9
CHAPTER
Amines

Level - 1 CORE SUBJECTIVE QUESTIONS

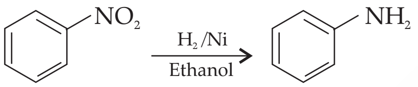
MULTIPLE CHOICE QUESTIONS (MCQs) (1 Mark)

1. Option (C) is correct

Explanation: Reacts with benzenesulphonyl chloride to form a product that is insoluble in alkali.

2. Option (A) is correct

Explanation:



3. Option (D) is correct

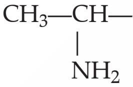
Explanation: Primary (1°) amines on reaction with Hinsberg reagent form product which is soluble in alkali.

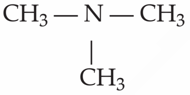
4. Option (A) is correct

Explanation:

5. Option (A) is correct

Explanation:


$CH_3—\underset{\underset{\displaystyle NH_2}{|}}{CH}—CH_3$ and $(C_2H_5)_2$ $CHNH_2$ are primary (1°) amines whereas $CH_3NH—CH_2\mathbf{CH_3}$ is (2°) amine.


$CH_3 — \underset{\underset{\displaystyle CH_3}{|}}{N} — CH_3$

is 3° amine

6. Option (A) is correct

Explanation:

$C_6H_5NH_2 < (CH_3)_3N < CH_3NH_2 < (CH)_2NH$

7. Option (C) is correct

Explanation: Aniline + Nitrous acid → Benzenediazonium chloride → Azodye (orange colour)

Ethanamine + Nitrous acid → Nitrogen + Ethanol (No colour change)

8. Option (D) is correct

Explanation: In the gaseous phase, basic strength depends mainly on the + I effect of alkyl groups, since solvation effects are absent.

More alkyl groups → more electron density on N → stronger base.

Order of +I effect: $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$

9. Option (B) is correct

Explanation: $CH_3CONH_2 + Br_2 + 4NaOH \rightarrow CH_3—NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$

10. Option (C) is correct

Explanation: In aniline, the lone pair of electrons on nitrogen atom is involved in resonance with the benzene ring making it less available for donation.

11. Option (D) is correct

Explanation: Benzylamine is strongest base than aniline because the lone pair of electron on N atom is localised and not involve in resonance.

12. Option (A) is correct

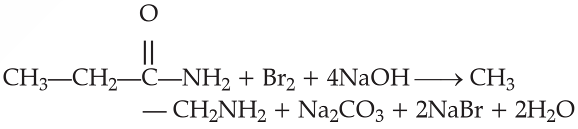
Explanation: $LiAlH_4$ is a strong reducing agent, but it is ineffective for reducing nitro groups in aromatic compounds under normal lab conditions. Nitrobenzene is typically reduced to aniline using catalytic hydrogenation (H_2/Ni) or metal + acid (Fe/HCl or Sn/HCl), which work efficiently.

13. Option (B) is correct

Explanation: $CH_3CN \xrightarrow{Na/C_2H_5OH} CH_3CH_2NH_2$

14. Option (D) is correct

Explanation:


$CH_3—CH_2—\overset{\overset{\displaystyle O}{||}}{C}—NH_2 + Br_2 + 4NaOH \longrightarrow CH_3—CH_2NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

15. Option (A) is correct

Explanation: Electron donating group increases basicity while electron withdrawing group decreases basicity.

ASSERTION-REASON QUESTIONS (1 Mark)

1. Option (D) is correct

Explanation: Assertion is false. Actually, aniline is a weaker base than ammonia because the lone pair on nitrogen gets delocalised into the benzene ring through resonance, making it less available to accept a proton.

Reason is true because resonance with the aromatic ring reduces the electron density on nitrogen.

