzylchloride is treated with ammonia followed by the reaction with chloromethane.

(iii) Aniline reacts with chloroform in the presence of alcoholic potassium hydroxide.

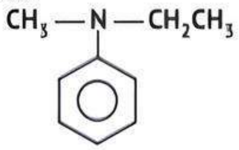
(CBSE SQP 2022 Term-2)

Ans. (i) When N-ethylethanamine reacts with benzenesulphonyl chloride, N,N-diethylbenzenesulphonamide is formed.

(ii) When benzylchloride is treated with ammonia, benzylamine is formed which on reaction with chloromethane yields a secondary amine, N-methylbenzylamine.

(iii) When aniline reacts with chloroform in the presence of alcoholic potassium hydroxide, phenyl isocyanide or phenyl isonitrile is formed.

Q 12. (i) Write the IUPAC name for the following organic compound:



(ii) Complete the following:

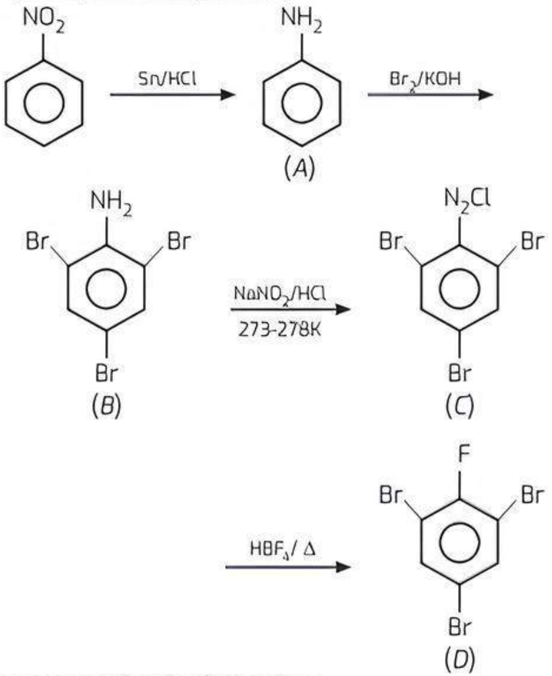
$$C_6H_5NO_2 \xrightarrow{Sn/HCl} A \xrightarrow{Br_2/H_2O} B \xrightarrow[273-278K]{NaNO_2/HCl} C \xrightarrow[\Delta]{HBF_4} D$$

(CBSE SQP 2022 Term-2)

Ans. (i) N-ethyl-N-methylbenzenamine

Or N-ethyl-N-methylaniline.

(ii)



Q 13. Write reasons for the following:

(i) Ethylamine is soluble in water whereas aniline is insoluble.

(ii) Amino group is *o* and *p*-directing in aromatic electrophilic substitution reactions, but aniline on nitration gives a substantial amount of *m*-nitroaniline.

(iii) Amines behave as nucleophiles. *(CBSE 2022 Term-2)*

Ans. (i) Ethylamine when added to water forms intermolecular H-bonds with water. Hence, it is soluble in water. But aniline can form H-bonding with water to a very small extent due to the presence of a large hydrophobic —C_6H_5 group. Hence, aniline is insoluble in water.

(ii) Nitration is carried out in an acidic medium, aniline is protonated to give anilinium ion which is *m*-directing. For this reason, aniline on nitration gives a substantial amount of *m*-nitroaniline.

(iii) A nucleophile is a substance that is attracted to and then attacks, a positive or slightly positive part of another molecule or ion. All amines contain an active lone pair of electrons on the very electronegative nitrogen atom. It is these electrons that are attracted to positive parts of other molecules or ions.

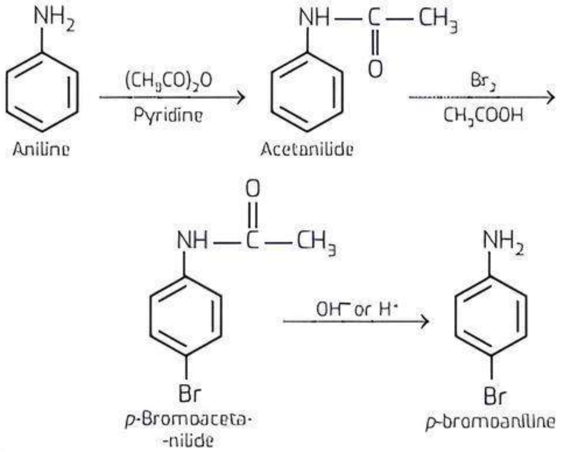
Q 14. How will you convert the following:

(i) Aniline to *p*-bromoaniline

(ii) Ethanoic acid to methanamine

(iii) Butanenitrile to 1-aminobutane *(CBSE 2023)*

Ans. **(i) Aniline to *p*-bromoaniline:**



(ii) Ethanoic acid to methanamine:

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{SOCl_2} \underset{\text{Ethanoyl chloride}}{CH_3COCl} \xrightarrow{NH_3\ (excess)}$$

$$\underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[\text{Hoffmann bromamide reaction}]{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(iii) Butanenitrile to 1-aminobutane:

$$\underset{\text{Butanenitrile}}{CH_3CH_2CH_2CN} \xrightarrow[\text{Partial hydrolysis}]{H_3O^+} \underset{\text{Butanoic acid}}{CH_3—CH_2—CH_2—COOH}$$

$$\xrightarrow{SOCl_2} \underset{\text{Butanyl chloride}}{CH_3—CH_2—CH_2—COCl}$$

$$\xrightarrow{NH_3\ (excess)} \underset{\text{Butanamide}}{CH_3CH_2CH_2CONH_2}$$

$$\xrightarrow[\text{Hoffmann bromamide reaction}]{Br_2/KOH} \underset{\text{1-amino butane}}{CH_3—CH_2—CH_2—CH_2NH_2}$$

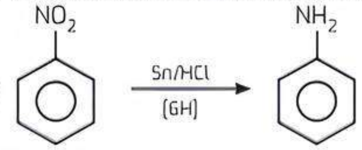
Q 15. How will you carry out the following conversions:

(i) Nitrobenzene to Aniline

(ii) Ethanamide to Methanamine

(iii) Ethanenitrile to Ethaneamine *(CBSE 2022 Term-2)*

Ans. (i)



Nitrobenzene Aniline

(ii) $$\underset{\text{Ethanamide}}{C_2H_5NH_2} \xrightarrow[273\text{–}278K]{HNO_2} C_2H_5OH \xrightarrow{[O]} CH_3COOH$$

$$\xrightarrow[(excess)]{NH_3} CH_3CONH_2 \xrightarrow[\text{(Hoffmann bromamide degradation)}]{Br_2/NaOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(iii) $$\underset{\text{Ethanenitrile}}{CH_3C\equiv N} \xrightarrow[\text{or } H_2/Ni]{LiAlH_4} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$$

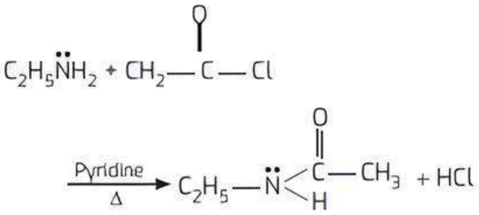
Q 16. Write equations involved in the following reactions:

(i) Ethanamine reacts with acetyl chloride.

(ii) Aniline reacts with bromine water at room temperature.

