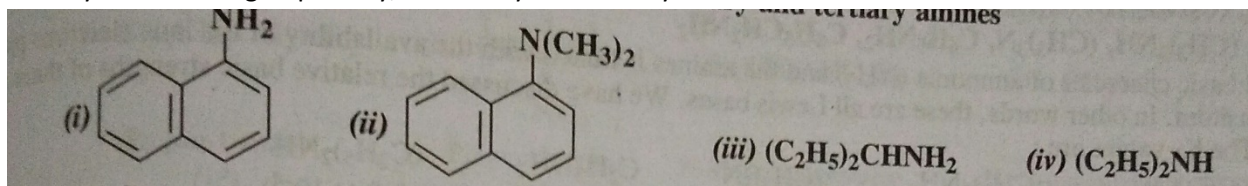


AMINES

Questions and answers

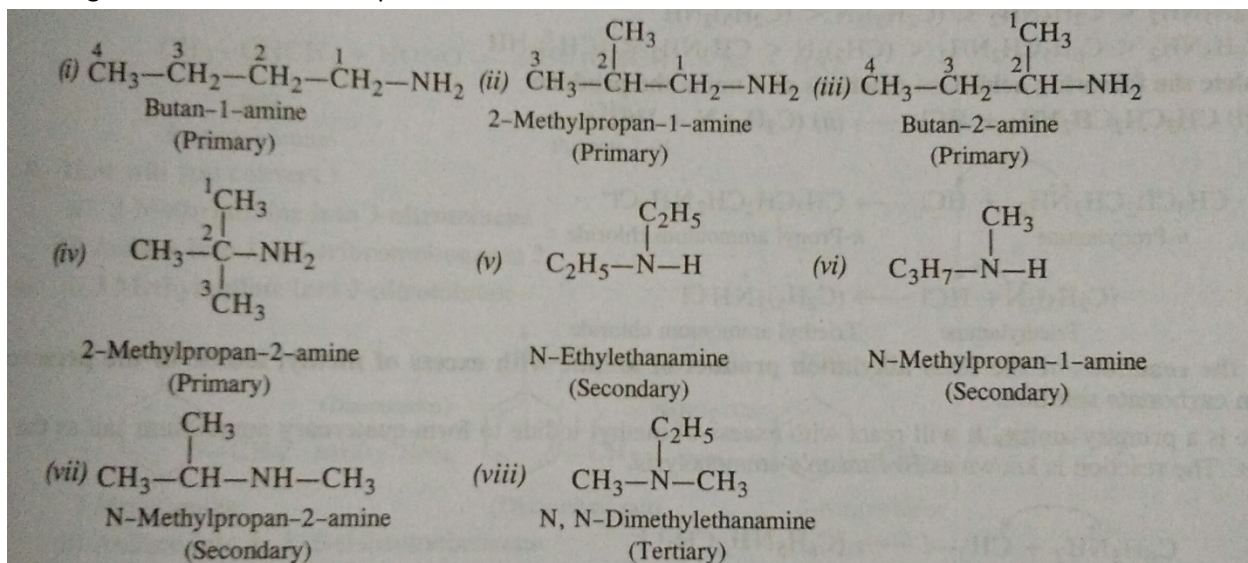
1. Classify the following as primary, secondary and tertiary amines.



Ans: i) primary ii) tertiary iii) primary iv) secondary

2. Write the structures of different isomeric amines corresponding to the molecular formula, $\text{C}_4\text{H}_{11}\text{N}$. i) Write the IUPAC names of all the isomers.

Ans: Eight isomeric amines are possible



3. pK_b of aniline is more than that of methylamine, why.

Ans. Because aniline is less basic than methylamine due to stabilisation lone pair of N by resonance effect.

4. 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 , $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$, $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$.

Ans. (i) $\text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$

- (ii) $C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$
 (iii) $C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

5. Arrange the following:

(i) In decreasing order of the pK_b values:

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

(ii) In increasing order of basic strength:

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

Ans. (i) $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

(ii) $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

6. Arrange the following: In increasing order of basic strength:

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

(ii) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$.

Ans. (i) p-nitroaniline < Aniline < p-toluidine

(ii) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$.

