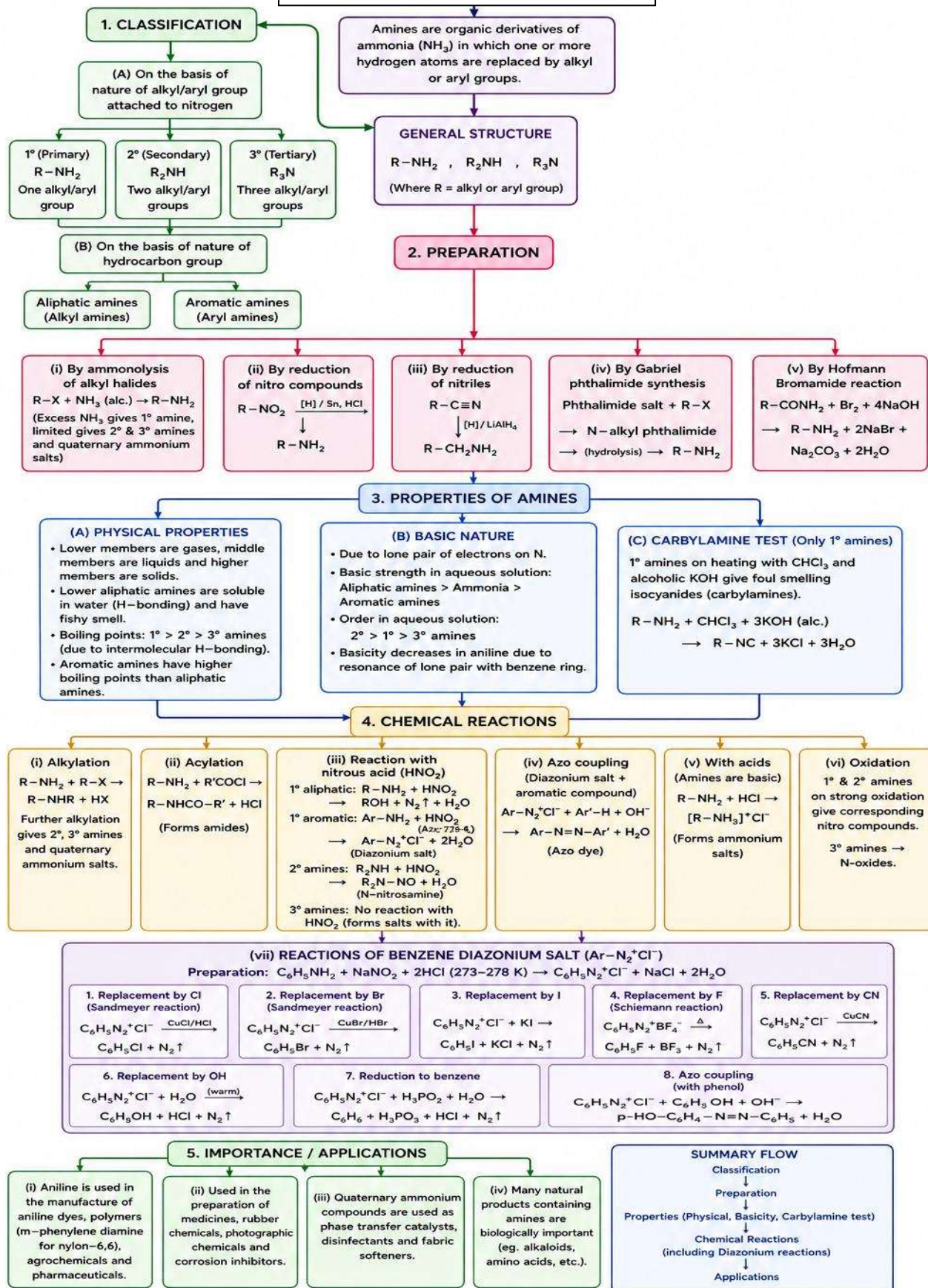


Unit-9 Amines



SECTION – A (1 Mark)

Q1. The correct order of decreasing basicities of $\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and $(\text{C}_2\text{H}_5)_3\text{N}$ in aqueous solution is :

- (A) $(\text{C}_2\text{H}_5)_3\text{N} > (\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2$ (B) $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_3\text{N}$
(C) $\text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N}$ (D) $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2$

Q2. Aniline reacts with Br_2 water to give.....