(iii) Aniline reacts with chloroform and ethanolic potassium hydroxide. *(CBSE 2022 Term-2)*

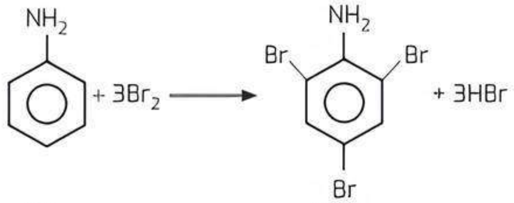
Ans. (i)



$$C_2H_5\ddot{N}H_2 + CH_2—\overset{\overset{O}{\|}}{C}—Cl \xrightarrow[\Delta]{Pyridine} C_2H_5—\ddot{N}\begin{matrix}\diagup \overset{\overset{O}{\|}}{C}—CH_3\\ \diagdown H\end{matrix} + HCl$$

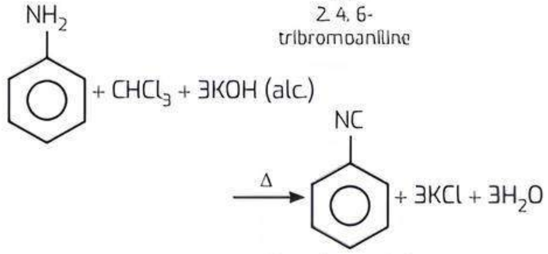
N-ethylacetamide
(N-acetylethylamine)

(ii)



2, 4, 6-tribromoaniline

(iii)



Phenylisocyanide

Q 17. Give reasons:

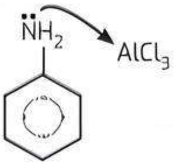
(i) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines.

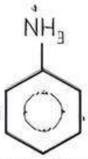
(ii) Aniline does not give Friedel-Crafts reactions.

(iii) Although —NH_2 group is *o/p*-directing in electrophilic substitution reactions, yet aniline on nitration gives good yield of *m*-anilium ion. *(CBSE 2022 Term-2)*

Ans. (i) Because it produce mixture of primary, secondary, tertiary and quaternary amines rather than primary amines.

(ii) Due to presence of lone pair electrons on N-atom of aniline, it co-ordinates with the catalyst (weak lewis acid) and it does not work like for anhydrous $AlCl_3$.



(iii) Due to formation of anilinium ion  , electron density at *o* and *p*-positions yield *m*-product.

Q 18. Reduction of an organic compound A having molecular formula C_2H_7N gives an amine, which on heating with chloroform and caustic potash gives a very bad smelling compound *B*. Write the structural formula and names of *A* and *B*.

Ans. $$\text{Organic compound } A \xrightarrow{\text{Reduction}} C_2H_7N\ \text{(Amine)}$$

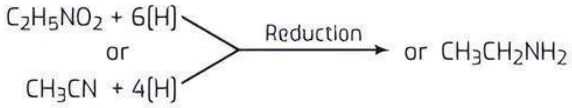
$$\xrightarrow{CHCl_3 + KOH} \text{very bad smelling compound } B.$$

Thus, the very bad smelling compound *B* is isocyanide, which is formed by the reaction of a primary amine with $CHCl_3$ and alcoholic KOH. Hence, C_2H_7N is a primary amine *i.e.*, $C_2H_5NH_2$, which is obtained by the reduction of CH_3CN or $C_2H_5NO_2$.
Thus, the organic compound *A* is $C_2H_5NO_2$ or CH_3CN.

$$\underset{\substack{\text{or } CH_3CN\\(A)}}{C_2H_5NO_2} \xrightarrow{\text{Reduction}} C_2H_5NH_2 \text{ (or } C_2H_7N)$$

$$\xrightarrow{CHCl_3\ +\ KOH\text{ (alc.)}} \underset{(B)}{C_2H_5NC}$$

Reactions:



$$\left.\begin{array}{c} C_2H_5NO_2 + 6[H] \\ \text{or} \\ CH_3CN\ + 4[H] \end{array}\right\rangle \xrightarrow{\text{Reduction}} \text{or } CH_3CH_2NH_2$$

$$C_2H_5NH_2 + CHCl_3 + 3KOH\text{ (alc.)} \longrightarrow \underset{\substack{\text{Ethyl isocyanide}\\ \text{(very bad smelling}\\ \text{compound B)}}}{C_2H_5NC} + 3KCl + 3H_2O$$

Q 19. An organic compound *'A'* on reduction gives compound *'B'* which forms ethanol with nitrous acid. Compound *'B'* gives a very bad smelling compound *'C'* on heating with chloroform and caustic potash, which on reduction forms ethylmethyl amine. Write the name and structural formula of *A*, *B* and *C* and explain the chemical equation of the chemical reactions involved.

Ans. Organic compound 'A' $\xrightarrow{\text{Reduction}}$ compound 'B'

$$\xrightarrow{HNO_2} C_2H_5OH$$

Thus compound 'B' is aliphatic primary amine because its —NH_2 group is converted into —OH group by HNO_2.
Compound 'B' is obtained by the reduction of compound. 'A'. Thus, compound A is a nitro (—NO_2) compound. On this basis:

$$\underset{\substack{\text{Nitroethane}\\ \text{(compound 'A')}}}{C_2H_5NO_2} + 6[H] \xrightarrow[\substack{\text{by reductant}\\ (-2H_2O)}]{\text{Reduction}} \underset{\substack{\text{Ethylamine}\\ \text{(compound 'B')}}}{C_2H_5NH_2}$$

$$\xrightarrow[(-N_2,\ -H_2O)]{HNO_2} \underset{\text{Ethanol}}{C_2H_5OH}$$

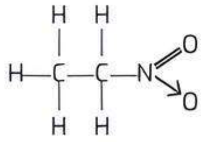
$$\underset{\substack{\text{Ethylamine}\\ \text{(compound 'B')}}}{C_2H_5NH_2} + CHCl_3 + 3KOH\text{ (alc.)} \longrightarrow$$

$$\underset{\substack{\text{Very bad smelling}\\ \text{ethyl isocyanide}\\ \text{(compound 'C')}}}{C_2H_5NC} + 3KCl + 3H_2O$$

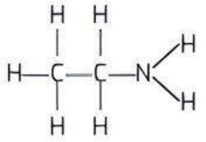
C_2H_5NC (compound *C*) on reduction gives ethylmethyl amine. Its reactions are as follows:

$$C_2H_5NC + 4[H] \xrightarrow{\text{Reaction}} \underset{\text{Ethylmethyl amine}}{C_2H_5NHCH_3}$$

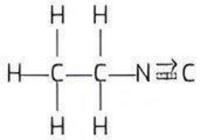
Thus, **compound *'A'*** is Nitroethane. Its structure is:



Compound *'B'* is Ethyl amine. Its structure is:



Compound *'C'* is Ethyl isocyanide. Its structure is:



Q 20. You are given four organic compounds *'A', 'B', 'C'* and *'D'*. The compounds *'A', 'B'* and *'C'* form an orange-red precipitate with 2, 4 DNP reagent. Compounds *'A'* and *'B'* reduce Tollen's reagent while compounds *'C'* and *'D'* do not. Both *'B'* and *'C'* give a yellow precipitate when heated with iodine in the presence of NaOH. Compound *'D'* gives brisk effervescence with sodium bicarbonate solution. Identify *'A', 'B', 'C'* and *'D'* given the number of carbon atoms in three of these carbon compounds is three while one has two carbon atoms. Give an explanation for your answer.

(CBSE SQP 2023-24)

Ans. *A*, *B* and *C* contain carbonyl group as they give positive 2, 4 DNP test.