7. Arrange the following In decreasing order of basic strength :

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

(ii) $(CH_3)_2NH$, $(CH_3)_3N$, NH_3 , CH_3NH_2

Ans. (i) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

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

8. Why are amines basic in character?

Ans. Like ammonia, the nitrogen atom in amines RNH_2 is trivalent and bears an unshared pair of electrons. Thus it acts like a Lewis base and donates the pair of electrons to electron-deficient species which further increases due to +I effect of alkyl radical.

9. Arrange the following in decreasing order of the basic strength:

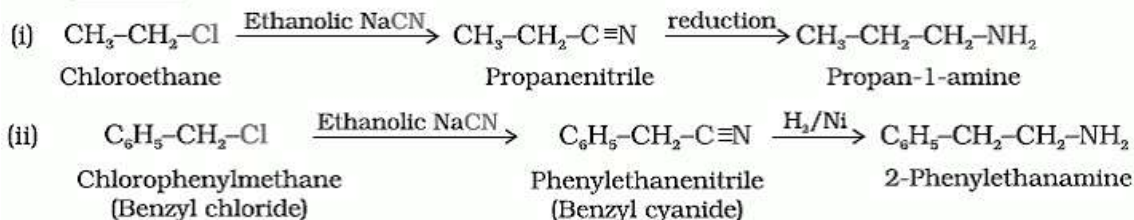
$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

Ans. The decreasing order of basic strength of the above amines and ammonia follows the following order: $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > C_6H_5NH_2$

10. Write chemical equations for the following conversions:

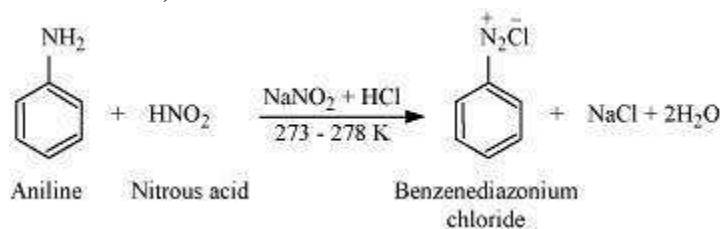
(i) CH_3-CH_2-Cl into $CH_3-CH_2-CH_2-NH_2$

(ii) $C_6H_5-CH_2-Cl$ into $C_6H_5-CH_2-CH_2-NH_2$

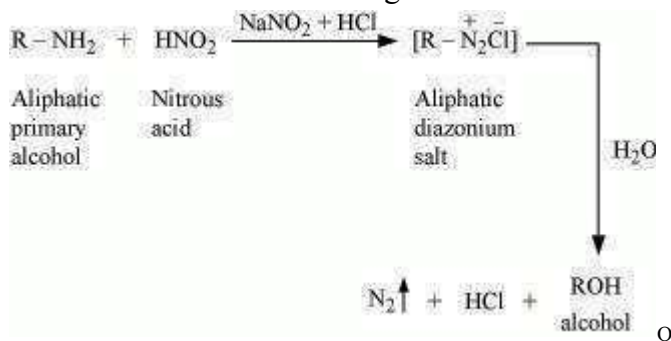


11. Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

Ans. (i) Aromatic amines react with nitrous acid (prepared in situ from NaNO_2 and a mineral acid such as HCl) at $273\text{--}278\text{K}$ to form stable aromatic diazonium salts i.e., NaCl and H_2O .



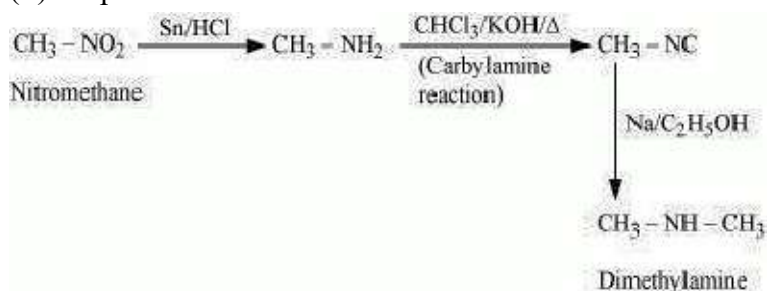
(ii) Aliphatic primary amines react with nitrous acid (prepared in situ from NaNO_2 and a mineral acid such as HCl) to form unstable aliphatic diazonium salts, which further produce alcohol and HCl with the evolution of N_2 gas.