- (a) 1-bromoaniline (b) 1,2- dibromoaniline (c) 2,4,6-tribromoaniline (d) No reaction

Q3. The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is.....

- (a) excess H_2 (b) Br_2 in aqueous NaOH
(c) iodine in the presence of red phosphorus (d) LiAlH_4 in ether

Q4 Which of the following compounds will dissolve in an alkali solution after it undergoes reaction with Hinsberg's reagent?

- (a) $(\text{CH}_3)_3\text{N}$ (b) CH_3NH_2 (c) $(\text{C}_2\text{H}_5)_2\text{NH}$ (d) $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_5$

Q5. The correct IUPAC for $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{C}_2\text{H}_5$ is.....

- (a) N-methyl-N-ethylpropan-1-amine (c) N-ethyl-N-methylpropan-1-amine
(b) N,N diethylpropane-1-amine (d) N,N-dimethylpropan-1-amine

Q6. Anilinium hydrogen sulphate on heating at 453-473 K produces which of the following as a major product?

- (A) 2-aminobenzene sulphonic acid (B) benzene sulphonic acid
(C) 2-aminobenzoic acid (D) sulphanilic acid

Q7. An amine 'X' reacts with Hinsberg reagent and the product obtained is insoluble in alkali. The amine 'X' is:

- (A) $(\text{CH}_3)_2\text{NH}$ (B) $(\text{CH}_3)_3\text{N}$ (C) $\text{CH}_3\text{-CH}_2\text{-NH}_2$ (D) $\text{C}_6\text{H}_5\text{-NH}_2$

Q8. Which of the following amines does not give foul smell of isocyanide on heating with chloroform and ethanolic KOH ?

- (A) $\text{CH}_3\text{-CH}_2\text{-NH}_2$ (B) $(\text{CH}_3)_3\text{CH-CH}_2\text{-NH}_2$
(C) $(\text{CH}_3\text{-CH}_2)_3\text{N}$ (D) $\text{C}_6\text{H}_5\text{-NH}_2$

Q9. When alkyl iodide is treated with large excess of ammonia, the major product obtained is:

- (A) Tertiary amine (B) Quaternary ammonium salt
(C) Secondary amine (D) Primary amine

Q10. Identify the false statement about amines.

- (a) Alkylamines are stronger bases than arylamines.
(b) Alkylamines react with nitrous acid to produce alcohols.
(c) Alkylamines are stronger bases than ammonia.
(d) Arylamines react with nitrous acid to produce phenols

The following questions has two statements; one is assertion and second is reason write;

- (a) If assertion and reason both are true and R is correct explanation of A
(b) Assertion and reason both are correct but R is not the correct explanation
(c) A is true but R is false (d) A is false but R is true

Q11. ASSERTION(A): Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

REASON(R): Diazonium salts of aliphatic amines undergo resonance.

Q12. ASSERTION (A): Aniline undergoes Friedel-Crafts reaction.

REASON (R): Aniline forms salt with AlCl_3 The Lewis acid in Friedel-Craft reaction..

Q13. ASSERTION(A): Gabriel phthalimide synthesis is not used for the preparation of primary aromatic amines.

REASON(R): Aryl halide do not undergo substitution reaction easily.

Q14. ASSERTION(A):): Monobromination of aniline can be conveniently done by protecting the amino group by acetylation.

REASON(R): Acetylation decrease the activation effect of the amino group.

Q15. ASSERTION(A): Nitration of aniline in strongly acidic medium give m-nitro aniline as major product.

REASON(R): $-\text{NH}_2$ group in aniline is ortho-para directing .

ANSWERS KEY:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
d	c	d	b	c	d	a	c	d	d	a	d	a	a	b

SECTION - B (2 marks)

Q1. a) Arrange the following in increasing order of their basic strength:

$\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NH}_2$, NH_3 , $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$

b) $(\text{CH}_3)_2\text{NH}$ is more basic than $(\text{CH}_3)_3\text{N}$ in an aqueous solution. Give reason.

Hint: Greater stability for ammonium cation of dimethyl amine than ammonium cation of trimethyl amine.

Q2. The $-\text{NH}_2$ group in aniline is acetylated before nitration, cite possible reason for it.

[Hint: Direct nitration of aniline gives tarry oxidation product]

Q3. Account for the following:

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

Hint: aniline is a weaker base than methylamine as lone pair of electron in aniline is delocalized over the benzene ring and less available for protonation.

