Chapter - 13 - AMINES

Level one

1) Write IUPAC names of the following compounds and classify them into primary,secondary andteritary amines.

a) $(CH_3)_2CHNH_2$ Ans:propan-2-amine(primary)

b)$CH_3(CH_2)_2NH_2$ Ans:propan-1-amine(primary)

c)$CH_3NHCH(CH_3)_2$ Ans:N-Methyl propan-2-amine(secondary)

d)$(CH_3)_3CNH_2$ Ans:2-Methylpropan-2-amine (primary)

e)$C_6H_5NHCH_3$ Ans:N-Methylaniline (secondary)

f)m-$BrC_6H_4NH_2$ Ans:3-Bromobenzenamine(primary)

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

a) Methylamine and dimethylamine

Ans:Methyl amine being a 1^0 amine will give carbyl amine test,while dimethylamine,a 2^0 amine will not

give this test.

b)Ethylamine and aniline

Ans:Aniline will give brilliantly coloured orange dye on diazotization and coupling with phenol.

ethylammine on treatment with HNO_3(NaOH+HCl) gives N_2 and ethanol fails to couple with phenol to give

adye

d)Aniline and benzylamine

Ans:Aniline (an aromatic primary amine) will give brilliantly coloured orange dye on diazotization and coupling

with phenol.Benzylamine which is not an aromatic primary amine will not give this test. It only give N_2 and

benzyl alcohol with HNO_2.

e)Aniline and N-methylaniline

Ans: Aniline is a primary amine it will give carbyl amine test while N-methylaniline is a secondary amine,and as such it will not give carbyamine test.

3) Arrange the following :

a) In decreasing order of the pKb values:

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

Ans: $C_6H_5NH_2 > C_6H_5NHCH+ > C_2H_5NH_2 > (C_2H_5)_2NH$

b) In increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

Ans: $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

c) In increasing order of basic strength:

a) Aniline, p-nitroniline and p-toluidine

b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$

Ans: a)p-nitroaniline<aniline<p-toluidine

b)$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

d) In decreasing order of basic strength in gas phase:

$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

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

e) In increasing order of boiling point:

C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

Ans: $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

f) In increasing order of solubility in water:

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

Ans: $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

4) Write short notes on the following:

i) Carbylamine reaction :All primary amines on heating with chloroform and an alcoholic solution of potassium hydroxide produce isocyanide

ii)Diazotisation:The conversion of aniline or other aromatic primary amines into diazonium salts by the action of nitrous acid and dilute hydrochloric acid is called diazotization.

iii)Hofmann's bromamide reaction :The heating of amine an amide with bromine and caustic alkali to yield an amine with one carbon less than the original amide this reaction is called Hofmann's bromamide reaction.

iv)Coupling reaction:Reaction of aromatic diazinium salt with phenols and amines to give azo compounds is called coupling reaction.

v)Ammonolysis :Alkyl halides react with alcoholic ammonia to primary,secondary and tertiary amines along with some quaternary ammonium salts.

vi) Acetylation:Introduction of acetyl group(CH_3CO-) into any molecule is known as acetylation.

vii) Gabriel phthalimide synthesis:This is an excellent method to prepare pure primary aliphatic amine form corresponding alkyl halide and amine.

5) Gabriel Phthalimide synthesis is not suitable for preparation of secondary and tertiary amines.

Ans- Since the reaction involves Sn_2 mechanism, only a primary alkyl group can approach the sterically hindered Phthalimide ring .

6) **pKb of aniline is more than that of methylamine.**

Ans- Since the lone pair on the N-atom remains in conjugation with the benzene ring and is unavailable for donation. The basic character of methylamine is enhanced due to +I effect of $–CH_3$ group.

7) **Aniline does not undergo Friedel Crafts reaction.**

Ans- Aniline is basic and reacts with anhyd. $AlCl_3$ to form a salt which deactivates 6the benzene ring towards electrophilic substitution.

Q.8 Give the IUPAC name of $H_2N - CH_2 - CH_2 - CH = CH_2$.

Soln: 4-amino-but-1-ene

Q.9 Write structure of methyl amine?

Ans- CH_3-NH_2

Q.10 Write the structure of methyl isocyanides?

Ans-CH_3NC

Q.11. Name the tests for Primary amine.