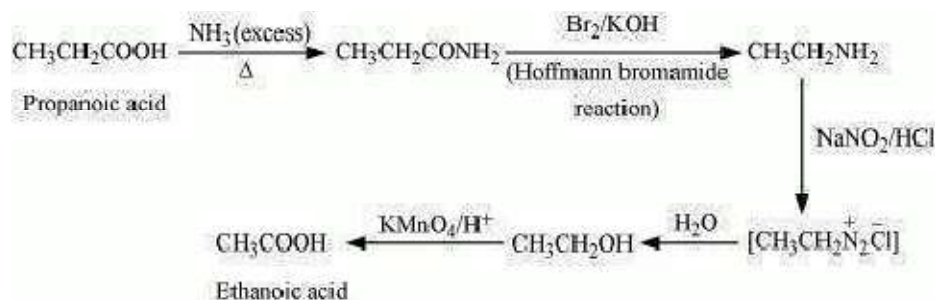


12. How will you convert

(i) Nitromethane into dimethylamine

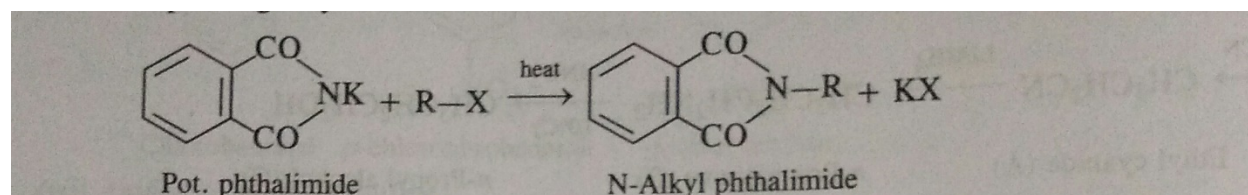
(ii) Propanoic acid into ethanoic acid?



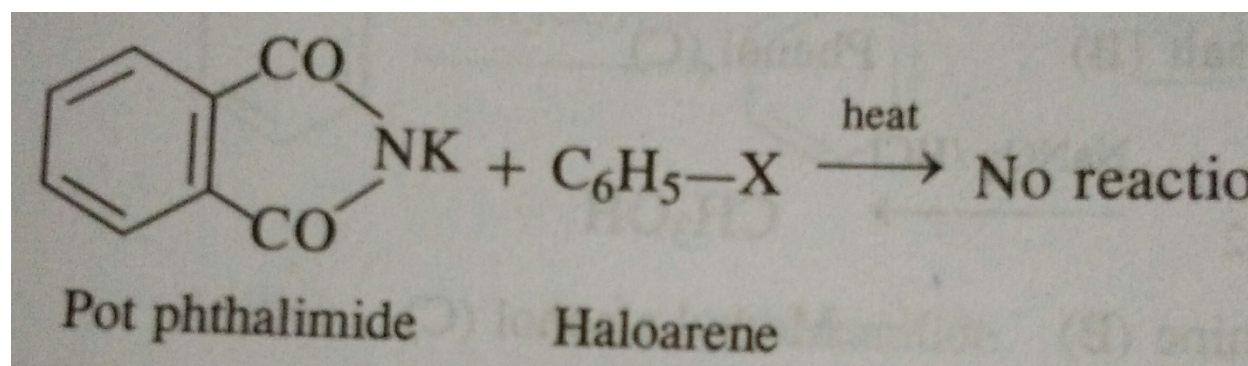


13. Why cannot aromatic amines be prepared by Gabriel phthalimide reaction?

Ans: In Gabriel phthalimide reaction, potassium salts of phthalimide is formed. It readily reacts with alkyl halides to form corresponding alkyl derivatives.

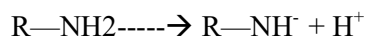


But it is not in a position to react with the aryl halide in case primary aromatic amines is to be prepared. Actually the cleavage of C-X bond in haloarene or aryl halide is quite difficult due to partial double bond character. Therefore, aromatic amines cannot be prepared by this method.



14. Why are amines less acidic than alcohols of comparable molecular masses?

Ans: The acidic character in both cases is due to the release of H^+ ion. Now, the anion in case of amine



Amines



RO^- ion is more stable than RNH^- ion because oxygen is more electronegative than nitrogen atom. Consequently alcohols are more stronger acid than amines.

15. What is the best reagent to convert nitrile into primary amines?

Ans: Lithium aluminium hydride (LiAlH_4) dissolved in anhydrous ether is the best reagent to convert a nitrile into primary amines.

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