A and *B* are aldehydes as aldehydes reduce Tollen's reagent.

C is a ketone, as it contains carbonyl group but does not give positive Tollen's test.

C is a methyl ketone as it gives positive iodoform test.

B is an aldehyde that gives positive iodoform test.

D is a carboxylic acid.

Since, the number of carbons in the compounds *A*, *B*, *C* and *D* is three or two, B is CH_3CHO as this is only aldehyde which gives a positive iodoform test.

The remaining compounds *A*, *C* and *D* have three carbons as shown:

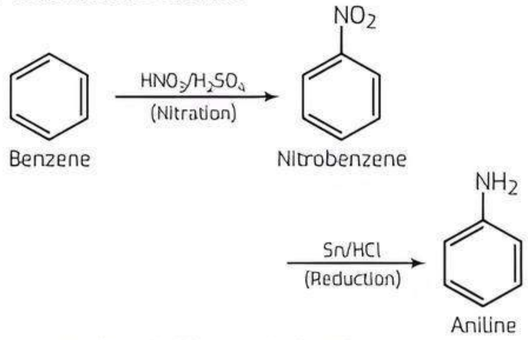
A is CH_3CH_2CHO, *C* is CH_3COCH_3 and *D* is CH_3CH_2COOH

Q 21. How will you convert:

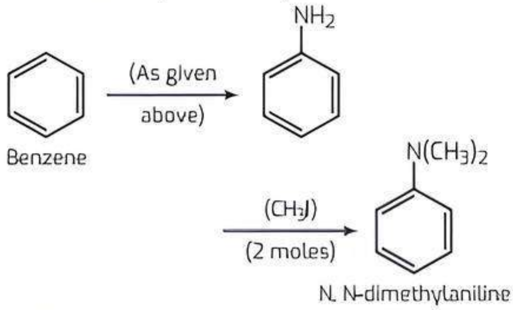
(i) Benzene into aniline
(ii) Benzene into N, N-dimethylaniline
(iii) $Cl(CH_2)_6$ Cl into hexane-1, 6-diamine

(NCERT INTEXT)

Ans. **(i) Benzene into aniline:**



(ii) Benzene into N, N-dimethylaniline:



(iii) $Cl—(CH_2)_6—Cl$ into hexane–1, 6–diamine:

$$\underset{\text{1, 6-Dichlorohexane}}{Cl—(CH_2)_6—Cl} + 4\,NH_3(alc.) \longrightarrow$$

$$\underset{\text{Hexane-1, 6-diamine}}{NH_2—(CH_2)_6—NH_2} + 2NH_4Cl$$

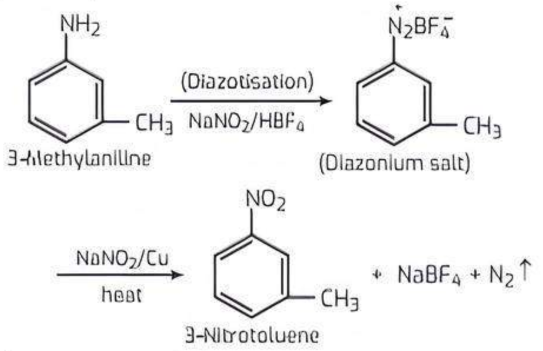
Q 22. How will you convert:

(i) 3-Methylaniline into 3-nitrotoluene

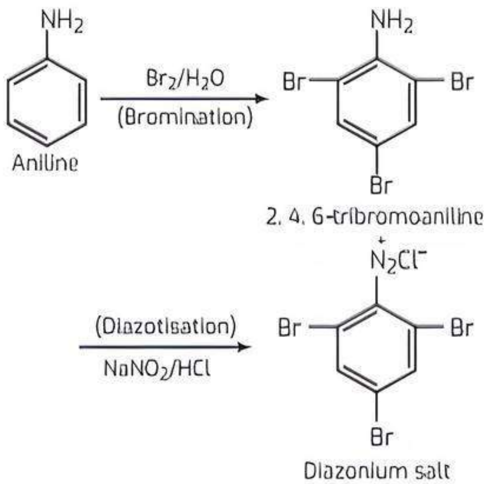
(ii) Aniline into 1, 3, 5-tribromobenzene?

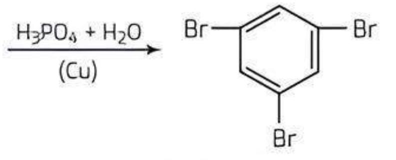
(NCERT INTEXT)

Ans. **(i) 3 Methylaniline into 3-nitrotoluene:**



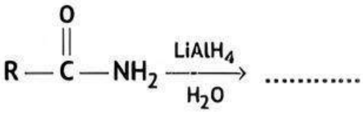
(ii) Aniline into 1, 3, 5-tribromobenzene:





1, 3, 5-tribromobenzene

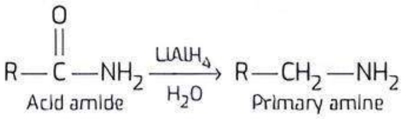
Q 23. Complete the following equations:



(i) $R—\overset{\overset{\large O}{||}}{C}—NH_2 \xrightarrow[H_2O]{LiAlH_4}$ ....

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$ ....

(iii) $C_6H_5NH_2 + Br_2\ (aq) \longrightarrow$ ....

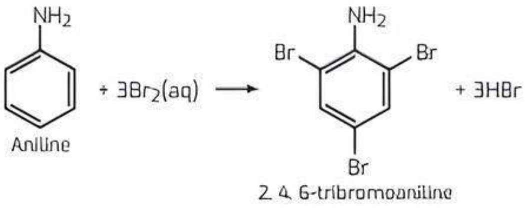


Ans. (i) $\underset{\text{Acid amide}}{R—\overset{\overset{O}{||}}{C}—NH_2} \xrightarrow[H_2O]{LiAlH_4} \underset{\text{Primary amine}}{R—CH_2—NH_2}$

(ii) $\underset{\text{Benzene diazonium chloride}}{C_6H_5N_2Cl} + H_3PO_2 + H_2O \longrightarrow$

$$C_6H_6 + \underset{\text{Phosphorus acid}}{H_3PO_3} + N_2\uparrow + HCl$$

(iii)

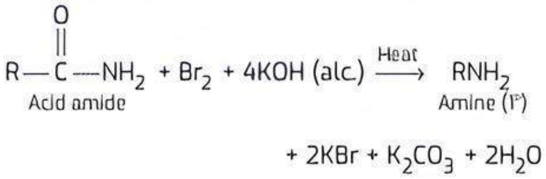


Q 24. Give equations for the following reactions:

(i) Hoffmann bromamide degradation reaction

(ii) Aniline treated with bromine water

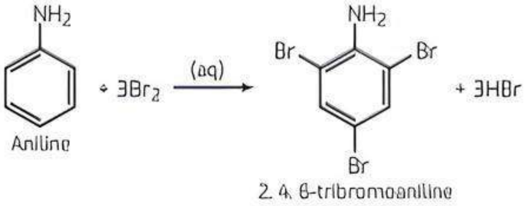
(iii) Benzene diazonium chloride treated with fluoroboric acid followed with heating.