2. Option (A) is correct
Explanation: Assertion is true. In *p*-nitroaniline, the $–NO_2$ group strongly withdraws electrons from the ring via –I (inductive) and –M (mesomeric) effects, reducing the electron density on nitrogen and making the lone pair less available for protonation.
Reason is also true and correct explanation of assertion.
3. Option (B) is correct
Explanation: Assertion is true. Aniline's $–NH_2$ group forms a complex with the Lewis acid catalyst (like $AlCl_3$) used in Friedel–Crafts, deactivating the ring and preventing the reaction.
Reason is also true but this fact does not explain why aniline fails to react.
4. Option (C) is correct
Explanation: Assertion is true. Aromatic diazonium salts (like benzene diazonium chloride) are stabilised by resonance between the benzene ring and the diazonium group.
Reason is false. Aliphatic diazonium salts cannot be stabilised by resonance because they lack an aromatic ring; they decompose easily, often releasing N_2.
5. Option (A) is correct
Explanation: Acetanilide is less basic than aniline because of the lone pair of nitrogen in acetanilide is involve in resonance with carbonyl group.
6. Option (B) is correct
Explanation: Assertion is true. The $–NH_2$ group is an electron-donating group through both resonance and +I effect, increasing electron density at the ortho and para positions of the aromatic ring.
Reason is also true. Aniline does not undergo Friedel–Crafts alkylation/acylation because the Lewis acid catalyst (like $AlCl_3$) forms a complex with the lone pair on nitrogen, making the ring less reactive.
Both assertion and reason are correct but the reason does not explain the assertion correctly because the ortho/para directing nature is due to electron donation, not because of inability to undergo Friedel–Crafts reaction.
7. Option (C) is correct
Explanation: Assertion is true. Acetylation converts $–NH_2$ to $–NHCOCH_3$, which reduces the strong activating effect of the amino group. This controls the reactivity of the ring, preventing excessive polysubstitution and giving mainly a monosubstituted product in electrophilic substitution reactions.
Reason is false. The $–NH_2$ group is more activating than $–NHCOCH_3$. Acetylation reduces activation, not increases it, by restricting resonance donation from nitrogen.
8. Option (A) is correct
Explanation: Acetylation of aniline decreases the activating effect of the amino group because the lone pair on the nitrogen atom is in conjugation with the carbonyl group in acetylated aniline.
9. Option (D) is correct
Explanation: Assertion is false. Benzene diazonium chloride is stable only at low temperatures (0–5 °C) in aqueous solution. It decomposes readily at higher temperatures, releasing N_2 gas. It cannot be stored for long periods under normal conditions. Reason is true.

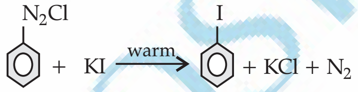
VERY SHORT ANSWER TYPE QUESTIONS (2 Marks)

1. (i) Carbylamine test: Ethanamine give a positives carbylamine test but dimethylamine does not give this test

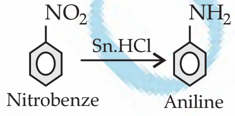
$$C_2H_5NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Ethyl isocyanide}}{C_2H_5–NC} + 3KCl + 3H_2O$$

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

(ii) Iodobenene is formed

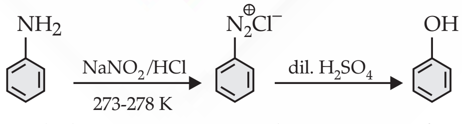


2. (i)



Nitrobenze Aniline

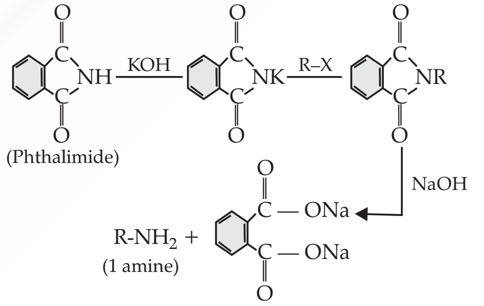
(ii)



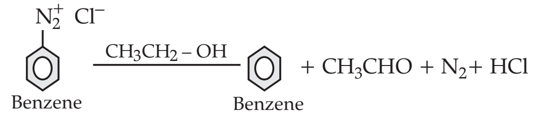
3. (i) Carbylamin reaction is the reaction of primary amine chloroform and a base to synthesise isocyanides.

$$\underset{1° \text{ Amine}}{CH_3 — NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Methyl Isocyanide}}{CH_3 — NC} + 3KCl + 3H_2O$$

(ii) Gabriel pthalimide synthesis is a chemical reaction that produces primary amines from primary alkyl halide.



