

AMINES

GIST OF THE CHAPTER

After studying this Unit, you will be able to

- describe amines as derivatives of ammonia having a pyramidal structure;
- classify amines as primary, secondary and tertiary;
- name amines by common names and IUPAC system;
- describe some of the important methods of preparation of amines;
- explain the properties of amines;
- distinguish between primary, secondary and tertiary amines;
- describe the method of preparation of diazonium salts and their importance in the synthesis of a series of aromatic compounds including azo dyes.

Amines are the organic which contain $-NH_2$ gp, $-NH$ gp, $-N - gp$. they are called primary (1°), secondary (2°) and tertiary (3°) amines.

They are considered as derivatives of ammonia obtained by replacement of hydrogen atoms with alkyl or aryl groups.

Amines are usually formed from nitro compounds, halides, amides, imides etc . Aromatic amines are called amines arenes.

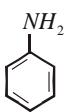
Structure :- Nitrogen is in sp^3 hybridised state and geometry of amines is pyramidal. The three hybridised orbital overlap with other and four one contain unshared pair & electron. Bond angle is 108° in trimethylamine

Nomenclature : Aliphatic Amine is named by prefixing alkyl group to amine. For eg. alkylamine as ethyl amine. In IUPAC system it is termed as Alkanamines for eg. CH_3NH_2 – methanamine

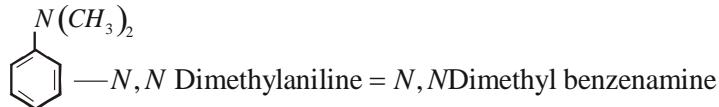
Secondaryamine : (R_2NH)

example - $CH_3NHCH_3 \rightarrow$ dimethylamine – N – Methylmethanamine-

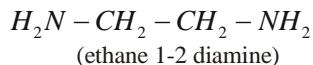
Tertiaryamines :- (R_3N) → tri alkyl amines , N,N dialkyl alkanamine .



Aromaticamines . -Aniline or Benzenamine



If more than one amine group is present at different position in the parent chain, their positions are specified by giving numbers to the carbon atoms bearing $-NH_2$ gp and suitable prefix as di, tri, etc is attached to the amines the letter 'e'

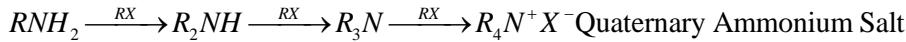
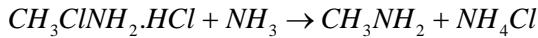
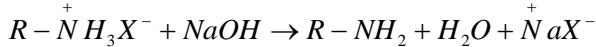
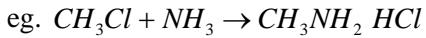
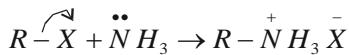


of the suffix of the hydrocarbon part is retained. For example

Preparation of Amines

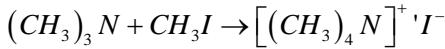
(I) **Ammonolysis** :- Alkyl halide + $NH_3 \rightarrow$ Primary Amines

(It is N.S.R as X is removed)



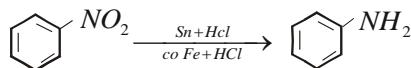
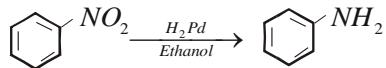
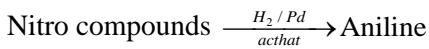
(ii) **Quaternary Ammonium Salts /Chlorides** :-

Tertiary Amines + Alkyl halides \rightarrow Quaternary Ammonium Chloride

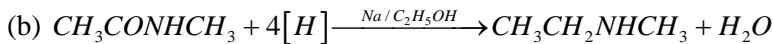
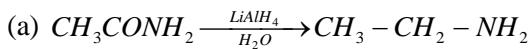


ORDER OF REACTIVITY OF HALIDE WITH AMINES $RI > RBr > RCl$

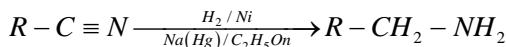
(II) **Reduction of Nitro Compounds** :-



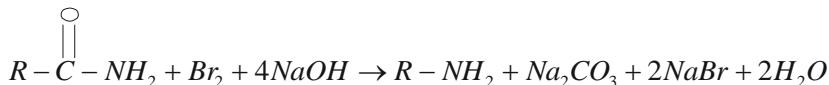
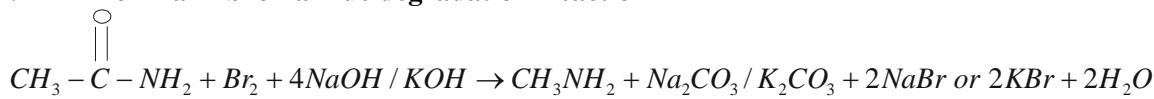
III **Reduction of Amides** :-



IV **From Cyanides** : Reduction or catalytic hydrogenation produce primary amines. It is used as ascent of seris.



