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CLASS XII CHEMISTRY NOTES

AMINES

KEY NOTES AND IMPORTANT
QUESTIONS WITH ANSWERS



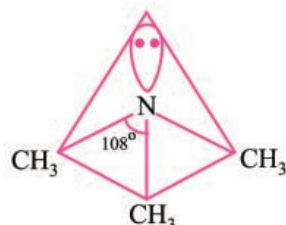
UNIT 13

AMINES

Points to Remember

1. Amines are alkyl and/or aryl derivatives of $\ddot{\text{N}}\text{H}_3$.
2. Functional groups of 1°, 2° and 3° amines are respectively as given below :
$$-\ddot{\text{N}}\text{H}_2, -\ddot{\text{N}}\text{H}- \text{ and } -\ddot{\text{N}}-$$
3. Gabriel phthalimide synthesis can't be used for the preparation of 2° and 3° amines. It gives aliphatic primary amine only.
4. Hoffmann's bromamide reaction gives 1° amines having one carbon atom less than parent primary amide.
5. The order of basic strength of aliphatic amines is :
 - (i) Aliphatic amines are more basic than $\ddot{\text{N}}\text{H}_3$.
 - (ii) In aqueous solution medium, the order is $2^\circ > 1^\circ > 3^\circ$ (for $-\text{CH}_3$ group) and $2^\circ > 3^\circ > 1^\circ$ for $-\text{C}_2\text{H}_5$ group.
 - (iii) In non-aqueous medium or gaseous phase, the order is $3^\circ > 2^\circ > 1^\circ$.
6. Basic strength of aromatic amines :
 - (i) Aromatic amines are weaker bases than $\ddot{\text{N}}\text{H}_3$.
 - (ii) ERGs like $-\text{CH}_3$, $-\text{OR}$, $-\text{NH}_2$ etc. increase basic strength while EWGs like $-\text{NO}_2$, $-\text{CN}$ etc. decrease the basic strength. The effect of substituents is more at para positions and less at meta position.
7. Basic strength of amines is expressed in terms of K_b or $\text{p}K_b$.
8. 1°, 2° and 3° amines can be distinguished by Hinsberg's test.
9. Hinsberg's reagent is benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$).
10. 3° amines like trimethylamine are used as insect attractants.
11. Diazonium salts are represented by the general formula $[\text{Ar N} \equiv \text{N}]^+ \text{X}^-$.

12. **Structure of amines :** Pyramidal for trimethyl amine $(\text{CH}_3)_3 - \ddot{\text{N}}$. They are Lewis bases.



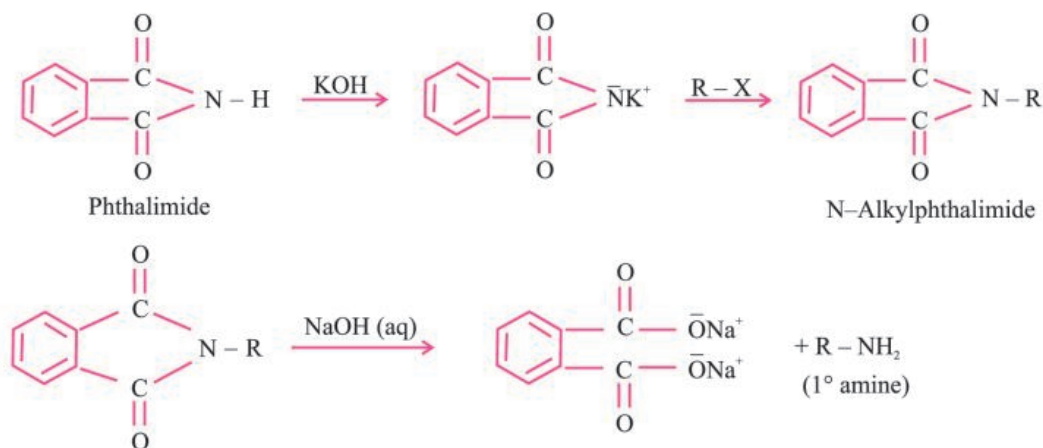
13. Carbylamine test only given by 1° amines.
14. Manich reaction involves the reaction of ketones with HCHO and NH_3 (or amine) in acidic medium to form Manich bases.
15. 1° amines give effervescence with HNO_2 .
16. $-\text{NH}_2$ group in aniline is *o*- and *p*- directing and is highly activating in nature.
17. Acylation of aniline is done before subjecting it to nitration or halogenation.
18. Aliphatic diazonium salts are very unstable and do not exist while aromatic salts are relatively stable.
19. These salts are prepared from 1° aryl amines by diazotization reactions.
20. Diazotised salts (diazonium salts) are used to prepare a variety of aromatic compounds.
21. $\text{R} - \text{C} \equiv \text{N}$ have generally pleasant odours but alkyl isocyanides have highly unpleasant odours.
22. Alkyl isocyanides have lower boiling points than that of isomeric alkyl cyanides due to lower dipole moments.
23. Arenediazonium salts are highly reactive compounds and reactivity is due to excellent leaving ability of diazo group as N_2 gas.