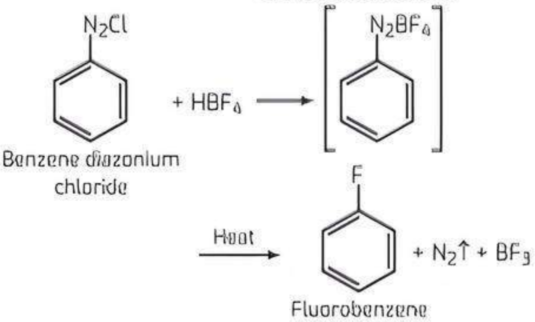
Ans. (i) $\underset{\text{Acid amide}}{R—\overset{\overset{O}{||}}{C}—NH_2} + Br_2 + 4KOH\ (alc.) \xrightarrow{Heat} \underset{\text{Amine (1°)}}{RNH_2}$

$$+ 2KBr + K_2CO_3 + 2H_2O$$

(ii)



(iii)



Q 25. Complete the following:

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

(ii) $C_6H_5N_2Cl + C_2H_5OH \longrightarrow$

(iii) $C_2H_5NH_2 + HONO \longrightarrow$

Ans. (i) $C_6H_5NH_2 + CHCl_3 + 3KOH\ (alc.) \longrightarrow$

$$C_6H_5N \equiv C + 3KCl + 3H_2O$$

Phenyl isocyanide

(ii) $C_6H_5N_2Cl + C_2H_5OH \longrightarrow C_6H_6 + CH_3CHO + N_2\uparrow + HCl$

(iii) $C_2H_5NH_2 + HONO \longrightarrow C_2H_5OH + N_2\uparrow + H_2O$

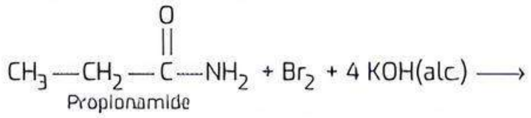
Q 26. How will you convert:

(i) Propionamide to ethylamine

(ii) Aniline to benzene

(iii) Aniline to chlorobenzene

Ans. (i)



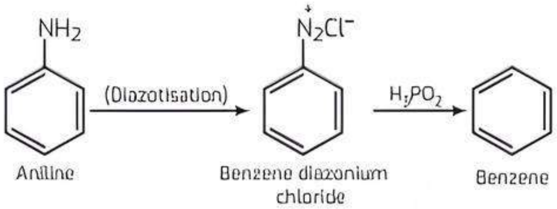
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4\ KOH(alc.) \longrightarrow$

Propionamide

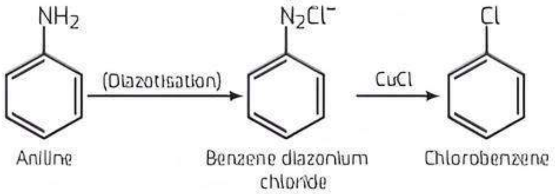
$CH_3-CH_2-NH_2 + 2KBr + K_2CO_3 + 2H_2O$

Ethylamine

(ii)



(iii)



Q 27. Give the structures of *A* and *B* in the following sequence of reactions:

(i) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B$

(ii) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[0^\circ\text{-}5^\circ C]{NaNO_2 + HCl} B$

(iii) $C_6H_5N_2^+Cl^- \xrightarrow[\Delta]{CuCN} A \xrightarrow{H_2O/H^+} B$

(CBSE 2020)

Ans. (i) $CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{(A)}{CH_3CONH_2} \xrightarrow{NaOBr} \underset{(B)}{CH_3NH_2}$

(ii) $C_6H_5NO_2 \xrightarrow{Fe/HCl} \underset{(A)}{C_6H_5NH_2} \xrightarrow[0^\circ\text{-}5^\circ C]{NaNO_2 + HCl} \underset{(B)}{C_6H_5N_2Cl}$

(iii) $C_6H_5N_2^+Cl^- \xrightarrow[\Delta]{CuCN} \underset{(A)}{C_6H_5CN} \xrightarrow{H_2O/H^+} \underset{(B)}{C_6H_5COOH}$

Q 28. (i) How will you distinguish between the following pairs of compounds:

(a) Aniline and Ethanamine

(b) Aniline and *N*-methylaniline.

(ii) Arrange the following compounds in decreasing order of their boiling points:

Butanol, Butane and Butanamine *(CBSE 2020)*

Ans. (i) (a) On adding ice-cold ($NaNO_2$ + HCl) followed by phenol or β-naphthol to both the compounds, aniline forms orange-red dye while ethylamine does not.

(b) On adding $CHCl_3$ and KOH (alc.) to both the compounds, aniline gives foul smelling isocyanide while *N*-methylaniline does not.

(ii) Decreasing order of the boiling points of the given compounds can be shown as follows:

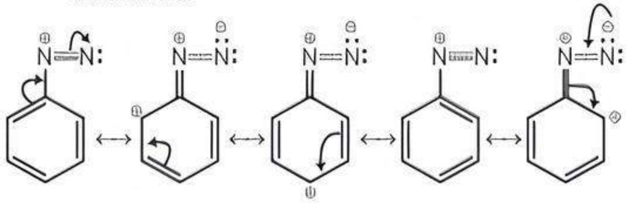
Butanol > Butanamine > Butane

Q 29. Account for the following by supporting your answer with diagrams or equations wherever possible:

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

(ii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide. *(CBSE 2019)*

Ans. (i) Diazonium salts of aromatic amines are more stable than those of aliphatic amines due to the delocalisation of the positive charge on the benzene ring as shown below by the resonating structures.



(ii) Methylamine being basic, gains a proton from water and releases hydroxyl ions which precipitate hydrated ferric oxide.

$$CH_3NH_2 \xrightarrow{H_2O} CH_3NH_3^{+} + OH^-$$

$$FeCl_3 \xrightarrow{3OH^-} Fe(OH)_3\downarrow + 3Cl^-$$

Q 30. Arrange the following in decreasing order of pK_b giving reason:

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

(ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ in gaseous state.

(CBSE 2019)

Ans. (i) *p*-nitroaniline > aniline > *p*-toluidine

Reason: pK_b decreases on increasing the basicity of the compound. Now, in *p*-toluidine, the presence of electron donating group (EDG)—CH_3 increases the electron density on the *n*-atom. Thus *p*-toluidine is more basic than aniline *i.e.*, pK_b of *p*-toluidine is less then aniline. On the other hand, the presence of electron withdrawing group (EWG)—NO_2 decreases the electron density over the *N*-atom in *p*-nitroaniline. Thus, *p*-nitroaniline is less basic than aniline *i.e.*, pK_b of *p*-nitroaniline is more than aniline.

(ii) $C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N$

Reason: In the gas phase, there is no solvation effect. As a result, the basic strength mainly depends upon the + *I* effect. The higher the + *I* effect, the stronger is the base. Also, the greater the number of alkyl groups, the higher is the + *I* effect. Therefore, the given compounds can be arranged in the above order as greater the basicity, lower the value of pK_b.

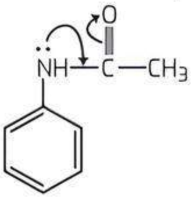
Q 31. Give reasons for the following:

(i) Acetylation of aniline reduces its activation effect.

(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$.

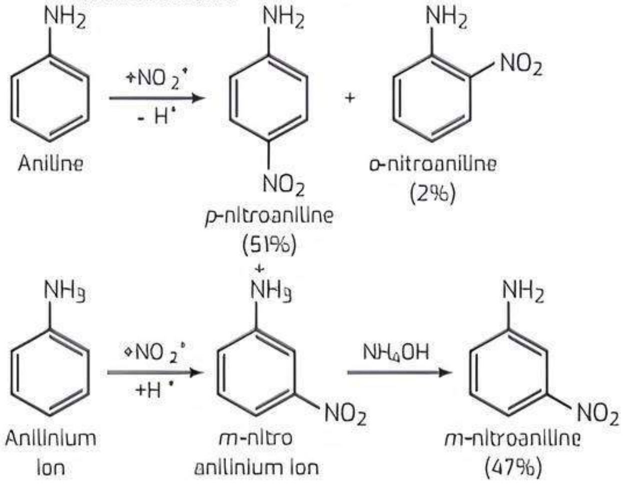
(iii) Although —NH_2 is *o/p* directing group, yet aniline on nitration gives a significant amount of *m*-nitroaniline.