V **Hoffmann bromamide degradation Reaction**

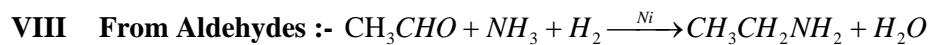


VI **From isocyanides** :- $CH_3NC + 4H \rightarrow CH_3NHCH_3$

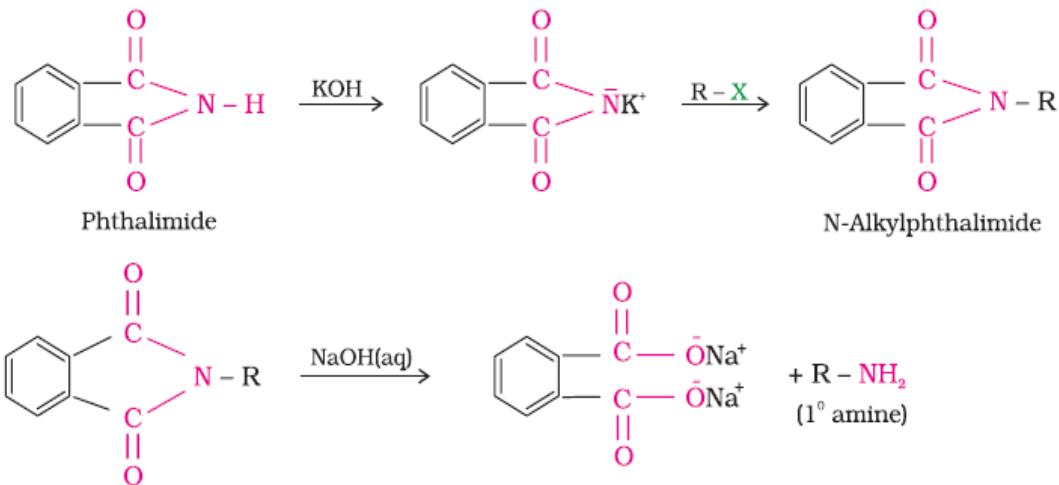
VII From alcohols :- $CH_3CH_2OH + NH_3 \xrightarrow[\Delta / 723K]{Al_2O_3} C_2H_5NH_2 + H_2O$

Primary amine + Alcohol $\xrightarrow{Al_2O_3}$ Sec Amine + Alcohol $\xrightarrow{Al_2O_3}$ Tertiaryamies

Tertiary amines+Alcohol → Quaternary ammonium hydroxide



IX Gabriel Phthalimide Synthesis

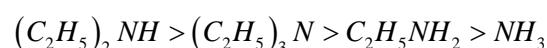


Physical Properties :- (1) Lower amines are gases followed by liquids. Higher members are solids .

- (ii) Polar in nature & form inter molecular Hydrogen Bonding.
- (iii) Lower amines are solids in water but solubility decrease with increase in alkyl group.
- (iv) Except methylamines and ethylamine other amines have fishy odour. Aromatic amines are toxic to easy oxidation in air.
- (v) Primary Amines have highest boiling point due to more extensive H-bonding. Therefore Primary amines >Secondary Amines>tertiary Amines
- (vi) Aniline is steam volatile & obtained by steam distillation.

Chemical Properties :-(Reactions involved)

(i) Basic Character

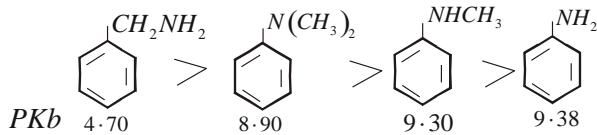


Amines are reactive due to difference in electro negativity between nitrogen and hydrogen atoms and presence of unshared pair of electrons over nitrogen . Amines behave as nucleophile .

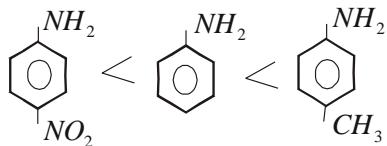
(2) PK_b Values of amines in aqueous phase and their basic character

$PK_b = -\log K_b$ – Higher value of K_b and lower value of PK_b , stronger will be amine.

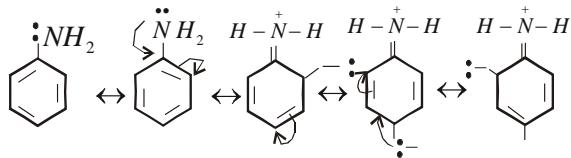
P – Toluidine > m – Toluidine > Aniline > O – Toluidine



The basic strength is also affected by $+I$ or $-I$ effect > solvation effect, steric hindrance structure etc.

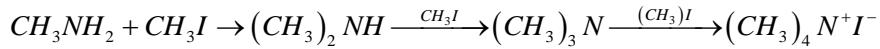


(3) Aniline is less basic than aliphatic amines due to +ve charge on nitrogen in '3' out of five resonating structures.

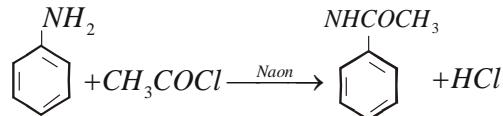
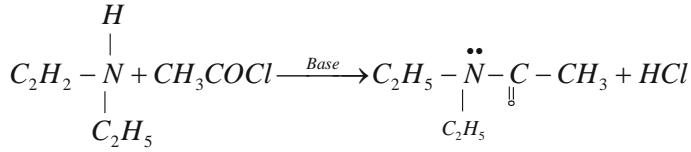
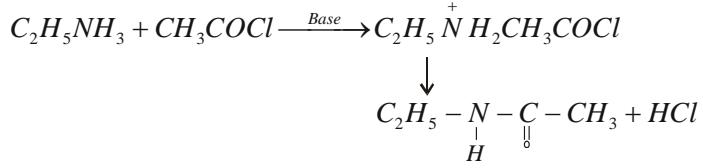


(4) The electron releasing groups like $-\text{OCH}_3, -\text{CH}_3$ increases basic strength but electron withdrawing groups like $-\text{NO}_2, -\text{SO}_3, -\text{COOH}, -\text{X}$ decreases it

(5) **Alkylation :-** P. Amine + Alkylhalide \rightarrow Sec Amine + AlkylHalide

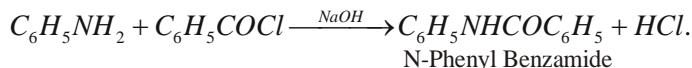


(6) **Acylation:-**

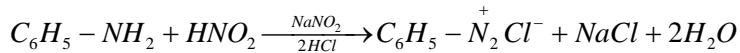
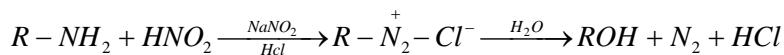