NAME REACTIONS

1. Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by

this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



2. Hoffmann bromamide degradation reaction

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. The amine so formed contains one carbon less than that present in the amide.



3. Carbylamine reaction

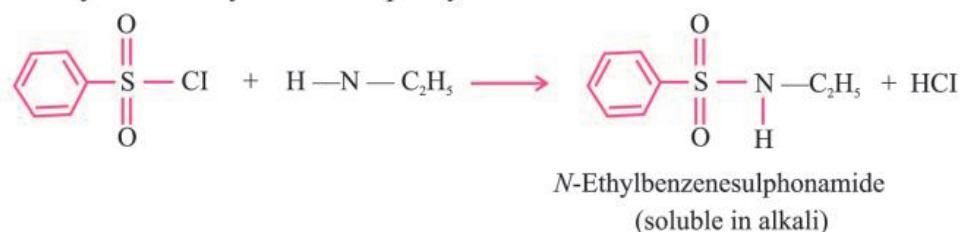
Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.



4. Hinsberg Test:

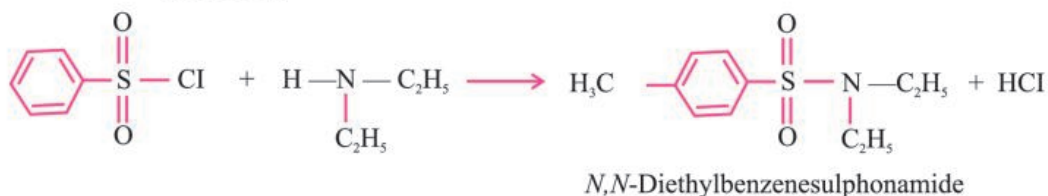
Benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

- (a) The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzenesulphonyl amide.



The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

- (b) In the reaction with secondary amine, *N,N*-diethylbenzenesulphonamide is formed.

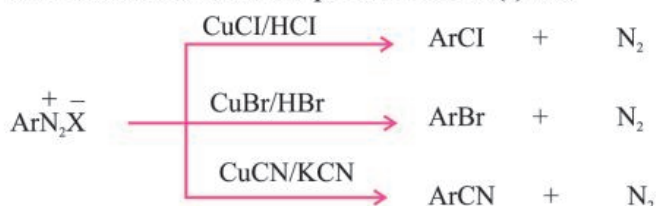


Since *N,N*-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

- (c) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.

5. Sandmeyer Reaction

The Cl⁻, Br⁻ and CN⁻ nucleophiles can easily be introduced in the benzene ring of diazonium salts in the presence of Cu(I) ion.



6. Gatterman Reaction

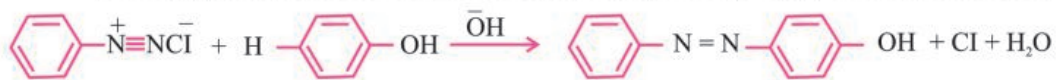
Chlorine or bromine can be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.



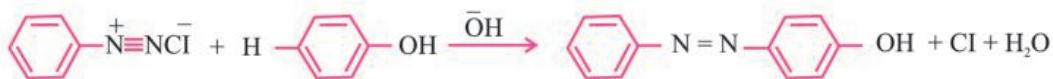
7. Coupling reactions

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the -N=N- bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form *p*-hydroxyazobenzene. This type of reaction is known as coupling reaction.