Ans. (i) Due to electron withdrawing effect of the acetyl group, the lone pair of electrons on *N*-atom is attracted by acetyl group. As a result, lone pair of electrons on *N*-atom is not exclusively available for donation to the benzene ring and hence, activating effect of the —NH_2 group is reduced.



(ii) In aromatic amines like $C_6H_5NH_2$, the lone pair of electrons present on nitrogen takes part in resonance and hence, not available for donation. Also aniline ($C_6H_5NH_2$) is more stable than anilinium ion. Hence, aniline has a very little tendency to accept a proton to form anilinium ion. However, in aliphatic amines like CH_3NH_2, the lone pair is easily available for donation. This is the reason, CH_3NH_2 is more basic than $C_6H_5NH_2$.

(iii) Nitration is usually carried out with a mixture of conc. HNO_3 and conc. H_2SO_4. So, in the presence of these acids, aniline gets protonated to form anilinium ion. Therefore, the reaction mixture consists of aniline and anilinium ion. Group —NH_2 in aniline is *ortho*, *para*-directing and activating, whereas the $\overset{+}{N}H_3$ group in anilinium is *m*-directing and deactivating. Now, nitration of aniline mainly gives *p*-nitroaniline due to steric hindrance at *o*-position and the nitration of anilinium ion gives *m*-nitroaniline.



Q 32. Write the structures of compounds *A*, *B* and *C* in the following reactions:

(i) $$CH_3—COOH \xrightarrow{NH_3/\Delta} \text{'}A\text{'} \xrightarrow{Br_2/KOH(aq)} \text{'}B\text{'} \xrightarrow{CHCl_3 + alc.\ KOH} \text{'}C\text{'}$$

(ii) $$C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} \text{'}A\text{'} \xrightarrow{Fe/HCl} \text{'}B\text{'} \xrightarrow{CH_3COCl/Pyridine} \text{'}C\text{'}$$

(CBSE 2017)

Ans. (i) $$\underset{\text{Acetic acid}}{CH_3—COOH} \xrightarrow[-H_2O]{NH_3/\Delta} \underset{\substack{\text{Acetamide}\\(A)}}{CH_3CONH_2} \xrightarrow[\substack{\text{Hoffmann bromamide}\\\text{degradation}}]{Br_2/KOH(aq)}$$

$$\underset{\substack{\text{Methylamine}\\(B)}}{CH_3NH_2} \xrightarrow[\text{Carbylamine reaction}]{CHCl_3 + alc.\ KOH} \underset{\substack{\text{Methylisocyanide}\\(C)}}{CH_3NC}$$

(ii) $$C_6H_5N_2^+ BF_4^- \xrightarrow[-N_2,\ -NaBF_4]{NaNO_2/Cu\ \Delta} \underset{\substack{\text{Nitrobenzene}\\(A)}}{C_6H_5NO_2} \xrightarrow[\text{Reduction}]{Fe/HCl}$$

$$\underset{\substack{\text{Aniline}\\(B)}}{C_6H_5NH_2} \xrightarrow[-HCl]{CH_3COCl/pyridine} \underset{\substack{\text{Acetanilide}\\(C)}}{C_6H_5NHCOCH_3}$$

COMMON ERR(!)R

While finding the final product, students write complete reactions and make mistakes.

Long Answer Type Questions

Q 1. (i) Write the reactions involved in the following:

(a) Hoffmann bromamide degradation reaction

(b) Diazotisation

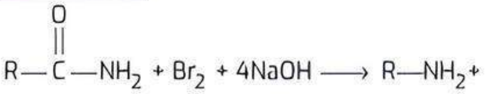
(c) Gabriel phthalimide synthesis

(ii) Give reasons:

(a) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.

(b) Aromatic diazonium salts are more stable than aliphatic diazonium salts. *(CBSE 2018)*

Ans. (i) (a) Hoffmann bromamide degradation reaction: This reaction is used for synthesising amine containing one carbon less than the starting amide. This method was developed for the preparation of primary amines by reacting an amide with Br_2/Cl_2 in NaOH/KOH. In this reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the *N*-atom.



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

e.g., $\underset{\text{Amide}}{CH_3CH_2CONH_2} + Br_2 + 4NaOH \longrightarrow$

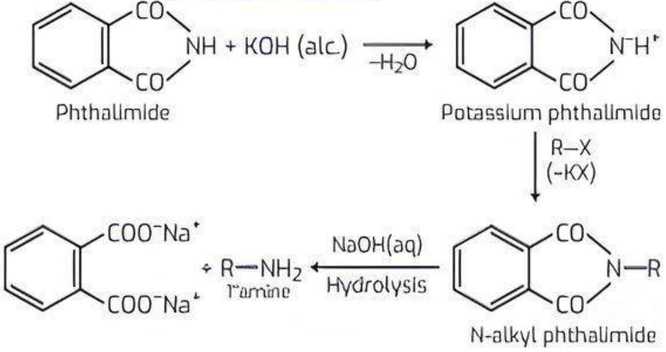
$3\underset{\text{Amine}}{CH_3CH_2NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$

(b) Diazotisation: The conversion of primary aromatic amines into their diazonium salts is called diazotisation. Benzene diazonium chloride is prepared by the reaction of aniline with nitrous acid, which is produced by the reaction of $NaNO_2$ and HCL at 273–278K or 0°-5°C as:

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

Due to its unstability, the diazonium salt is not generally stored and is used immediately after its preparation.

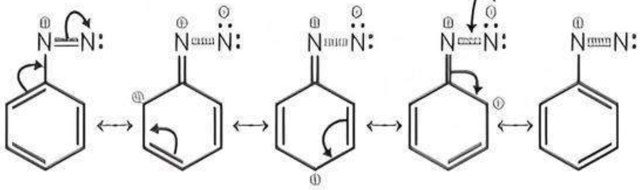
(c) Gabriel phthalimide synthesis: When a phthalimide is treated with alcoholic KOH, it forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis forms corresponding primary amines as:



Primary amines are produced through this method without the traces of secondary or tertiary amines. So, this method is preferred for the synthesis of primary amines.

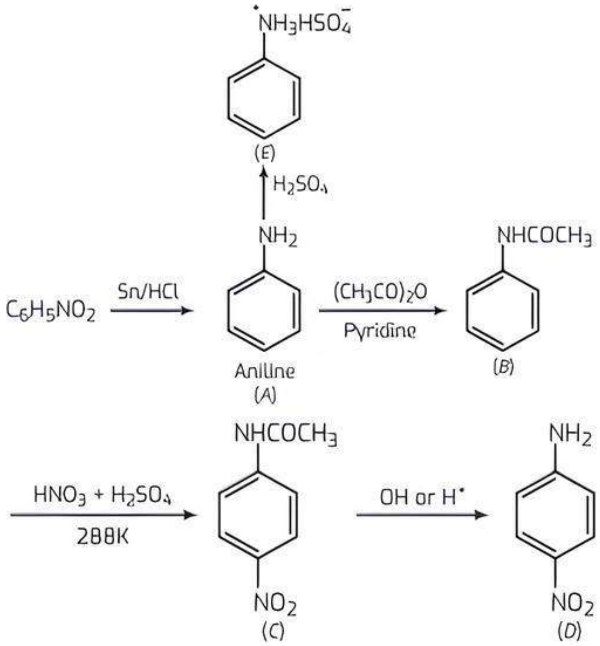
(ii) (a) Basicity of $(CH_3)_2NH$ and $(CH_3)_3N$ depends upon the stabilisation of their conjugate acids by a number of factors such as H-bonding, steric hindrance of alkyl groups and +I effect of alkyl groups. The first two factors are favourable for 2° amines, hence $(CH_3)_2NH$ is a stronger base than $(CH_3)_3N$ in aqueous medium.