(7) **Benzoylation:-** $\text{C}_6\text{H}_5\text{COCl} + \text{CH}_3\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{CONHCH}_3 + \text{HCl}$

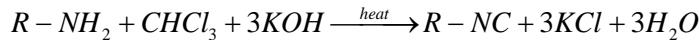
Benzoylchloride Methanamine N-methyl benzamide



(8) **With HNO_2 :-** $\text{C}_2\text{H}_5\text{NH}_2 + \text{HNO}_2 \longrightarrow \text{C}_2\text{H}_5\text{OH} + \text{N}_2 + \text{H}_2\text{O}$



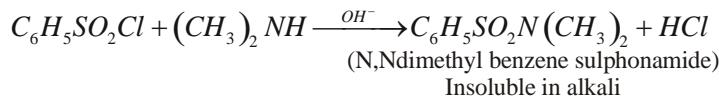
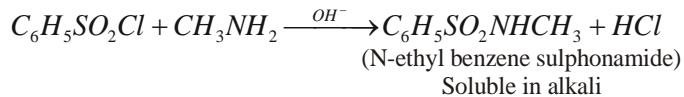
(9) Carbylamine reaction :- (Isocyanide test)



(Only primary amines give this reaction and not Sec or Tertiary amines)

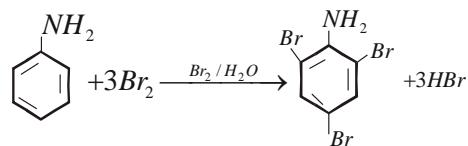
(10) With Aryl Sulphonyl chloride :- (Hinsberg's test)

Benzene sulphonyl chloride ($C_6H_5SO_2Cl$) called as Hinsberg's reagent. It is used to distinguish between primary secondary and tertiary amines.

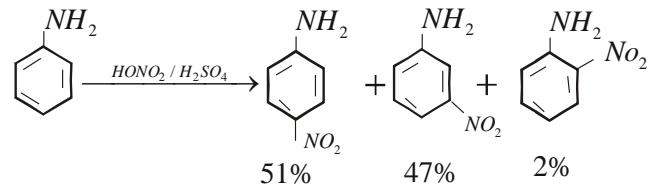


(11) Bromination, Nitration Sulphonation (as E.S.R. in Amines)

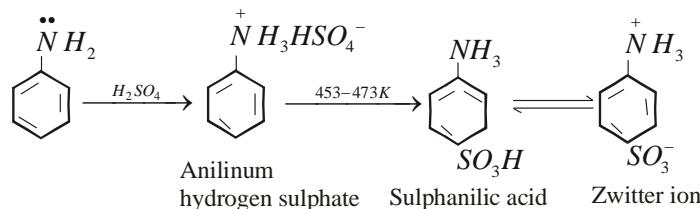
(a)



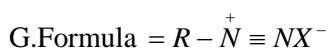
(b)



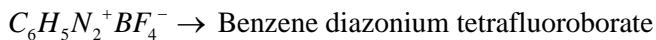
(c)



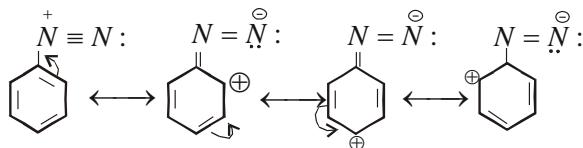
DIAZONIUM SALTS :-



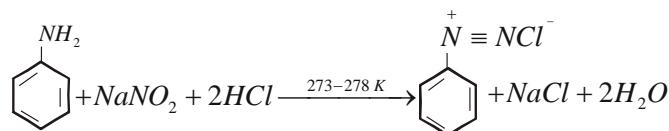
R = Aryl gp, $X - Cl^-, Br^-, HSO_4^-, BF_4^-$ etc



The salts i.e diazonium salts of primary amines are highly unstable . Primary aromatic amines form large no of arene diazonium salts which are stable due to resonance, diazonium ion is stable.

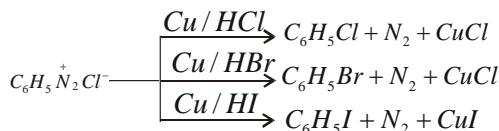


Preparation :-

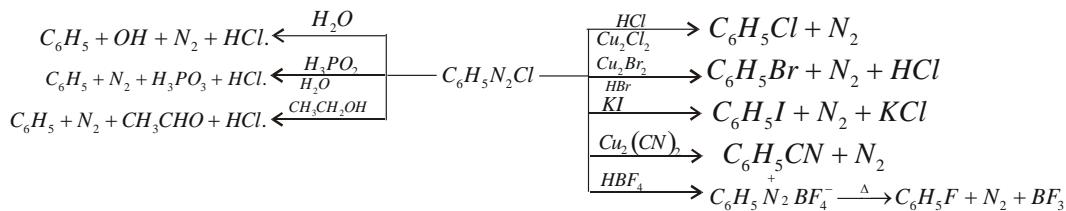


IMPORTANT CHEMICAL REACTIONS

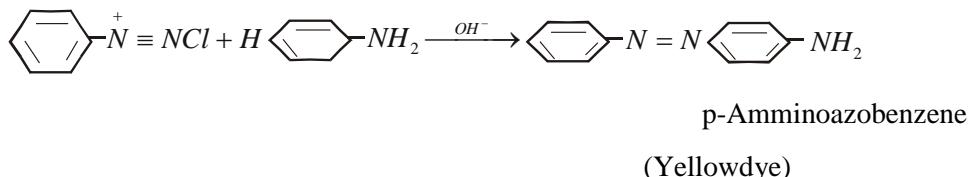
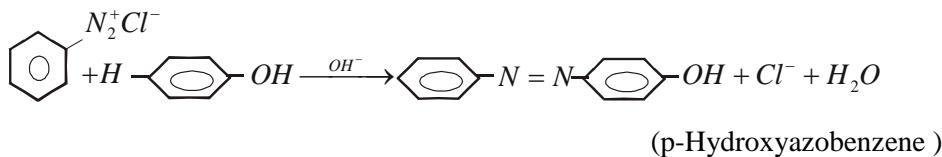
(1) Gattermann reaction :-