4. (i)



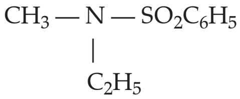
Benzene diazonium chloride Benzene

(ii) $CH_3 — CH_2 — Br + KCN \longrightarrow CH_3CH_2 — CN \xrightarrow{LiAlH_4} \underset{\text{Propanemine}}{CH_3 — CH_2 — CH_2NH_3}$

SHORT ANSWER TYPE QUESTIONS (3 Marks)

1. Since the compound C_3H_9N react with $C_6H_5SO_2Cl$ to give a produce which is insoluble in alkali it shows there is no H-atom attached to N in the product. Hence, the compound X is a secondary amine.

$CH_3 — NH — C_2H_5 + C_6H_5SO_2Cl \longrightarrow$
2° Amine



$$CH_3 — \underset{\underset{C_2H_5}{|}}{N} — SO_2C_6H_5$$

N-ethyl-N-methy benzenesulphonamide

IUPAC name of C_3H_9N is N-methylethanamine

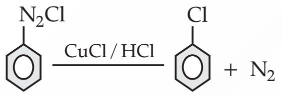
The reaction involved is Hinsberg reaction.

2. (i) Diazonium salts of aromatic amines are stable because of resonance, which disperse the positive charge over the benzene ring.

(ii) Aniline does not undergo Friedel-Crafts reaction because the amino group in aniline react with aluminium chloride $AlCl_3$, a Lewis acid catalyst to form a salt that deactivates the aromatic ring.

(iii) Aniline produces a substantial amount of meta product when nitrated because the amino group in aniline is protonated in the acidic medium of the nitration reaction resulting in anilinium ion which is meta directing.

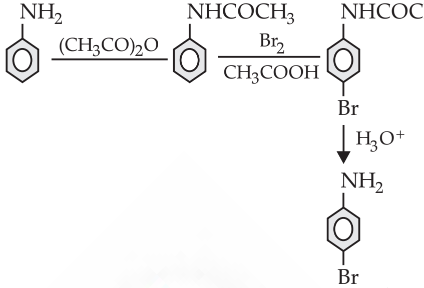
3. (i) The sandmeyer reaction is a chemical reaction used to synthesise aryl halide from aryl benzene diazonium salts.



Benzene diozonium chloride Chlorobenzene

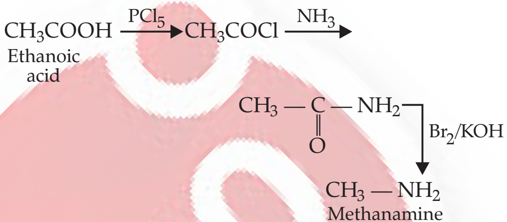
(ii) It is because $(CH_3)_2 NH_2^+$ is hydrated to a greater extent than $(CH_3)_3 NH^+$. As the number of methyl group increases, the extent of hydration decreases due to steric hindrance. Greater is the extent of hydration greater is the stability of ion and greater is the basic strength of amine.

4. (i)



p-Bromoaniline

(ii)



$$CH_3COOH \xrightarrow{PCl_5} CH_3COCl \xrightarrow{NH_3} CH_3 — \underset{\underset{O}{\|}}{C} — NH_2 \xrightarrow{Br_2/KOH} CH_3 — NH_2$$

Ethanoic acid Methanamine

(iii) $C_3H_7C \equiv N \xrightarrow{LiAlH_4/H^+} C_4H_9NH_2$

Butanenitrile 1-Aminobutane

5. (i) It is because the iron chloride formed during the reaction is hydrolysed to release hydrochloric acid. This means that only a small amount of hydrochloric acid is needed to start the reaction.

(ii) Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules.

(iii) Pyridine is used to remove the side product (HCl) formed in the acylation reaction.

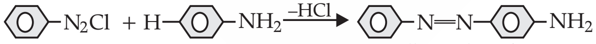
(iv) Nitration involves acidic medium. So protonation of aniline take place forming anilinium ion which being m-directing forms mainly m-nitro aniline.

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. (i) N, N-diethyl benzene sulphonomide is insoluble in alkali because it does not contain any hydrogen atom attached to a nitrogen atom making it insoluble in alkai.

(ii) It is because it react with lewis acid catalyst, typically aluminium chloride ($AlCl_3$) to form a salt which places a positive charge on the nitrogen atom, effectivly deactivating the benzene ring towards further electrophillic substitution reaction crucial for the Friedel-Crafts process.

(iii) Aniline give azodye test in which it react with benzene onium chloride and form a dye.