(b) Diazonium salts of aromatic amines are more stable than those of aliphatic amines due to the delocalisation of the positive charge on the benzene ring as shown below by the resonating structures.



Q 2. **Write the structures of *A*, *B*, *C*, *D* and *E* in the following reactions:**

$$\begin{tikzcd}
C_6H_5NO_2 \arrow[r, "Sn/HCl"] & \text{'}A\text{'} \arrow[r, "(CH_3CO)_2O", "Pyridine"'] \arrow[d, "H_2SO_4"] & \text{'}B\text{'} \arrow[r, "HNO_3 + H_2SO_4", "288\ K"'] & \text{'}C\text{'} \arrow[d, "OH^- \text{ or } H^+"'] \\
 & E & & D
\end{tikzcd}$$



Q 3. **(i) Account for the following:**

(a) N-ethylbenzenesulphonyl amide is soluble in alkali.

(b) Reduction of nitrobenzene using Fe and HCl is preferred over Sn and HCl.

(ii) Arrange the following in:

(a) decreasing order of pK_b values

$C_6H_5NH_2, C_6H_5NHCH_3, C_6H_5CH_2NH_2, CH_3NH_2, NH_3$

(b) increasing order of solubility in water

$C_2H_5Cl, C_2H_5NH_2, C_2H_5OH$

(c) decreasing boiling point

$CH_3COOH, C_2H_5OH, CH_3NH_2, CH_3OCH_3$

(CBSE SQP 2023-24)

Ans. (i) (a) The hydrogen attached to N-Ethylbenzene sulphonamide is acidic in nature. This is due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

(b) 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.

(ii) (a) $C_6H_5NH_2 > C_6H_5NHCH_3 > NH_3 > C_6H_5CH_2NH_2 > CH_3NH_2$

(b) $C_2H_5Cl < C_2H_5NH_2 < C_2H_5OH$

(c) $CH_3COOH > C_2H_5OH > CH_3NH_2 > CH_3OCH_3$

Q 4. (i) Give reasons:

(a) Aniline on nitration gives good amount of m-nitroaniline, though —NH_2 group is *o/p* directing in electrophilic substitution reactions.

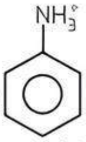
(b) $(CH_3)_2$ NH is more basic than $(CH_3)_3N$ in an aqueous solution.

(c) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines.

(ii) Write the reaction involved in the following:

(a) Carbyl amine test

(b) Gabriel phthalimide synthesis *(CBSE 2023)*

Ans. (i) (a) Due to the formation of anilinium ion 

electron density at *o* and *p*-positions yield *m*-product.

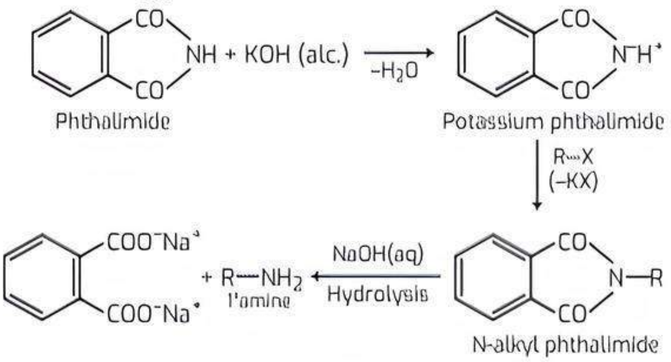
(b) $(CH_3)_2NH$ is hydrated to a greater extent than $(CH_3)_3N$. As the number of methyl group increases, the extent of hydration decreases due to steric hindrance. Greater is the extent of hydration, greater is the stability of ion and greater is the basic strength of amine.

(c) Because it produce mixture of primary, secondary, tertiary and quaternary amines rather than primary amines.

(ii) (a) Carbylamine test: When an organic compound having $-NH_2$ group is heated with chloroform and alcoholic KOH solution, it releases a bad smelling gas called isocyanide or carbylamine. This reaction is called carbylamine reaction and it is used to confirm the presence of $-NH_2$ group in the organic compound.

$$CH_3CH_2NH_2 + CHCl_3 + 3KOH\ (alc.) \longrightarrow \underset{\text{Ethyl isocyanide}}{CH_3CH_2NC} + 3KCl + 3H_2O$$

(b) Gabriel phthalimide synthesis: When a phthalimide is treated with alcoholic KOH, it forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis forms corresponding primary amines as:



Primary amines are produced through this method without the traces of secondary or tertiary amines. So, this method is preferred for the synthesis of primary amines.

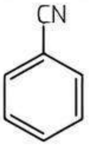
Q 5. (i) Write the structures of the main products when benzene diazonium chloride reacts with the following reagents:

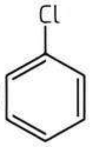
(a) CuCN, (b) CH_3CH_2OH, (c) Cu/HCl

(ii) Arrange the following in the increasing order of their basic strength:

CH_3NH_2, $(CH_3)_2NH$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$

(iii) Write one chemical test to distinguish between Aniline and Ethyl amine. *(CBSE 2017)*

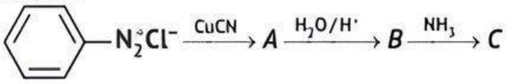
Ans. (i) (a) 

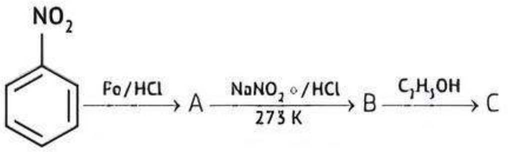
(b) 
(c) 

(ii) $C_6H_5NH_2 < C_6H_5CH_2NH_2 < CH_3NH_2 < (CH_3)_2NH$

(iii) When we add ($NaNO_2$ + HCl) to both aniline and ethylamine at 273 K and then followed by addition of phenol, only aniline gives orange dye. So, in this way we can distinguish between aniline and ethylamine.

Q 6. (i) Write the structures of A, B and C in the following reactions:

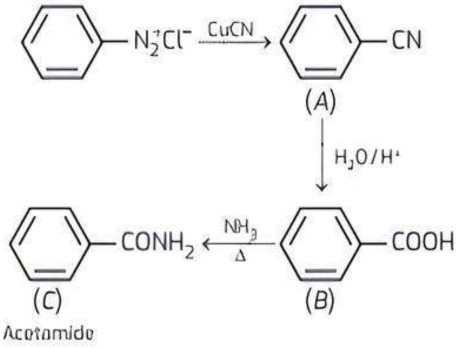
(a) 

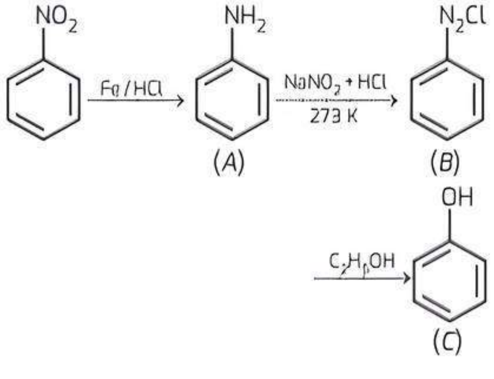
(b) 

(ii) Why aniline does not undergo Friedel-Crafts reaction?