Ans- Carbylamines test

Q.12. Primary amines have higher b.p than tertiary amines.

Ans- Due to inter molecular hydrogen bonding.

Q.13. Why is alkyl amine more basic than ammonia?

Ans Due to +I effect of alkyl group.

Q**.14 why do amine react as nucleophile.**

Ans-due to lone pair of electron on nitrogen.

Q.15. Why are aqueous solution of amine basic in nature?

Ans- Because of high electron density on nitrogen it gains H^+ from water.

Level Two Questions

Q.1 **Name one test to distinguish between ethyl cynide and ethyl isocynide.**

Ans- ethyl cynide on hydrolysis with acids form propionic acid, whereas ethyl isocynide with dilute HCl forms ethylamine and formic acid.

Q2.**Identify A and B**

$$C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} A \xrightarrow{CuBr} B$$

Q3.**Name the reaction in which amide directly converted into amines.**

Ans:Hofmann'sbromamide reaction.

Q4.**Complete the following:**

$RNH_2 + CHCI_3 + 3KOH \longrightarrow$?

Q5. .**Complete the following:**

$RCONH_2 + Br_2 + 4\ NaOH \longrightarrow$?

Q6.**Write the formula of hinsberg's reagent.**

Ans:Benzoyl chloride.

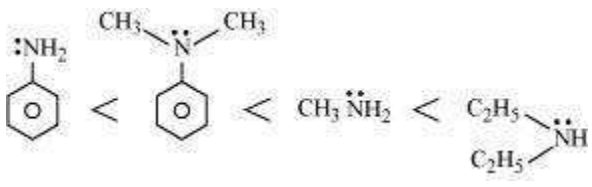
Q7.**What is meant by diazotization?**

Ans:Conversion of primary aromatic amines into diazonium salts.

Q.8 In an increasing order of basic strength:

$C_6H_5NH_2$,$C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ & CH_3NH_2

Ans:
Basic strength:

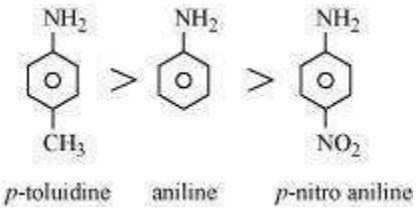


Aliphatic amines are stronger bases than aromatic amines due to the presence of lone pair of e- on nitrogen atom. In case of aromatic amines the lone pair gets delocalised by resonance. Diethyl amine has greater + I effect. Hence, e- density over the nitrogen atom is more in this case. Similarly N, N − dimethyl aniline has greater + I effect than aniline.

Q.9 In a decreasing order of basic strength:

Aniline, p-nitroaniline& p-toluidine

Ans-



Methyl ($-CH_3$) is an e- donating group. It increases the e- density on the ring. Therefore, the lone pair of nitrogen is available for donation. Hence, it is most basic. On the other h& nitro ($-NO_2$) is an e- withdrawing group. It decreases the e- density of the ring. Therefore, the lone pair is more delocalized in this case & is less available for donation. Thus, it will be least basic among the three.

Level Three Questions

Q.1 In an increasing order of pK_b value

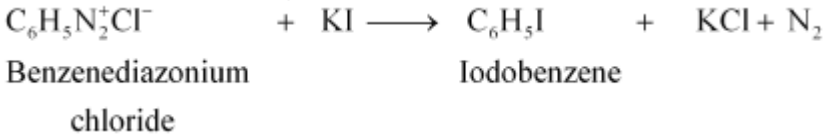
$C_2H_5NH_2$, C_6H_5 $NHCH_3$, $(C_2H_5)_2$ NH & $C_6H_5NH_2$

Ans-

Stronger the base is lesser is the pK_b value. $(C_2H_5)_2NH$ is the strongest base due to two e- releasing group followed by $C_2H_5NH_2$ which has only one e- releasing group. $C_6H_5NHCH_3$ is the next stronger base because of the presence of one e- releasing alkyl group & e- delocalising phenyl group. $C_6H_5NH_2$ is the least basic wherein the e- get delocalised by resonance.

Q.2.Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt.

Ans-:



Q.3Why is an alkylamine more basic than ammonia?

Ans: An alkylamine is more basic than ammonia because of inductive effect (+I effect). Alkyl group or 'R' has an e--releasing effect, which increases e- density over nitrogen atom. This increases its basicity.