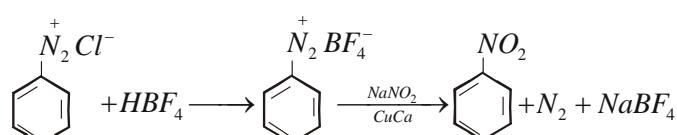
(2) Sandmeyer Reaction :



(3) Coupling Reaction :-



(4)



Uses :- (1) Used to prepare halobenzene, phenol, nitro benzene

(2) Used in preparation of methyl orange and dyes and also substituted aromatic compound.

OBJECTIVE TYPE QUESTIONS (MULTIPLE CHOICE)

1. The conversion of benzene diazonium chloride to bromobenzene can be accomplished by

- (a) Reimer-Tiemann reaction
- (b) Friedel-Crafts reaction
- (c) Gattermann reaction
- (d) Azo-Coupling reaction

2. The correct IUPAC name for $\text{CH}_2 == \text{CHCH}_2\text{NHCH}_3$ is

- (a) Allylmethylamine (b) 2-amino-4-pentene
- (c) 4-aminopent-1-ene (d) N-methylprop-2-en-1-amine

3. In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as source of nitrogen is _____

- (a) Sodium amide, NaNH_2 (b) Sodium azide, NaN_3
- (c) Potassium cyanide, KCN (d) Potassium phthalimide, $\text{C}_6\text{H}_4(\text{CO})_2\text{N}^-\text{K}^+$

4. 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

5. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?

- (a) H_2 (excess)/Pt (b) LiAlH_4 in ether (c) Fe and HCl (d) Sn and HCl

6. Amongst the given set of reactants, the most appropriate for preparing 2° amine is _____.

- (a) 2° R—Br + NH_3
- (b) 2° R—Br + NaCN followed by H_2/Pt
- (c) 1° R—NH₂ + RCHO followed by H_2/Pt
- (d) 1° R—Br (2 mol) + potassium phthalimide followed by $\text{H}_3\text{O}^+/\text{heat}$

7. The best reagent for converting, 2-phenylpropanamide into 1-phenylethanamine is _____.

- (a) excess H_2/Pt (b) NaOH/Br_2 (c) $\text{NaBH}_4/\text{methanol}$ (d) $\text{LiAlH}_4/\text{ether}$

8. The source of nitrogen in Gabriel synthesis of amines is _____.

- (a) Sodium azide, NaN_3 (b) Sodium nitrite, NaNO_2
- (c) Potassium cyanide, KCN (d) Potassium phthalimide, $\text{C}_6\text{H}_4(\text{CO})_2\text{N}^-\text{K}^+$

9. Which of the following statements about primary amines is 'false'?

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

10. Amongst the following, the strongest base in aqueous medium is _____.

- (a) CH_3NH_2 (b) NCCH_2NH_2 (c) $(\text{CH}_3)_2\text{NH}$ (d) $\text{C}_6\text{H}_5\text{NHCH}_3$

The following questions given below consist of an "Assertion" (A) and "Reason" (R) Type questions. Use the following Key to choose the appropriate answer.

(A) If both (A) and (R) are true, and (R) is the correct explanation of (A).

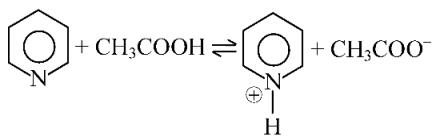
(B) If both (A) and (R) are true but (R) is not the correct explanation of (A).

(C) If (A) is true but (R) is false.

(D) If (A) is false but (R) is true.

Q.1 Assertion :

this equilibrium favours backward direction.



Reason : is stronger base than CH_3COO^-

Q.2 Assertion (A). The major product of reaction $\text{Ph}-\text{C}\equiv\text{C}-\text{N}(\text{CH}_3)_2$ with $\text{H}^\oplus/\text{H}_2\text{O}$ will contain amide as only function group .

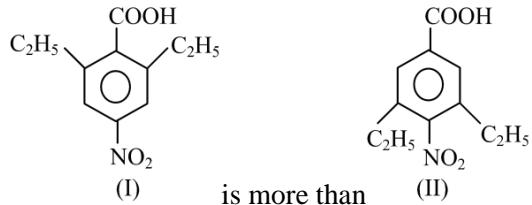
Reason (R) : The major product obtained will be formed due to formation of benzylic carbocation which is stabilised due to + M–effect of benzene ring.

Q.3 Assertion : $\text{CH}_3\text{CH}_2\text{NH}_2$, ethylamine, on treatment with CS_2 followed by HgCl_2 , gives mustard oil smell.

Reason : $\text{CH}_3\text{CH}_2\text{NH}_2$ on treatment with CS_2 produces dithiocarbamic acid

Sol. The mustard oil smell is caused due to alkyl isothiocyanate $\text{R}-\text{N}=\text{C}=\text{S}$.