(yellow colour dye)

where as methylamine give unstable diazonium salt of aliphatic amines. It means it does not form any dye.

(iv) Gabrielphthalimide synthesis reaction is a method used to prepare primary amines from phthalimide.

Reaction:

Phthalimide $\xrightarrow[KOH]{Alcohol}$ Potassium plithalimide

Potassium phthalimide + R – X $\xrightarrow{SN2}$ N-alkyl phthalimide

N-alkyl phthalimide + H_2O / H_2NNH_2 $\longrightarrow$ Primary amine (R – NH_2) + Phthalic acid / Hydrazide

Example:

$C_6H_4(CO)_2NH + KOH \longrightarrow C_6H_4(CO)_2NK$

$C_6H_4(CO)_2NK + CH_3CH_2Br \longrightarrow C_6H_4(CO)_2NCH_2CH_3$

$C_6H_4(CO)_2NCH_2CH_3 + H_2NNH_2 \downarrow CH_3CH_2NH_2 + C_6H_4(CO)_2N_2H_2$

(v) Direct bromination of aniline with Br_2 gives 2, 4, 6-tribromoaniline because the $-NH_2$ group is a very strong activator. To get only the *p*-substituted product, we first protect the amino group by acetylation, then brominate, and finally hydrolyse.

Step 1: Protect $-NH_2$ group by acetylation

$$C_6H_5NH_2 + CH_3COCl \xrightarrow[\text{Base}]{} C_6H_5NHCOCH_3$$

Product: Acetanilide

Step 2: Bromination

$$C_6H_5NHCOCH_3 + Br_2 \xrightarrow[\text{AeOH}]{} p — BR — CH_4NHCOCH_3$$

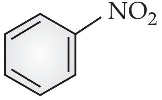
The $-NHCOCH_3$ group is less activating, so bromination occurs mainly at the para position.

Step 3: Hydrolysis of the amide

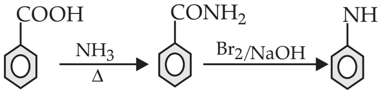
$$p - Br - C_6H_4NHCOCH_3 + H_2O \xrightarrow[H^+ \text{ or } OH^+\text{, heat}]{} p - Br - C_6H_4NH_2$$

Final Product: *p*-Bromoaniline

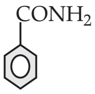
(vi)



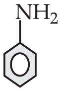
(vii)



(A)



(B)



2.

$$\begin{tikzcd} A \arrow[r, "Br_2 + KOH"] & B \arrow[r, "HNO_2"] \arrow[d, "CHCl_3" ', "KOH" '] & C \arrow[d, "C_2H_5OH"] \\ & D & E \end{tikzcd}$$

A = C_6H_5 $CONH_2$(Benzamide)

B = $C_6H_5NH_2$ (Aniline)

C = $C_6H_5N_2Cl$ (Benzene diazonium chloride)

D = C_6H_5NC (Phenyl isocyanide)

E = C_6H_6 (Benzene)

3. (i) (1) Benzene sulphonyl chloride ($C_6H_5SO_2Cl$) is called Hinsberg reagent. It is used to distinguish between primary secondary and tertiary amines.

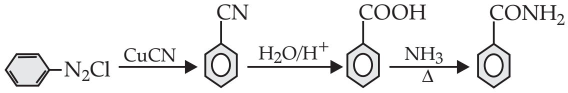
(2) $C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$

(ii) (1) In case of aliphatic amine as inductive effect of alkyl group increases the electron density of the nitrogen atom which increases the basicity. In case of anline ($C_6H_5NH_2$) due to conjugation the lone pair density is less than that of methyl amine. That's why methyl amine is more basic.

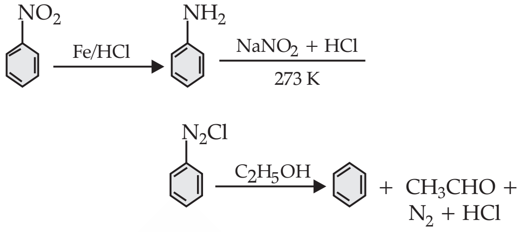
(2) It is because the amino group in aniline activates the benzene ring and making it more susceptible to an electrophilic attack on ortho and para position.

(3) In tertiary amino no hydrogen atom is present hence it cannot form hydrogen bond. On the other hand primary amines can form inter molecular hydrogen bonds due to which it has higher boiling point than tertiary amines.