(ii) Although trimethylamine and n-propylamine have the same molecular weight, but the former boils at a lower temperature (276 K) than the latter (322 K). Explain.

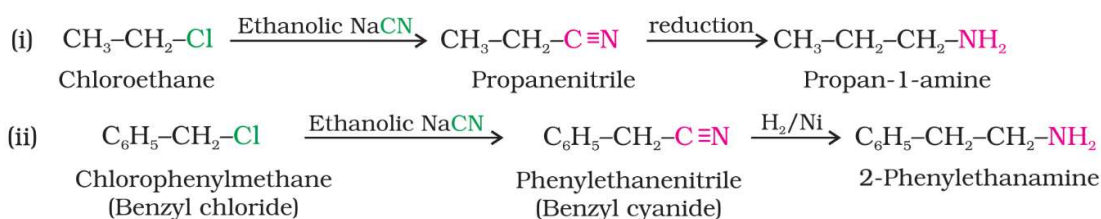
Hint: $(\text{CH}_3)_3\text{N}$, is a tertiary amine does not have any H-atom on the N-atom & thus it does not undergo H-bonding.

Q4. Write chemical equations for the following conversions:

(i) $\text{CH}_3-\text{CH}_2-\text{Cl}$ into $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2$

(ii) $\text{C}_6\text{H}_5-\text{CH}_2-\text{Cl}$ into $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\text{NH}_2$

Hint:



Q5. Give a chemical test to distinguish between the following pair of compounds

(a) Aniline & Methanamine

(b) Ethanamine & N-methylethanamine

[Hint: a- azodye test, b- Carbyl amine or Hinsberg test]

SECTION – C (3 marks)

Q1. Arrange the following in increasing order of their basic strength:

(i) $\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NH}_2$, NH_3 , $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ and $(\text{C}_2\text{H}_5)_2\text{NH}$

- (ii) $\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $(\text{C}_2\text{H}_5)_3\text{N}$, $\text{C}_6\text{H}_5\text{NH}_2$
 (iii) CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$, $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$.

[Hint: ref, NCERT Ch.9 q.n. 9.4]

Q2. Illustrate the following reactions:

- (a) Sandmeyer's reaction
 (b) Gabriel phthalimide reaction
 (c) Carbylamine reaction

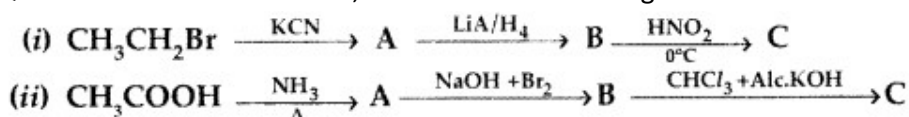
[Hint: ref summary]

Q3. Cite the reasons for the following :

- (i) Although amino group is o- and p-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.
 (ii) Ethylamine is soluble in water whereas aniline is not soluble in water.
 (iii) Primary amines have higher boiling points than tertiary amines

[Hint: ref. Summary]

Q4. Predict the structure of A, B and C in the following reactions:



[Hint: (i) A- $\text{CH}_3\text{CH}_2\text{CN}$, B- $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, C- $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$]

(ii) A- CH_3CONH_2 , B- $\text{CH}_3\text{CH}_2\text{OH}$, C- $\text{CH}_3\text{CH}_2\text{NC}$

Q5. Complete & give names to the following reactions:

- (a) $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{CuCl} + \text{H}^+$
 (b) $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{CHCl}_3 + \text{KOH}$
 (c) $\text{C}_6\text{H}_5\text{CONH}_2 + \text{Br}_2 + \text{KOH}$

[Hint: a- Sandmeyer's reaction, b- Carbylamine reaction c- Hoffmann bromamide reaction]

SECTION D Case Based Questions (4 Marks)

Q1. Read the following passage carefully and give answers of following questions:

Amines are usually formed from amides, imides, halides, nitro compounds, etc. They exhibit hydrogen bonding which influences their physical properties. In alkyl amines, a combination of electron releasing, steric and H-bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. Alkyl amines are found to be stronger bases than ammonia. Amines being basic in nature, react with acids to form salts. Aryldiazonium salts, undergo replacement of the diazonium group with a variety of nucleophiles to produce aryl halides, cyanides, phenols and arenes.