Q.4 Assertion : Acidic character of



Reason : In Ist alkyl groups show + R effect while in IInd it shows + I effect.

Q.5 Assertion :: Ammonolysis of alkyl halides is not a suitable method for the preparation of pure primary amines.

Statement-II : Ammonolysis of alkyl halides yields mainly secondary amines.

Q.6 Assertion :: Carbonylamine reaction involves chemical reaction between 1° amine and chloroform in basic medium.

Statement-II : In carbonylamine reaction, –NH₂ group changes into –NC group.

Q.7 Assertion :: The main product of reaction of alcoholic silver nitrite and ethyl bromide is nitroethane.

Statement-II : Silver nitrite is predominantly covalent compound.

Q.8 Assertion : In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagent

Statement-II : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

Q.9 Assertion :: Carbonyl compounds take part in nucleophilic addition reactions.

Statement II: These reactions are initiated by nucleophilic attack at the electron deficient carbon atom.

Q.10 Assertion :: The addition of ammonia derivatives on carbonyl compounds is carried in weakly acidic medium.

Statement II: In weakly acidic medium attacking nucleophile is also protonated.

Q.11 Assertion :: Formic acid reduces mercuric chloride solution.

Statement II : Formic acid has reducing aldehydic group.

Q.12 Assertion :: Acetaldehyde undergoes aldol condensation with dilute NaOH.

Statement II : Aldehyde which do not contain α -hydrogen undergoes aldol condensation.

Q.13 Assertion :: Crossed Cannizzaro reaction between formaldehyde and benzaldehyde give benzyl alcohol and formate ion.

Statement II : Formaldehyde is a better hydride donor than benzaldehyde.

Q.14 . Assertion: Hoffmann's ammonolysis can be used to prepare pure primary amines.

Reason: Ammonolysis of haloalkanes lead to multiple substitution of alkyl groups on nitrogen.

Q. 15. Assertion: Aniline is less basic than ammonia.

Reason: The lone pair on nitrogen in aniline is donated into the ring through resonance.

SUBJECTIVE TYPES QUESTIONS 2 MARKS QUESTIONS

Q. 1. (i) Arrange the following in increasing order of boiling points.

$(CH_3)_3N$, C_2H_5OH , $C_2H_5NH_2$

(ii) Arrange the following in increasing order of base strength in gas phase:

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

Q. 2. (i) Arrange the following in decreasing order of solubility in water:

$(CH_3)_3N$, $(CH_3)_2NH$, CH_3NH_2

(ii) Arrange the following in decreasing order of the basic character:

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

Q. 3. (i) Arrange the following in increasing order of pK_b values:

$C_6H_5CH_2NH_2$, $C_6H_5NHCH_3$, $C_6H_5NH_2$

(ii) Arrange the following in decreasing order of solubility in water:

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

Q.4.-(i) Write IUPAC name of the following compound:

$(CH_3CH_2)_2NCH_3$

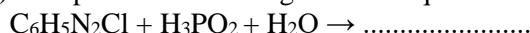
(ii) Write IUPAC name of the following compound:

$CH_3NHCH(CH_3)_2$

Q. 5. (i) Write IUPAC name of the following compound:

$(CH_3)_2N — CH_2CH_3$

(ii) Complete the following reaction equation:



Q. 6- Account for the following:

(i) Aniline gets coloured on standing in air for a long time.

(ii) $MeNH_2$ is stronger base than $MeOH$.

Q. 7. Account for the following:

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

(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.

Q.8. Give the chemical tests to distinguish between the following pairs of compounds :

(i) Methylamine and dimethylamine

(ii) Aniline and *N*-methylaniline

3 MARKS QUESTIONS

Q. 1. (i) Arrange the following compounds in increasing order of dipole moment.



(ii) Give possible explanation for each of the following:

(a) The presence of a base is needed in the ammonolysis of alkyl halides.

(b) Amides are more acidic than amines.

Q. 2. How are the following conversions carried out:

(i) Aniline to fluorobenzene

(ii) Benzene diazonium chloride to benzene

(iii) Methyl chloride to ethylamine

Q.3.- Give reasons:

(i) Acetylation of aniline reduces its activation effect.

(ii) CH_3NH_2 is more basic than $\text{C}_6\text{H}_5\text{NH}_2$.

(iii) Although $-\text{NH}_2$ is o/p directing group, yet aniline on nitration gives a significant amount of m nitroaniline.

Q.4. How will you convert the following:

(i) Nitrobenzene into aniline,

(ii) Ethanoic acid into methanamine,

(iii) Aniline to N-phenylethanamide.

(Write the chemical equations involved.)

Q. 5. How are the following conversions carried out:

(i) Aniline to fluorobenzene

(ii) Benzene diazonium chloride to benzene

(iii) Methyl chloride to ethylamine

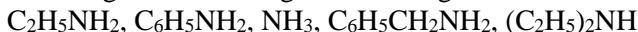
CASE STUDY BASED QUESTIONS

Q.1- Read the passage given below and answer the following questions:

Amines have a lone pair of electrons on nitrogen atom due to which they behave as Lewis base. Larger the value of K_b or smaller the value of pK_b stronger is the base. Amines are more basic than alcohols, ethers, esters, etc. The basic character of aliphatic amines should increase with the increase of alkyl substitution. But it does not occur in a regular manner as a secondary aliphatic amine is unexpectedly more basic than a tertiary amine in solutions.

Aromatic amines are weaker bases than ammonia and aliphatic amines. Electron-donating groups such as $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{NH}_2$, etc., increase the basicity while electron-withdrawing substituents such as $-\text{NO}_2$, $-\text{CN}$, halogens, etc. decrease the basicity of amines. The effect of these substituents is more at *p*- than at *m*-positions.