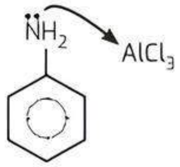
(iii) Arrange the following in increasing order of their boiling point: *(CBSE 2023)*

C_2H_5OH, $C_2H_5NH_2$, $(C_2H_5)_3N$

Ans. (i) (a) 

(b) 

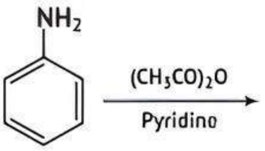
(ii) Due to presence of lone pair electrons on N-atom of aniline, it co-ordinates with the catalyst (weak lewis acid) and it does not work like for anhydrous $AlCl_3$.



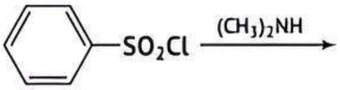
(iii) $(C_2H_5)_3N < C_2H_5NH_2 < C_2H_5OH$

Q 7. (i) Write the structures of the main products of the following reactions:

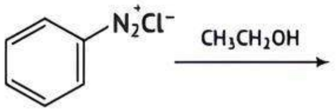
(a)



(b)



(c)

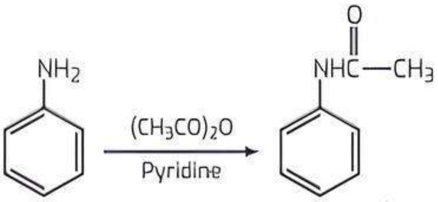


(ii) Give a simple chemical test to distinguish between Aniline and N, N-dimethylaniline.

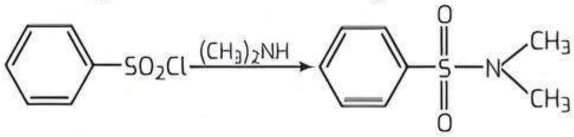
(iii) Arrange the following in the increasing order of their pK_b values.

$C_6H_5NH_2$, $C_2H_5NH_2$, $C_6H_5NHCH_3$ *(CBSE 2018)*

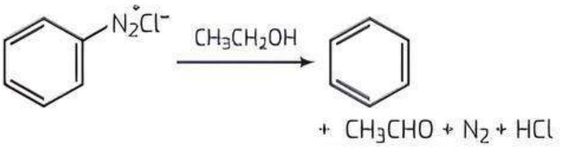
Ans. (i) (a)



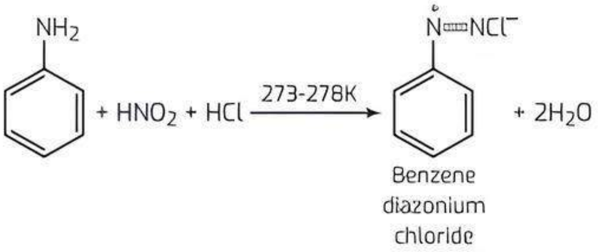
(b)



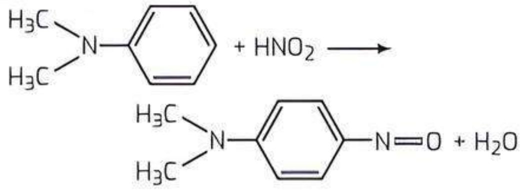
(c)



(ii) Aniline and N, N-dimethyl aniline can be distinguished using reaction with nitrous acid. Aniline is primary aromatic amine. It reacts with nitrous acid at low temperature forming arenediazonium salt.



N, N-dimethylamine is tertiary aromatic amine, it reacts with nitrous acid to form green coloured *p*-nitrosoamine.



(iii) Increasing order of pK_b value is

$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2$

with pK_b values in the order 9.38 > 9.30 > 3.29 respectively.

Aliphatic amines are more basic than aromatic amines because in aromatic amine, the lone pair is delocalised within benzene ring due to resonance and hence, it is not available for donation.

Q 8. An organic compound with molecular formula $C_7H_7NO_2$ exists in three isomeric forms, the isomer '*A*' has the highest melting point of the three. '*A*' on reduction gives compound '*B*' with molecular formula C_7H_9N. '*B*' on treatment with $NaNO_2/HCl$ at 0-5°C to form compound '*C*'. On treating *C* with H_3PO_2, it gets converted to *D* with formula C_7H_8, which on further reaction with CrO_2Cl_2 followed by hydrolysis forms '*E*' C_7H_6O. Write the structure of compounds *A* to *E*. Write the chemical equations involved. *(CBSE SQP 2023-24)*

Ans. Compound '*A*' is *p*-methylnitrobenzene

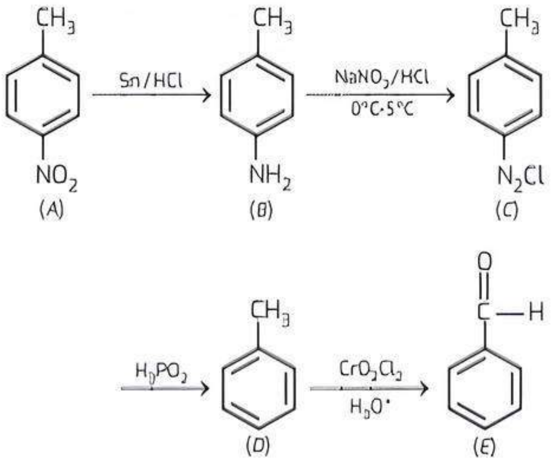
Compound '*B*' is *p*-methylbenzenamine

Compound *C* is *p*-methylbenzenediazoniumchloride

Compound *D* - Toluene

Compound *E* - Benzaldehyde

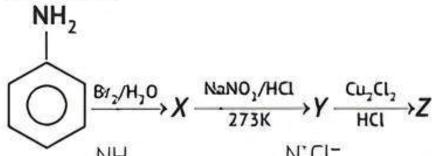
The chemical reactions involved are:

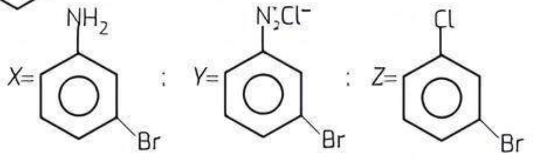


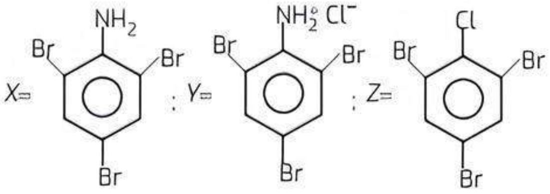
Chapter Test

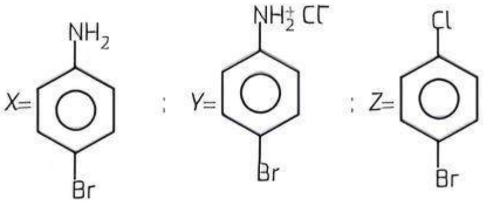
Multiple Choice Questions

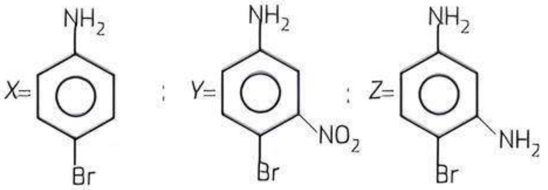
Q 1. Identify *X*, *Y* and *Z* in the given sequence of reactions:



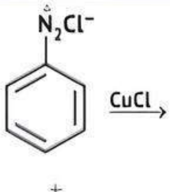
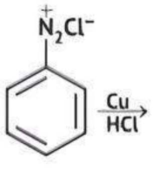
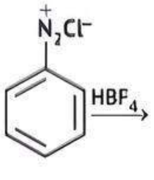
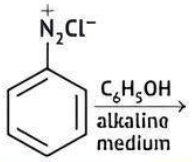
a. 

b. 

c. 