Answer the following questions:

(a) How can you convert the following?

- (i) Ethanoic acid to methanamine (ii) Propanenitrile to 1-aminopropane

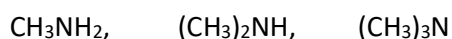
[Hint: i) Heat with NH_3 followed by Hoffmann bromamide reaction

ii) reduce with suitable reducing agent]

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

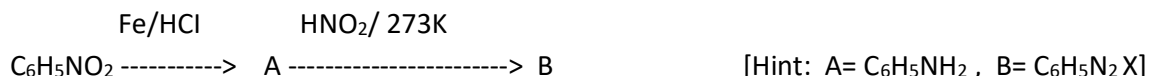
[Hint: 1° amines have intermolecular H-bonding but 3° do not.]

(c) (1) Arrange the following in increasing order of their basic strength in aqueous solution:



OR

(2) Give the structures of A and B in the following reaction:



Q2. Read the passage given below and answer the following questions:

The amines are basic in nature due to the presence of a lone pair of electron on N-atom of the -NH_2 group. Aliphatic amines are stronger bases than NH_3 because of the +I effect of the alkyl groups. Thus, the order of basic nature of amines is expected to be $3^\circ > 2^\circ > 1^\circ$ (in gaseous phase), however the observed order is $2^\circ > 1^\circ > 3^\circ$ (for Methyl substitution) and $2^\circ > 3^\circ > 1^\circ$ (for ethyl substitution). This is explained on the basis of crowding on N-atom of the amine by alkyl groups which hinders the approach and bonding by a proton, consequently, the electron pair which is present on N is unavailable for donation. Aromatic amines are weaker bases than ammonia and aliphatic amines. Electron -donating groups such as -CH_3 , -OCH_3 , etc. increase the basicity while electron-withdrawing substitutes such as -NO_2 , -CN , halogens, etc. decrease the basicity of amines. The effect of these substituents is more at p than at m-positions.

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

- (a) Methyl amine (b) Trimethylamine (c) Aniline (d) Dimethylamine

(ii) Choose the correct statement

- (a) Methylamine is slightly acidic (b) Methylamine is stronger base than ammonia
(c) Methylamine is less basic than ammonia (d) Methylamine forms salt with alkali

(iii) The electron donating groups like -OCH_3 , -CH_3 etc. increases basicity of amines, Comment on the statement.

(iv) The decreasing order of basicity of primary, secondary and tertiary ethylamines and NH_3 will be

- (a) $\text{NH}_3 > \text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N}$ (b) $(\text{C}_2\text{H}_5)_3\text{N} > (\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$
(c) $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_3\text{N} > \text{NH}_3$ (d) $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$

[Hint: (i)-d, (ii)-b, (iii)-Resonance, (iv)-d]

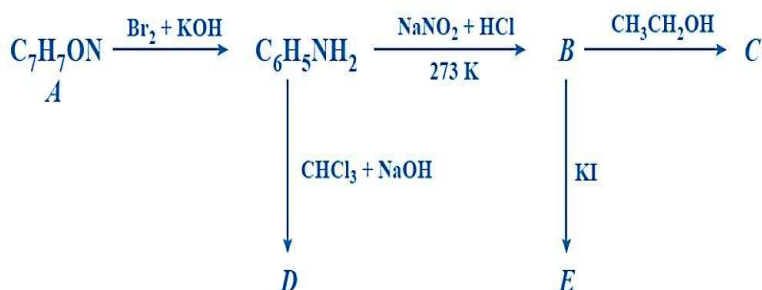
SECTION –E (5 Marks)

Q1. An aromatic compound 'A' of molecular formula $\text{C}_7\text{H}_7\text{ON}$ undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions:

[Hint : A = $\text{C}_6\text{H}_5\text{-CONH}_2$ B = $\text{C}_6\text{H}_5\text{N}_2$

C = C_6H_6 D = $\text{C}_6\text{H}_5\text{NC}$ E =

$\text{C}_6\text{H}_5\text{I}$]



Q2. a. $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ reacts with the following reagents to give :

- (i) $\text{H}_3\text{PO}_2 + \text{H}_2\text{O}$ (ii) CuCN/KCN (iii) H_2O

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

(ii) Aniline does not give Friedel Craft reaction.

[Hint : ref. summary]