Similarly the reaction of diazonium salt with aniline yields p-aminoazobenzene.



P-Hydroxyazobenzene (orange dye)



p-Aminoazobenzene
(yellow dye)

DISTINCTION BETWEEN PAIRS OF COMPOUNDS

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

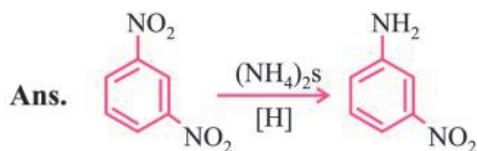
- Methylamine and dimethylamine
- Secondary and tertiary amines
- Ethylamine and aniline

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

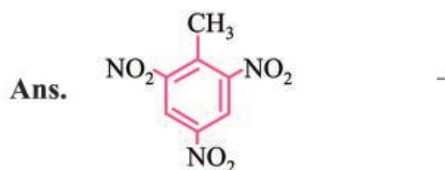
Q. 1. Write IUPAC name of CH_3NC .

Ans. Methane carbylamine.

Q. 2. Convert *m*-dinitrobenzene to *m*-nitro aniline.



Q. 3. Draw structure of TNT, an explosive.



Q. 4. Write IUPAC name of $\text{CH}_3-\underset{\text{CH}_3}{\text{N}}-\overset{\text{CH}_3}{\underset{\text{C}_2\text{H}_5}{\text{C}}}-\text{CH}_2-\text{CH}_3$

Ans. 3-Methyl-N,N-dimethyl pentanamine

Q. 5. Give one use of quaternary ammonium salts.

Ans. It is used as detergents, e.g., $[\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_2]^+\text{Cl}^-$.

Q. 6. What is Hinsberg's reagent ?

Ans. Benzene sulphonyl chloride, -SO₂Cl

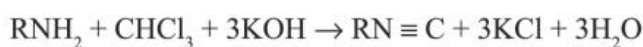
Q. 7. Why aniline dissolves in HCl ?

Ans. $\text{C}_6\text{H}_5\text{NH}_2 + \text{HCl} \rightarrow [\text{C}_6\text{H}_5\text{NH}_3]^+\text{Cl}^-$.

It dissolves due to its basic nature.

Q. 8. How will you test the presence of primary amine ?

Ans. By carbyl amine test.



Q. 9. What is vapour phase nitration ?

Ans. $\text{CH}_4 + \text{HNO}_3 \xrightarrow{623 \text{ K}} \text{CH}_3\text{NO}_2$
(High temperature and nitration in vapour phase only)

Q. 10. Write one use of dopamine and atropine alkaloid.

Ans. Dopamine : Neurotransmitter

Atropine alkaloid : 0.5-1.0% solution ophthalmic examination.

Q. 11. Direct nitration of aniline is not carried out. Explain.

Ans. ($\text{H}_2\text{SO}_4 + \text{HNO}_3$) easily oxidized aniline into tarry complex product due to high e^- density on the benzene ring of aniline.

Q. 12. Among the compounds as following which will react with  to give product containing >C=N- ?

(i) $\text{C}_6\text{H}_5\text{NH}_2$

(ii) $(\text{CH}_3)_3\text{N}$

(iii) $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_5$

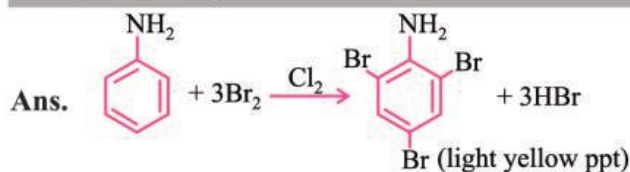
(iv) $\text{C}_6\text{H}_5\text{NHNH}_2$

Ans. $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NHNH}_2$.