4. (i) (1)



(2)



(ii) Aniline does not undergo Friedel–Crafts alkylation or acylation because on the way its $-NH_2$ group interacts with the Lewis acid catalyst used in the reaction.

(iii) $(C_2H_5)_3N < C_2H_5NH_2 < C_2H_5 — OH$

5. (i) (1) Under nitration conditions (conc. HNO_3 + conc. H_2SO_4), the $-NH_2$ group of aniline gets protonated to form $-NH_3{}^+$:

$$C_6H_6NH_2 + H^+ \rightarrow C_3H_5NH_3 + C_9H_5NH_2 + H^+$$

The $-NH_3{}^+$ group is strongly deactivating and meta-directing in electrophilic substitution reactions. Therefore, nitration occurs mainly at the meta position, giving a good yield of m-nitroaniline, despite $-NH_2$ normally being o/p directing.

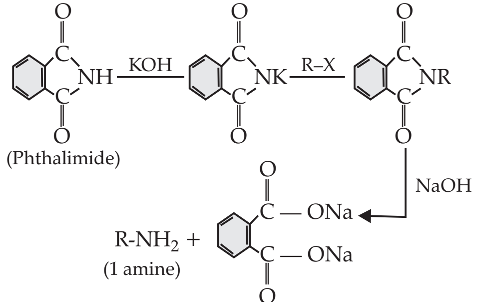
(2) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution because the lone pair of electrons on nitrogen atom in $(CH_3)_2NH$ is more available for protonation. This is due to less steric hindrance and favourable solvation.

(3) The reaction between ammonia and alkyl halide can form a mixture of primary secondary and tertiary amines. along with quaternary ammonium salts separation of this mixture is difficult due to their similar chemical properties This make it difficult to obtain a pure primary amines.

(ii) (1) Carbylamin reaction is the reaction of primary amine chloroform and a base to synthesise isocyanides.

$$\underset{\text{1° Amine}}{CH_3 — NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Methyl Isocyanide}}{CH_3 — NC} + 3KCl + 3H_2O$$

(2) Gabriel pthalimide synthesis is a chemical reaction that produces primary amines from primary alkyl halide.



Level - 2 ADVANCED COMPETENCY FOCUSED QUESTIONS

MULTIPLE CHOICE QUESTIONS (MCQs) (1 Mark)

1. Option (D) is correct

   Explanation: The solubility of amines decreases in the order 1° > 2° > 3° due to tendency of forming H-bonds with water.

2. Option (C) is correct

   Explanation: In excess of ammonia primary amine is formed as major product

   $$\underset{\text{(Alkyl halide)}}{R-X} + \underset{\text{(Excess)}}{NH_3} \longrightarrow \underset{\text{(1° Amine)}}{R-NH_2} + HX$$

3. Option (C) is correct

   Explanation: Antihistamines are amine-based compounds that work by blocking histamine receptors (H_1-receptors) in the body. Histamine is released during allergic reactions, causing symptoms like sneezing, itching, and runny nose. By blocking these receptors, antihistamines reduce these symptoms.

4. Option (B) is correct

   Explanation: Aniline is an aromatic amine with the formula $C_6H_5NH_2$.The $-NH_2$ group (amino group) on the benzene ring activates the ring towards electrophilic substitution reactions such as nitration, sulphonation, and diazotisation. Through diazotisation, aniline forms diazonium salts, which are key intermediates in the synthesis of azo dyes — a major class of synthetic dyes used in fabrics and inks.

5. Option (C) is correct

   Explanation: Ignocaine (also called Lidocaine) is a local anaesthetic and pain-relief agent commonly used in topical creams, injections, and sprays. Lignocaine is a substituted amide, specifically, an amide derived from a secondary amine. It has both amine and amide functional groups in its structure, and it belongs to the class of amino amides used in anaesthesia.

6. Option (A) is correct

   Explanation: Aliphatic tertiary amines have three alkyl groups attached to the nitrogen atom and no hydrogen atom on nitrogen. This structure makes them incapable of forming hydrogen bonds with water (because H-bonding requires a hydrogen directly attached to a nitrogen, oxygen, or fluorine atom). As a result, their solubility in water is less than that of primary amines, which have $-NH_2$ groups and can form strong hydrogen bonds with water molecules.