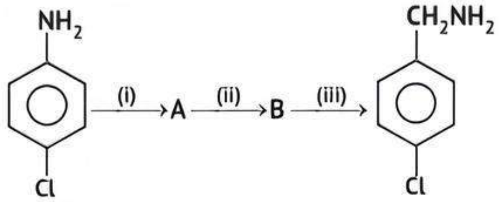
d. 

Q 2. Match the column I with column II and mark the appropriate choice.

	Column I		Column II
(A)		(i)	Coupling reaction
(B)		(ii)	Balz-Schiemann reaction
(C)		(iii)	Gattermann reaction
(D)		(iv)	Sandmeyer reaction

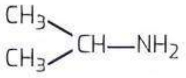
a. (A) → (iv), (B) → (iii), (C) → (ii), (D) → (i)
b. (A) → (iii), (B) → (iv), (C) → (i), (D) → (ii)
c. (A) → (ii), (B) → (iii), (C) → (iv), (D) → (i)
d. (A) → (i), (B) → (ii),(C) → (iii), (D) → (iv)

Q 3. Mark the correct route of the conversion of *p*-chloroaniline to *p*-chlorobenzylamine:

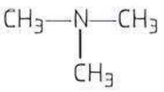


	(i)	(ii)	(iii)
a.	Alkylation	KCN	H_2/Pt
b.	Diazotisation	CuCN	H_2/Pt
c.	Oxidation	H_2/Pt	Hydrolysis
d.	Diazotisation	H_2O/H^+	Sn/HCl

Q 4. An organic compound (C_3H_9N) (*A*), when treated with nitrous acid, gave an alcohol and N_2 gas was evolved. (*A*) on warming with $CHCl_3$ and caustic potash gave (*C*) which on reduction gave isopropylmethyl amine. Predict the structure of (*A*).

a. 
$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH—NH_2$

b. $CH_3CH_2—NH—CH_3$

c. 
$CH_3—\underset{\underset{CH_3}{|}}{N}—CH_3$

d. $CH_3CH_2CH_2—NH_2$

Assertion and Reason Type Questions

Directions (Q. Nos. 5-6): *Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:*

a. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
b. Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
c. Assertion (A) is true but Reason (R) is false.
d. Assertion (A) is false but Reason (R) is true.

Q 5. Assertion (A): Hoffmann degradation of benzamide gives aniline.

Reason (R): Hoffmann bromamide degradation reaction can be used for the preparation of primary amines from amides.

Q 6. **Assertion (A):** Controlled nitration of aniline at low temperature mainly gives *m*-nitroaniline.

Reason (R): In acidic medium, $-NH_2$ group gets converted into *m*-directing group.

Case Study Based Question

Q 7. The chemical reactivity of amines is mainly due to the presence of a lone pair of electrons on N atom due to which amines act as nucleophiles or bases. A nucleophile is a species that attacks an electron deficient carbon and a base is a species that attacks an electron deficient hydrogen, *i.e.*, proton. In aromatic amines, the lone pair of electrons on nitrogen atom activates the aromatic ring towards electrophilic substitution. The number of hydrogen atoms on the amine nitrogen also affect the course of some reactions.

Read the given passage carefully and give the answer of the following questions:

(i) Write the chemical reaction to obtain methylamine form acetamide.

(ii) Write the chemical reaction of hydrolysis of $R - N \geqq C$.

(iii) How is *m*-nitroaniline obtained from nitrobenzene?

OR

What happens when phenyl cyanide is treated with dilute mineral acid?

Very Short Answer Type Questions

Q 8. Why electrophilic substitution takes place more readily in aromatic amines than benzene?

Q 9. Propanamine and N, N-dimethylmethanamine contain the same number of carbon atoms, even though propanamine has higher boiling point than N, N-dimethylmethanamine. Why?

Short Answer Type-I Questions

Q 10. Explain the following reactions:

(i) Gabriel phthalimide reaction

(ii) Coupling reaction

Q 11. Identify *A* and *B* in each of the following processes:

(i) $CH_3CH_2Cl \xrightarrow{NaCN} A \xrightarrow[Ni/H_2]{Reduction} B$

(ii) $C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} A \xrightarrow[OH^-]{C_6H_5NH_2} B$

Q 12. How will you convert:

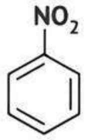
(i) Aniline to benzonitrile

(ii) Ethanamine to ethanoic acid

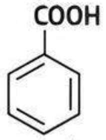
Short Answer Type-II Questions

Q 13. An aromatic compound '*A*' on heating with Br_2 and KOH forms a compound '*B*' of molecular formula C_6H_7N which on reacting with $CHCl_3$ and alcoholic KOH produces a foul smelling compound '*C*'. Write the structures and IUPAC names of compounds *A*, *B* and *C*.

Q 14. Write the products A and B in the following.

(i) 

$\xrightarrow{Sn/HCl} A \xrightarrow{CHCl_3 + aq.\ NaOH} B$

(ii) 

$\xrightarrow{NH_3} A \xrightarrow{Heat} B$

(iii) $C_6H_5\overset{+}{N}_2Cl^- \xrightarrow{Cu/HCl} A \xrightarrow{Cl_2/FeCl_3} B$

Q 15. Write the structures of compounds *A*, *B* and *C* in the following reactions.

(i) $CH_3-COOH \xrightarrow{NH_3/\Delta} A \xrightarrow{Br_2/KOH\ (aq.)} B \xrightarrow{CHCl_3 + (alc.)KOH} C$

(ii) $C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Fe/HCl} B \xrightarrow{CH_3COCl/pyridine} C$

Long Answer Type Questions

Q 16. (i) Write the structures of main products when benzene diazonium chloride reacts with the following reagents:

(a) $H_3PO_2 + H_2O$, (b) CuCN/KCN, (c) H_2O

(ii) Arrange the following in the increasing order of their basic character in an aqueous solution:

$C_2H_5NH_2, (C_2H_5)_2NH, (C_2H_5)_3N$

(iii) Give a simple chemical test to distinguish between the following pair of compounds.

$C_6H_5-NH_2$ and $C_6H_5-NH-CH_3$

Q 17. An aromatic compound '*A*' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of *A*, *B*, *C*, *D* and *E* in the following reactions:

$$\begin{tikzcd}
 & D & \\
(C_7H_7ON)A \arrow[r, "Br_2 + KOH"] & C_6H_5NH_2 \arrow[u, "CHCl_3 + NaOH"'] \arrow[d, "NaNO_2 + HCl\ 273K"] & \\
 & B \arrow[r, "CH_3CH_2OH"] \arrow[d, "KI"] & C \\
 & E &
\end{tikzcd}$$