Q. 13. How will you give expression for K_b to indicate its basic strength ?

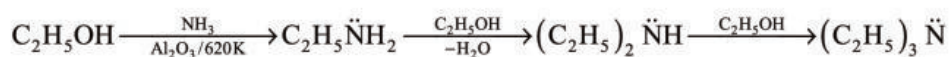
Ans.
$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{R}-\text{NH}_2]}$$

Q. 14. What happens when aniline is treated with bromine ?

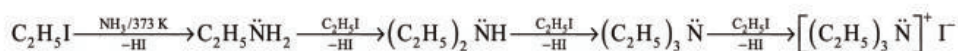


Q. 15. Write a chemical equation to illustrate the ammonolysis.

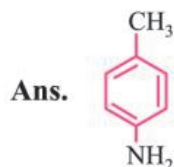
Ans. For alcohols :



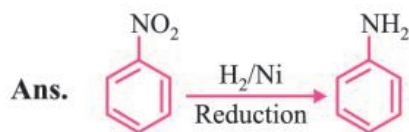
For alkyl halides :



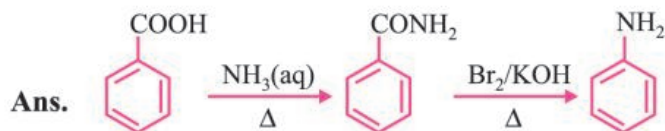
Q. 16. Write the structure of p-toluidine.



Q. 17. Prepare/convert nitrobenzene into aniline.



Q. 18. Convert $\text{C}_6\text{H}_5\text{COOH}$ to $\text{C}_6\text{H}_5\text{NH}_2$.



Q. 19. Write isomerism exhibited by different amines.

Ans. Chain, position, metamerism, functional.

Q. 20. Arrange the following compounds in increasing order of solubility in water:



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

SHORT ANSWER TYPE QUESTIONS (2 Marks)

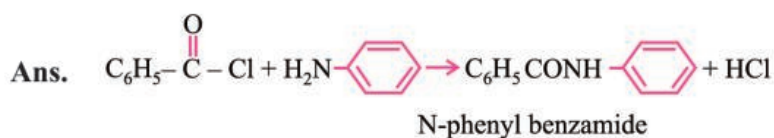
Q. 1. Complete the following acid-base reactions and name the products :



Ans. (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}^+\text{H}_3\text{Cl}^-$ (n-propyl ammonium chloride)

(ii) $(\text{CH}_3\text{CH}_2)_3\text{N} - \text{N}^+\text{HCl}^-$ (Triethyl ammonium chloride)

Q. 2. Write chemical reaction of $\text{C}_6\text{H}_5\text{NH}_2 + \text{C}_6\text{H}_5\text{COCl}$ and name product obtained.



Q. 3. How will you convert :

(i) 3-methylaniline $\rightarrow$ 3-nitrotoluene

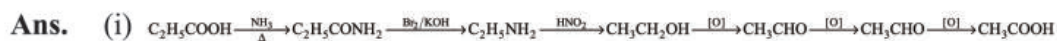
(ii) Aniline $\rightarrow$ 1, 3, 5-tribromobenzene



Q. 4. How will you convert :

(i) Propanoic acid $\rightarrow$ Ethanoic acid

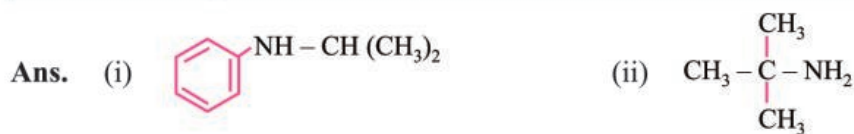
(ii) Nitromethane $\rightarrow$ Dimethylamine



Q. 5. Draw the structures of the following compounds :

(i) N-isopropylaniline

(ii) t-butylamine



Q. 6. Why $\text{C}_6\text{H}_5\text{N}^+(\text{CH}_3)_3\text{OH}^-$ a stronger base than NH_4OH ?

Ans. Due to $-I$ effect of phenyl group, it decreases e^- density on nitrogen atom but no such group in NH_4OH .