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



b. Arrange the following compounds in increasing order of their acidic strength:

Methylamine, dimethylamine, aniline, N-methylaniline

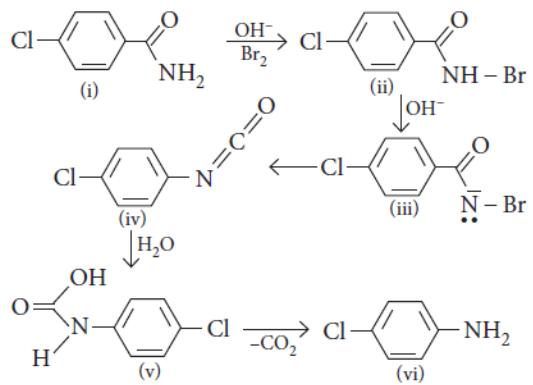
c. Rearrange the following in increasing order of their basic strength:

p-toluidine, N, N-dimethyl-*p*-toluidine, *p*-nitroaniline, aniline

d. Which is more acidic, aniline or ammonia?

Q. 2 Read the passage given below and answer the following questions: (1×4=4).

RCONH_2 is converted into RNH_2 by means of Hoffmann bromamide degradation. During the reaction amide is treated with Br_2 and alkali to get amine. This reaction is used to descend the series in which carbon atom is removed as carbonate ion (CO_3^{2-}). Hoffmann bromide degradation reaction can be written as :



a. Hoffmann bromamide degradation is used for the preparation of

- (a) primary amines (b) secondary amines
- (c) tertiary amines (d) secondary aromatic amines.

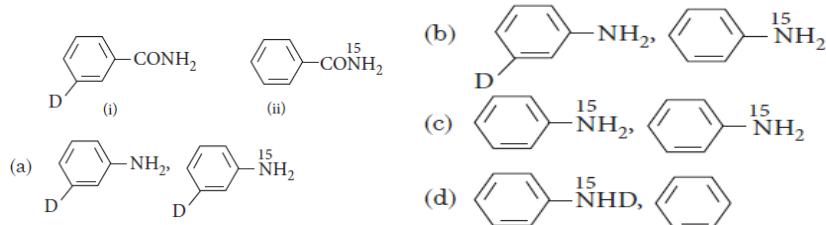
b. Which is the rate determining step in Hoffmann bromamide degradation?

- (a) Formation of (i) (b) Formation of (ii)
- (c) Formation of (iii) (d) Formation of (iv)

c. Which of the following is used for the conversion of (i) to (ii)?

- (a) KBr (b) KBr + CH₃ONa
- (c) KBr + KOH (d) Br₂ + KOH

d. What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hoffmann bromamide degradation?



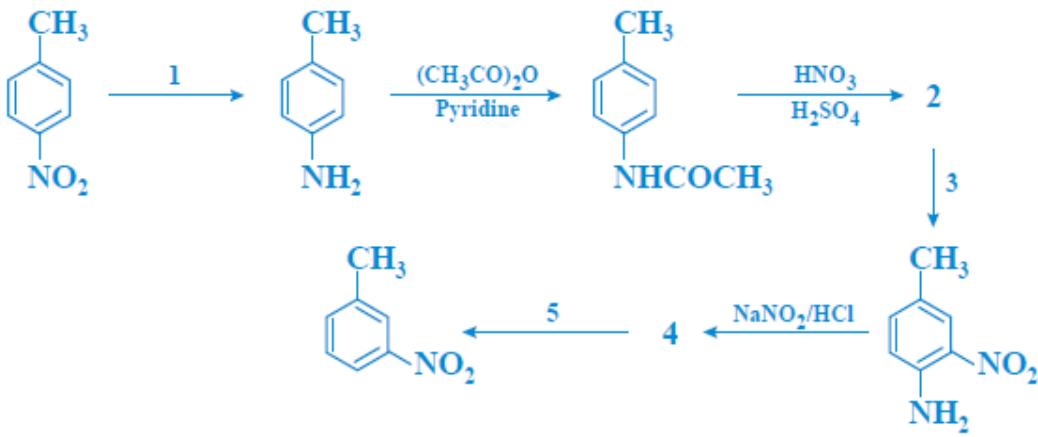
5 MARKS QUESTIONS

Q. 1 Give plausible explanation for each of the following :

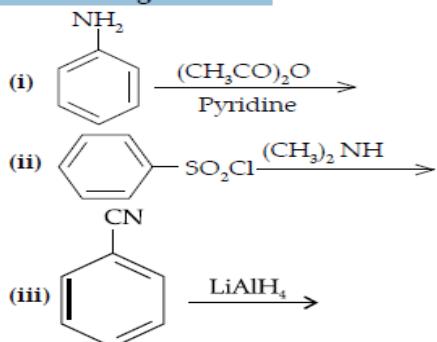
- (i) Why are amines less acidic than alcohols of comparable molecular masses?
- (ii) Why do primary amines have higher boiling point than tertiary amines?
- (iii) Why are aliphatic amines stronger bases than aromatic amines?

Q. 2- A hydrocarbon 'A', (C₄H₈) on reaction with HCl gives a compound 'B', (C₄H₉Cl), which on reaction with 1 mol of NH₃ gives compound 'C', (C₄H₁₁N). On reacting with NaNO₂ and HCl followed by treatment with water, compound 'C' yields an optically active alcohol, 'D'. Ozonolysis of 'A' gives 2 moles of acetaldehyde. Identify the compounds 'A' to 'D'. Explain the reactions involved.