7. Option (A) is correct

   Explanation: In medicinal chemistry, amines play a crucial role because many neurotransmitters (like dopamine, serotonin, histamine) are amines or amine derivatives. Amines can bind to specific receptors in the body due to their structural similarity to natural molecules. This interaction with biological receptors makes them highly effective in drug design for treating conditions like depression, allergies, and neurological disorders.

ASSERTION-REASON QUESTIONS (1 Mark)

1. Option (A) is correct

   Explanation: Assertion is true. Antihistamines are indeed effective in treating allergies such as sneezing, itching, watery eyes, etc.

   Reason is also true. Antihistamines work by blocking histamine (H_1) receptors. They have a structure similar to histamine, allowing them to bind to these receptors and prevent histamine from triggering allergic responses.

2. Option (A) is correct

   Explanation: Assertion is true. Aniline is indeed widely used in the synthesis of dyes and pH indicators due to its reactivity and functional versatility.

   Reason is also true. The $-NH_2$ (amino) group in aniline is an electron-donating group, which activates the benzene ring toward electrophilic substitution reactions, especially at the ortho and para positions. This enhanced reactivity makes it valuable in dye synthesis, where substitution reactions are key.

3. Option (A) is correct

   Explanation: Assertion is true. Tertiary amines are indeed less soluble in water than primary amines of similar molecular mass.

   Reason is also true. Primary amines have an $-NH_2$ group, which can form strong hydrogen bonds with water molecules due to the presence of two hydrogen atoms bonded to nitrogen. In tertiary amines, there are no hydrogen atoms directly bonded to nitrogen, so they cannot form hydrogen bonds with water effectively. This reduces their solubility in water.

4. Option (C) is correct

   Explanation: Assertion is true. Amines are indeed commonly used in medicinal drugs. Many drugs, such as antihistamines, antidepressants, and local anaesthetics, contain amine groups because they interact effectively with biological receptors.

   Reason is false. Amines are basic, not acidic, in nature. They do not neutralise stomach acid like antacids do. Instead, compounds like magnesium hydroxide or sodium bicarbonate are used to neutralise stomach acid.

5. Option (A) is correct

   Explanation: Assertion is true. Aromatic amines, such as *p*-aminophenol, are indeed used in the synthesis of paracetamol (acetaminophen). It is one of the key starting materials.

   Reason is also true. Aromatic amines can undergo acylation (reaction with acyl chlorides or acid anhydrides) to form amide derivatives, which is exactly what happens in the synthesis of paracetamol. In the synthesis of paracetamol, *p*-aminophenol (an aromatic amine) reacts with acetic anhydride to form the amide compound paracetamol.

VERY SHORT ANSWER TYPE QUESTIONS (2 Marks)

1. The sulphonyl group is a stronger electron withdrawing group compared to the carbonyl group which makes the H atom attached to the N atom more acidic in nature. Hence P is more likely to be acidic in nature than Q.

2. The orange coloured dye will be produced in larger amounts by process P. The diazonium salt X is unstable at higher temperatures and hence should be prepared at low temperature or used immediately.

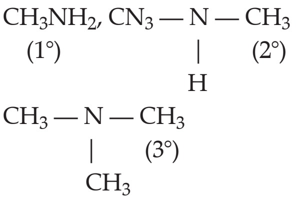
SHORT ANSWER TYPE QUESTIONS (3 Marks)

1. (i) Test tube M = Secondary amine

Test tube N = Tertiary amine

Test tube O = Primary amine

(ii)



CH_3NH_2 (1°), $CN_3—\underset{|\atop H}{N}—CH_3$ (2°)

$CH_3—\underset{|\atop CH_3}{N}—CH_3$ (3°)

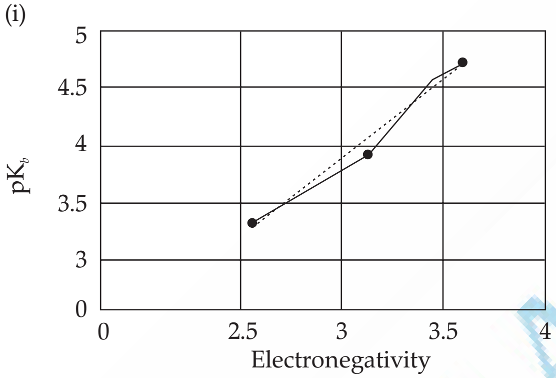
2. Test tube A contains benzylamine

The lone pair of electrons on N-atom of aniline is conjugated with an is delocalised over the benzene ring and hence is less available for protonation.