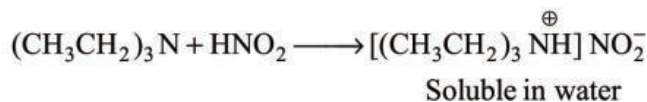
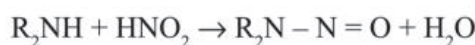
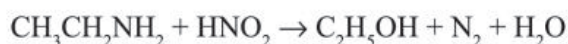
Q. 7. Explain Kb order : $\text{Et}_2\text{NH} > \text{Et}_3\text{N} > \text{EtNH}_2$ in aqueous solution.

Ans. Basicity of amines in aqueous solution depends upon :

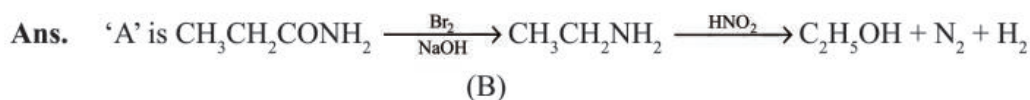
- $+I$ effect of an alkyl group.
- Extent of hydrogen bonding with H_2O .
- Steric effects of alkyl groups.

Q. 8. Distinguish between 1° , 2° and 3° amines by HNO_2 acid test.

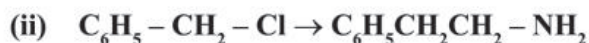
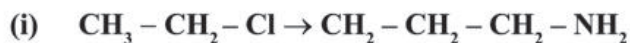
Ans. 1° gives N_2 gas. 2° gives yellow oily compound. 3° form water soluble salts.



Q. 9. A compound 'A' having molecular formula $\text{C}_3\text{H}_7\text{ON}$ reacts with Br_2 in presence of NaOH to give compound 'B'. This compound 'B' reacts with HNO_2 to form alcohol and N_2 gas. Identify compound 'A' and 'B' and write the reaction involved.

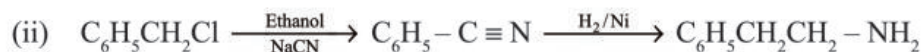


Q. 10. Write chemical equation for the following conversions :



Ans. (i) With NaCN and reduction.





Q. 11. Account for :

- (i) **Amino group in aniline is *o*- and *p*- directing in aromatic electrophilic substitution reactions. Aniline on nitration gives a substantial amount of *m*-nitroaniline.**
- (ii) **Aniline does not go Friedel Crafts reaction.**

- Ans.** (i) It is because aniline is formed by protonation with NH_3^+ *i.e.*, EWG hence it is *m*-directing *i.e.*, 47%.
- (ii) It is because aniline is basic, can form adduct with $AlCl_3$, electrophile cannot be generated.

Q. 12. Account for the following :

- (i) **Electrophilic substitution in aromatic amines takes place more readily than benzene.**
- (ii) **Nitro compounds have higher boiling points than hydrocarbons having almost same molecular mass.**

- Ans.** (i) $-NH_2$ is ERG, electrophilic substitution takes place faster.
- (ii) Nitro compounds are more polar than hydrocarbons therefore have more van der Waal's forces of attraction.

Q. 13. Write short notes on :

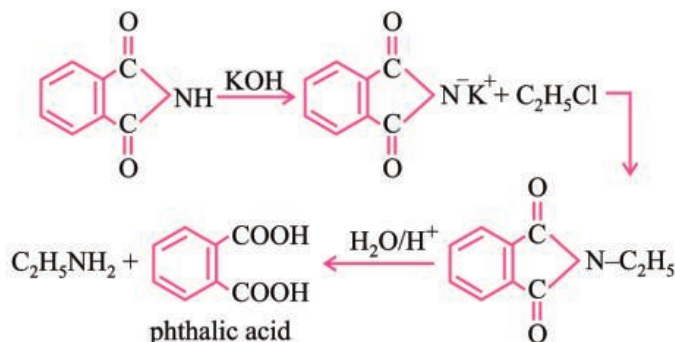
- (i) **Coupling reaction**
- (ii) **Ammonolysis**



- (ii) Ammonolysis :
- $$R-X + NH_3 \rightarrow R-NH_2 + HX$$
- $$RNH_2 + R-X \rightarrow (R)_2N + HX$$
- $$(R)_2NH + R-X \rightarrow (R)_3N + HX$$
- $$(R)_3N + R-X \rightarrow [R_4N]^+X^-$$

Q. 14. Prepare pure sample of 1° amine from 1° alkyl halide.

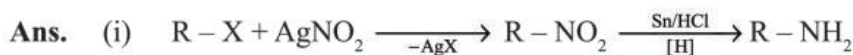
Ans. By Gabriel Phthalimide Reaction



ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. What happens when :

- (i) An alkyl halide reacts with AgNO_2 and product is reduced.
- (ii) An alkyl halide is treated with AgCN and product is hydrolysed.
- (iii) Methyl magnesium is treated with cyanogens chloride.