4marks questions

Q.4.Describe the Hofmann's bromamidereaction

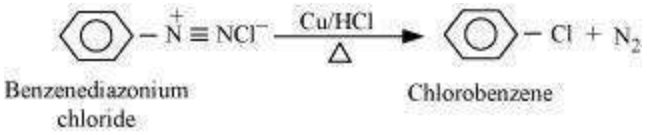
Ans: *Hofmann's bromamidereaction*: It involves the reaction of bromine with an acid amide in the presence of an alkali. It results in the formation of a primary amine with one carbon less than the parent compound. Here, the alkyl group migrates from carbonyl, with the elimination of CO_2. For example:

$$RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$$

$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + H_2O$$

Q.5.Describe the Gattermanreaction

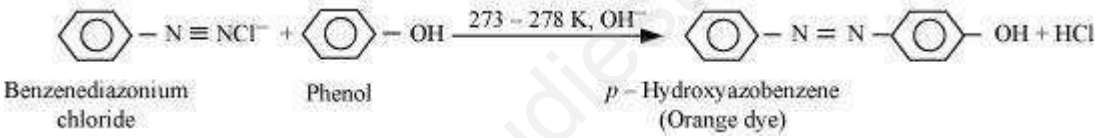
Ans- *Gattermanreaction*: This is a modification of *S&meyer* reaction in which benzenediazonium chloride is treated with copper powder & halogen acid to form aryl halides.



Q.6.Describe the couplingreaction

Ans

Coupling reaction: It is the reaction of diazonium salts with phenols & aromatic amines to form *azo* compounds of the general formula Ar − N = N − Ar. The coupling of phenol takes place in a mildly alkaline medium.



Q.7.pK_b for aniline is more than that for methylamine.

Ans:
In aniline, the lone pair of e- on the N atom is delocalised over the benzene ring. As a result, the e- density on the nitrogen atom decreases. In contrast, in CH_3NH_2, the +I effect of CH_3increases the e- density on the N atom. Therefore, aniline is a weaker base than methylamine. Hence, its pK_b value is higher than that of methylamine.

Q.8 Methylamine Soln in water reacts with ferric chloride Soln to give a precipitate of ferric hydroxide.

Ans- Being more basic than water, methylamine accepts a proton from water-liberating OH^- ions.

$$CH_3NH_2 + H_2O \longrightarrow CH_3NH_3OH^- \longrightarrow CH_3NH^+ + OH^-$$

These OH^- ions combine with Fe^{3+} ions present in H_2O to form a brown precipitate of hydrated ferric oxide.

$$FeCl_3 \rightarrow Fe^{3+} + 3\,Cl^-$$

$$2Fe^{3+} + 6OH^- \longrightarrow 2Fe(OH)_3$$

Hydrated ferric oxide

(Brown ppt.)

Q9.An aromatic compound ' A' on treatment with aqueous ammonia and heating forms compound 'B ' which on heatiog with Br_2 and KOH forms a compound ' C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B andC.

Ans:-((A) Benzoic acid (B) Benzamide (c) Aniline

Q10.Complete the following reactions:

(i)$C_6H_5NH_2$ +$CHCI_3$ +alc.KOH---------→

(II)$C_6H_5N_2Cl$ +H_3PO_2 +H_2O----------→

(III)$C_6H_5NH_2$ +H_2SO_4(CONC)----------→

(IV)$C_6H_5N_2Cl$ +C_2H_5OH----------→

(V)$C_6H_5NO_2$ + Fe/HCI----------→

Ans:-

(i)$C_6H_5NH_2$ +$CHCI_3$ +alc.KOH----------→C_6H_5NC +3KCl +$3H_2O$

(II)$C_6H_5N_2Cl$ +H_3PO_2 +H_2O----------→C_6H_6 +H_3PO_3 +N_2 +HCl

(III)$C_6H_5NH_2$ +H_2SO_4(CONC)----------→NH_2-Ph-SO_3H +H_20

(IV)$C_6H_5N_2Cl$ +C_2H_5OH----------→C_6H_6 +N_2+CH_3CHO +HCI

(V)$C_6H_5NO_2$ + Fe/HCI----------→$C_6H_5NH_2$