In arylalky lamines, the lone pair of electrons on the N-atom is not conjugated with the benzene ring and therefore is not delocalised. Hence, the lone pair of electrons on the N-atom in arylalky lamines is more readily available for protonation than that on the N-atom of aniline. So aniline has high value of pK_b. That's why compound B is aniline and compound A is benzyl amine.

CASE BASED QUESTIONS (4 Mark)

1. (i)



------ Is the line of best fit

The pK_b increases with an increase in the electronegativity of the substituent, therefore the basic strength decreases with an increase in the electronegativity of the substituent.

(ii) (D) 9.1

(iii) (A) 3.5

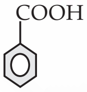
OR

(C) 10.15

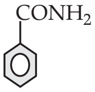
2. (i) $(C_2H_5)_2NH < (C_2H_5)_3N < C_2H_5NH_2$

(ii) It is because the amino group is protonated to form an anilinium ion which is meta directing in the acidic medium used for nitration.

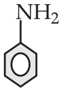
(iii) (a) (A)

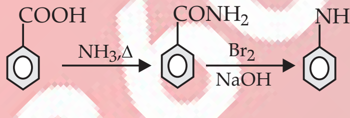


(B)



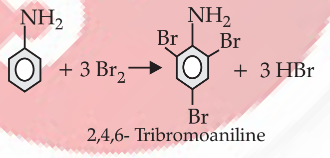
(C)



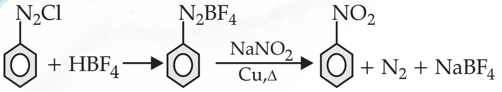


OR

(b) (1)



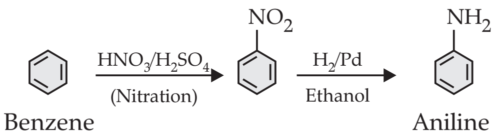
(2)



3. (i) Benzene ring in aniline is highly activated. This is due to the sharing of lone pair of nitrogen with the ring which results in increase in the electron density on the ring and hence facilitates the electrophilic attack.

(ii) In aniline, the electron density is more at ortho and para positions than meta position, so, the substitution mainly takes place at ortho and para positions.

(iii) (a)



OR

(b) The amino group is an activating group and activate the ring at *o*- and *p*- positions. In benzene, no group is present, so it does not respond to the electrophilic substitution reaction readily.

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. (i) Benzene sulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent. Benzene sulphonyl chloride is replaced by p-toluene sulphonyl chloride

(ii) Amine V and W have the structural formula of R-NH-R

(iii) The hydrogen attached to nitrogen in the product formed after the amine U reacts with Heisenberg's reagent is strongly acidic due to the presence of hydrogen atom with nitrogen atom. Hence, it is soluble in aqueous NaOH.

Amine V and W do not contain any hydrogen atom attached to the nitrogen atom in the product formed are not acidic and hence insoluble in aqueous NaOH.

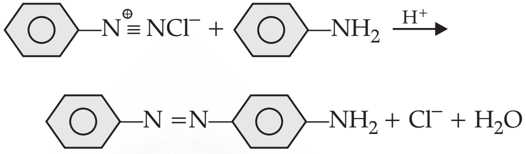
(iv) Amine U may be prepared in aqueous NaOH So, it is a primary amine Gabriel synthesis is used for the preparation of primary amines.

2. (i) Aqueous solution of compound X can conduct electricity due to the presence of ions in it.

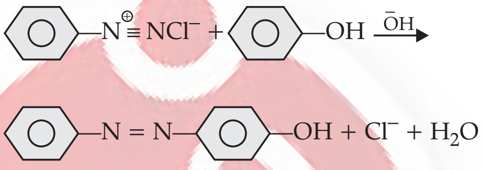
(ii) $C_6H_5NH_2 + NaNO_2 + 2HCl \rightarrow C_6H_5N_2^+Cl^-$ (compound X) + NaCl + $2H_2O$

(iii) Due to its unstability, the benzene diazonium chloride salt is not generally stored and is used immediately after its preparation.

(iv)



(Yellow dye)



(Orange dye)