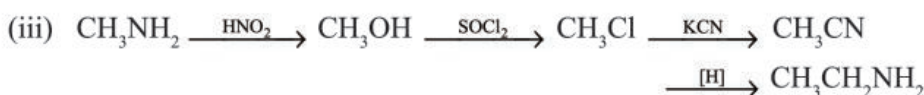
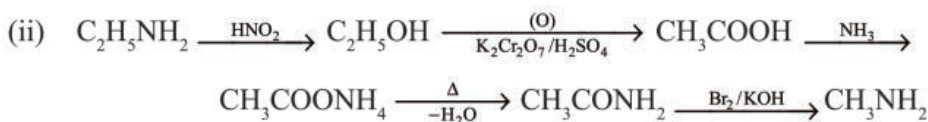
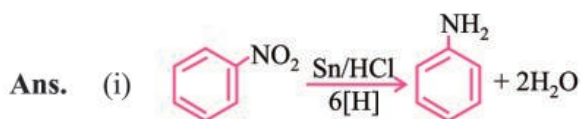


Q. 2. How would you prepare :

(i) $\text{C}_6\text{H}_5\text{NH}_2$ from $\text{C}_6\text{H}_5\text{NO}_2$

(ii) CH_3NH_2 from $\text{C}_2\text{H}_5\text{NH}_2$

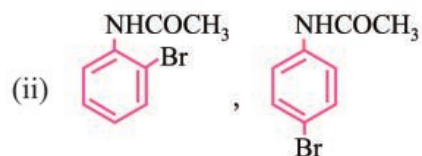
(iii) $\text{C}_2\text{H}_5\text{NH}_2$ from CH_3NH_2



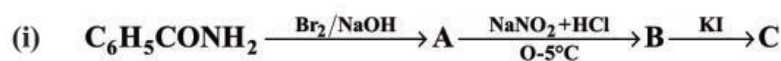
Q. 3. Write the structure of the products in each case :



Ans. (i) $\text{CH}_3\text{CH}_2\text{NHCOCH}_3, \text{CH}_3\text{COOH}$



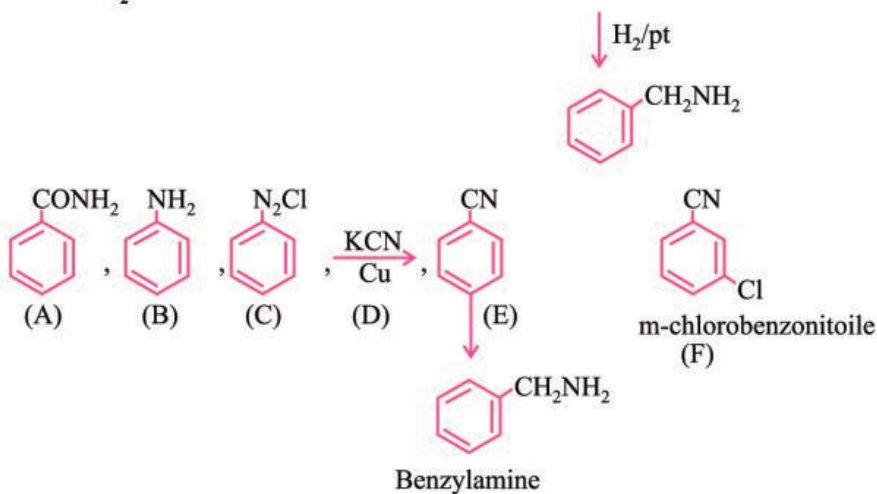
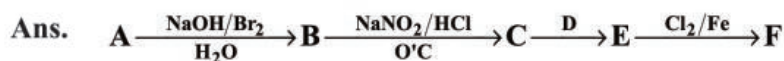
Q. 4. Write the structures of A, B and C in following