Q. 3- Predict the reagents or the products in the following reaction sequence:



Q. 4- (a) Write the structures of the main products of the following reactions:



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

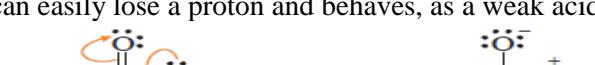
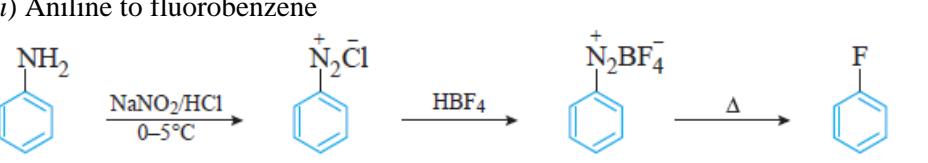
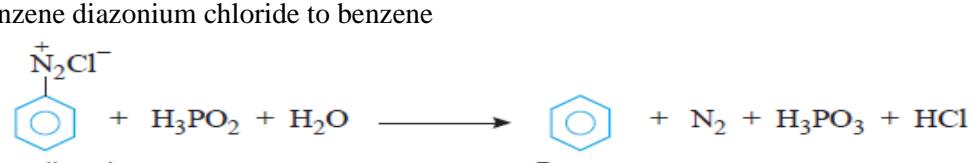
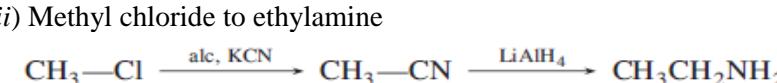
(c) Arrange the following in the increasing order of their pK_b values:



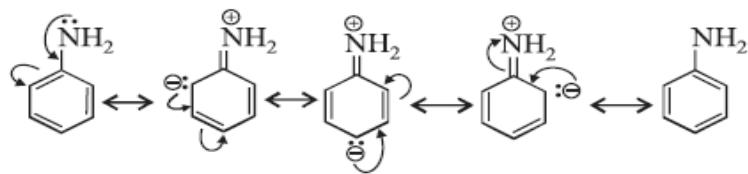
Q. 5- An organic compound A with molecular formula C₇H₇NO reacts with Br₂/aq. KOH to give compound B, which upon reaction with NaNO₂ and HCl at 0°C gives C. Compound C on heating with CH₃CH₂OH gives a hydrocarbon D. Compound B on further reaction with Br₂ water gives white precipitate of compound E. Identify the compound A, B, C, D and E; also justify your answer by giving relevant chemical equations.

ANSWERS KEY

| OBJECTIVE TYPE QUESTIONS (MULTIPLE CHOICE) | |
|---|--|
| | ANSWERS 1-c, 2-d , 3- c, 4-d , 5-b , 6-c ,7-b, 8-d, 9-d, 10-c. |
| REASON ASSERTION TYPES QUESTIONS | |
| | ANSWERS -1- d, 2- c, 3-b, 4-b, 5-c, 6-a, 7-a, 8-d, 9-a, 10-c, 11-a,12-c,13-a,14-d,15-a |
| SUBJECTIVE TYPES QUESTIONS 2 MARKS QUESTIONS | |
| Ans. 1 | <p>(i) (CH₃)₃N < C₂H₅NH₂ < C₂H₅OH</p> <p>(ii) C₂H₅ NH₂ < (C₂H₅)₂ NH < (C₂H₅)₃N</p> <p>Base strength is the ability to donate lone pair. Due to inductive +I effect of C₂H₅, the negative charge density on nitrogen atom increases. Therefore, lone pair is easily available for donation. C₂H₅ NH₂ < (C₂H₅)₂ NH < (C₂H₅)₃N</p> |
| Ans. 2 | <p>(i) CH₃NH₂ > (CH₃)₂NH > (CH₃)₃N</p> <p>(ii) (CH₃)₃N > C₂H₅NH₂ > C₆H₅NH₂</p> |
| Ans. 3 | <p>(i) C₆H₅CH₂NH₂ < C₆H₅NHCH₃ < C₆H₅NH₂</p> <p>(ii) C₂H₅NH₂ > (C₂H₅)₂NH > C₆H₅NH₂</p> |
| Ans. 4 | <p>(i) N-Ethyl-N-methylethanamine.</p> <p>(ii) N-Methylpropan-2-amine.</p> |

| | |
|--------------------------|--|
| Ans. 5 | (i) N, N-Dimethylethanamine (ii) $\text{ArN}^+_{\text{C}_6\text{H}_5}\text{Cl}^- + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \rightarrow \text{ArH} + \text{N}_2 + \text{H}_3\text{PO}_3 + \text{HCl}$ (where Ar is C ₆ H ₅) Benzene |
| Ans. 6 | (i) Due to electron-donating effect (+R-effect) of —NH ₂ group, the electron density on the benzene ring increases. As a result, aniline is easily oxidised on standing in air for a long time to form coloured products. (ii) Nitrogen is less electronegative than oxygen therefore lone pair of electrons on nitrogen is readily available for donation. Hence, MeNH ₂ is more basic than MeOH |
| Ans. 7 | (i) Refer to Ans. 3(i) NCERT Textbook Exercises. (ii) n-Propylamine has two H-atoms on the N-atom and hence undergoes intermolecular H-bonding, thereby raising its boiling point. Trimethylamine, (CH ₃) ₃ N, being a tertiary amine does not have any H-atom on the N-atom. As a result, it does not undergo H-bonding and hence its boiling point is low. |
| Ans. 8 | (i) Methylamine gives carbylamine test, i.e., on treatment with alc. KOH and chloroform, followed by heating it gives offensive odour of methyl isocyanide. Dimethylamine does not give this test. (ii) Aniline gives carbylamine test, i.e., on treatment with alc. KOH and chloroform followed by heating it gives offensive odour of phenylisocyanide but N-methylaniline being secondary amine, does not show this test. |
| 3 MARKS QUESTIONS | |
| Ans. 1 | (i) CH ₃ CH ₂ CH ₃ < CH ₃ CH ₂ NH ₂ < CH ₃ CH ₂ OH (ii) (a) To remove HX formed so that the reaction shifts in the forward direction. (iii) Due to +R effect, availability of lone pair of electron on N of —NH ₂ group decreases. As a result, acid amide is much weaker base than amines. Because of the positive charge on N, as a result of resonance, N can easily lose a proton and behaves, as a weak acid.  |
| Ans. 2 | (i) Aniline to fluorobenzene  (ii) Benzene diazonium chloride to benzene  (iii) Methyl chloride to ethylamine  |
| Ans. 3 | (i) Due to the resonance, the electron pair of nitrogen atom gets delocalised towards carbonyl group / resonating structures. (ii) Because of +I effect in methylamine electron density at nitrogen increases whereas in aniline resonance takes place and electron density on nitrogen decreases / resonating structures. (iii) Due to protonation of aniline / formation of anilinium ion. |