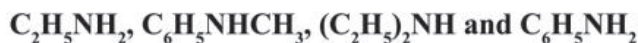
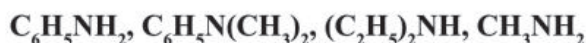
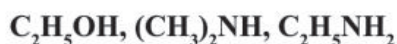
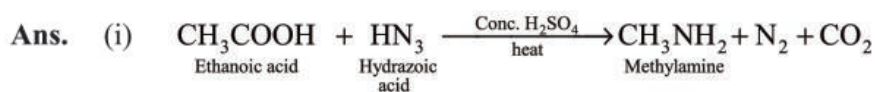


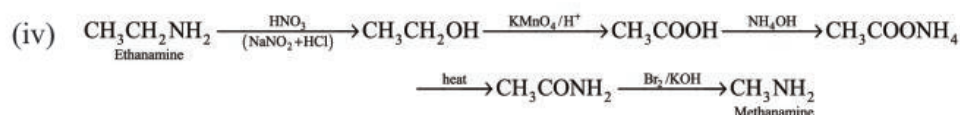
Ans. (i) $\text{C}_6\text{H}_5\text{NH}_2, \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-, \text{C}_6\text{H}_5\text{I}$

(ii) $\text{CH}_3\text{CN}, \text{CH}_3\text{CH}_2\text{NH}_2, \text{CH}_3\text{CH}_2\text{NC}$

Q. 5. Write the structure of reagents/organic compounds 'A' to 'F' :



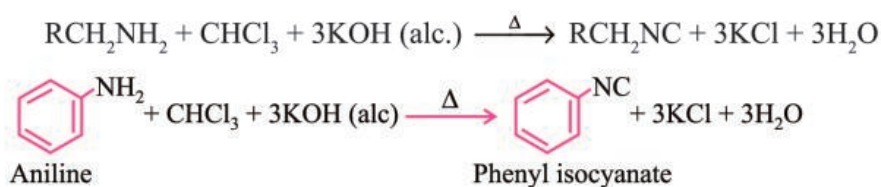
LONG ANSWER TYPE QUESTIONS (5 Marks)**Q. 1. Arrange the following :****(i) In decreasing order of pK_b values :****(ii) In increasing order of basic strength :****(a) Aniline, p-nitroaniline and p-toluidine****(iii) In decreasing order of basic strength :****(iv) Decreasing order of basic strength in gas phase :****(v) Increasing order of boiling point :****Ans. (i) $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$** **(ii) (a) p-nitroaniline < aniline < p-toluidine****(iii) $(C_2H_5)_2NH > CH_3NH_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2$** **(iv) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$** **(v) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$** **Q. 2. How will you convert :****(i) Ethanoic acid into methanamine****(ii) Hexane nitrile into 1-aminopentane****(iii) Methanol into ethanoic acid****(iv) Ethanamine into methanamine**



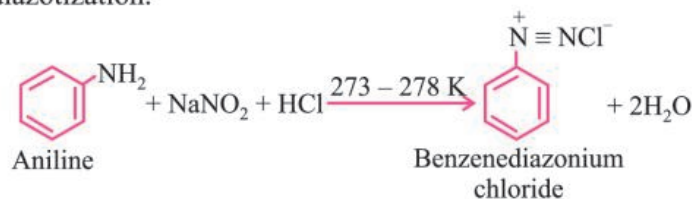
Q. 3. Write short note on the following :

- (i) Carbylamine reaction
- (ii) Diazotization
- (iii) Hoffmann's bromide reaction
- (iv) Coupling reaction
- (v) Ammonolysis

Ans. (i) Carbylamine reaction : When primary amine (aromatic or aliphatic) warmed with chloroform and alc. KOH, isocyanides are formed which can be identified by their offensive smell. This test is used to identify the presence of primary amine or chloroform.



(b) **Diazotization :** When primary aromatic amine is treated with NaNO_2 and HCl at 273-278 K, diazonium salt is obtained. This reaction is known as diazotization.