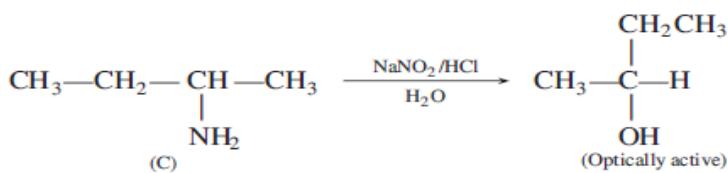
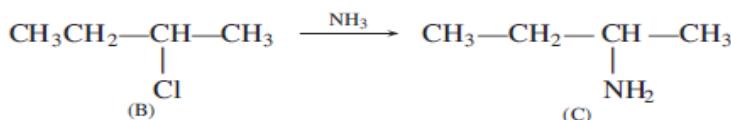
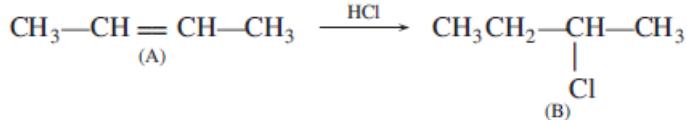
| | |
|-----------------------------------|--|
| Ans4 | <p>(i) Nitrobenzene into aniline</p> <p>(ii) Ethanoic acid into methanamine</p> $\text{CH}_3\text{COOH} \xrightarrow{\text{NH}_3} \text{CH}_3\text{CONH}_2 \xrightarrow{\text{Br}_2} \text{CH}_3\text{NH}_2$ <p>(iii) Aniline to N-Phenylethanamide</p> |
| Ans. 5 | <p>(i) Aniline to fluorobenzene</p> <p>(ii) Benzene diazonium chloride to benzene</p> <p>(iii) Methyl chloride to ethylamine</p> |
| CASE STUDY BASED QUESTIONS | |
| Ans. 1 (a) | $\text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$ |
| Ans.b | dimethylamine < methylamine < N-methylaniline < aniline. |
| Ans.c | <i>p</i> -nitroaniline < aniline < <i>p</i> -toluidine < N, N-dimethyl- <i>p</i> -toluidine. |
| Ans.d | Due to delocalization of the lone pair of electrons of the N-atom of aniline over the benzene ring, aniline is more acidic than ammonia. |
| Ans 2(a) | A |
| B | D |
| C | D |
| D | B |
| 5 MARKS QUESTIONS | |
| Ans. 1 | <p>(i) In alcohols, the hydrogen atom is attached to more electronegative oxygen atom whereas nitrogen of amines is less electronegative. After the loss of H^+ ion, the negative charge is more easily accommodated on oxygen than in case of nitrogen in amines. Hence, amines have lesser tendency to lose H^+ ions, so they are less acidic than alcohols.</p> <p>(ii) Primary amines ($R - \text{NH}_2$) have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines ($R_3\text{N}$). So primary amines boil at a higher temperature than tertiary amines.</p> <p>(iii) In aromatic amines, the lone-pair of electrons on nitrogen atom is involved in resonance with the benzene ring as shown below for aniline.</p> |



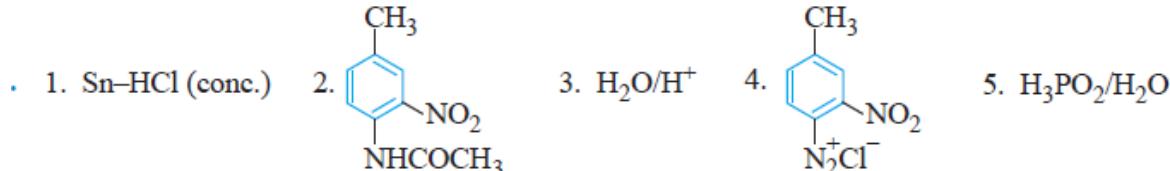
It shows that this pair of electrons is less available for protonation. In case of aliphatic amines electron releasing alkyl groups increase electron density on nitrogen atom. So, aliphatic amines are stronger bases than aromatic amines.

Ans-2

On the basis of structure of 'A', the reactions can be explained as follows:



Ans-3



Ans-4

- (a) (i) $\text{C}_6\text{H}_5\text{NHCOCH}_3$
(ii) $\text{C}_6\text{H}_5\text{SO}_2\text{N}(\text{CH}_3)_2$
(iii) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

(b) Add chloroform in the presence of KOH and heat, then, aniline gives a offensive smell while N, N dimethylaniline does not. (or any other correct test)

(c) $\text{C}_2\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{NHCH}_3 < \text{C}_6\text{H}_5\text{NH}_2$

Ans-5