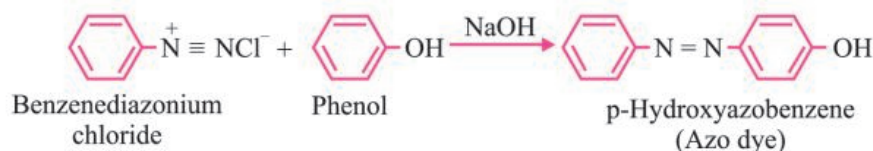
Benzenediazonium chloride is a very important synthetic compound, which can be changed into haloarenes, phenol, cyanobenzene, benzene etc.

- (c) **Hoffmann's bromide reaction** : When any primary amide (aliphatic or aromatic) is treated with bromine and alkali, it gives the amine with one less carbon atom.

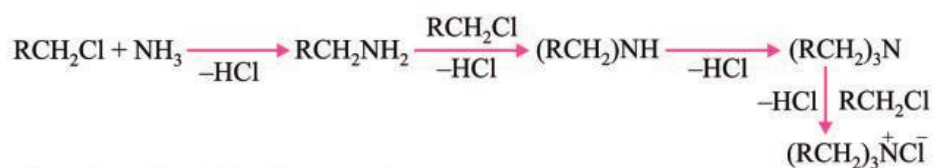


This reaction is used to reduce one carbon atom from a compound.

- (d) **Coupling reaction** : When benzenediazonium chloride is treated with phenols or aromatic amines, azo dyes are produced in which diazo ($-\text{N}=\text{N}-$) group is retained. Coupling reactions generally take place at p-position of phenol or aromatic amines.

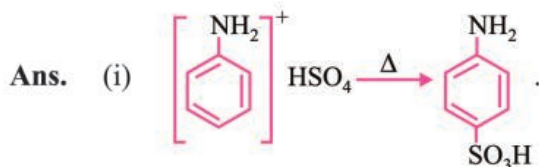


- (e) **Ammonolysis** : Reaction of alkyl halides with ammonia is known as ammonolysis. Ammonolysis generally gives the mixture of 1°, 2°, 3° amines and quaternary ammonium salt.

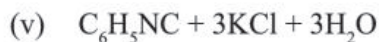


Q. 4. Complete the following reactions :

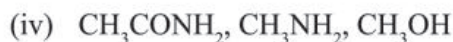
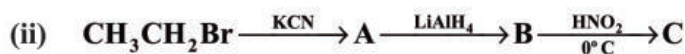
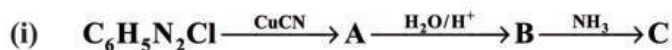
- (i) $\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{SO}_4 \text{ (conc.)} \rightarrow$
- (ii) $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow$
- (iii) $\text{C}_6\text{H}_5\text{NH}_2 + (\text{CH}_3\text{CO})_2\text{O} \rightarrow$
- (iv) $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \rightarrow$
- (v) $\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH (alc.)} \rightarrow$



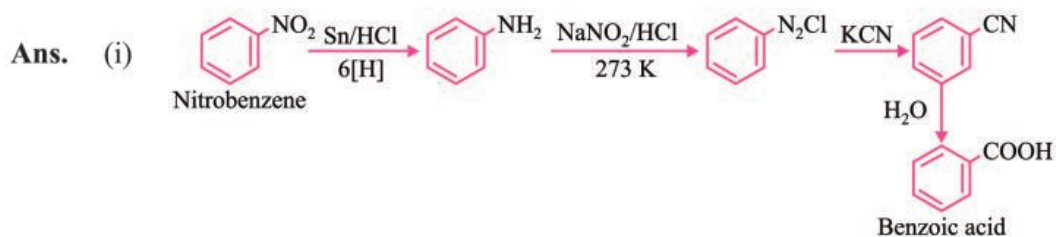
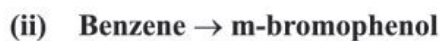
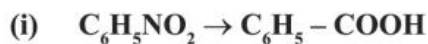
- (ii) $\text{C}_6\text{H}_6 + \text{N}_2 + \text{HCl} + \text{CH}_3\text{CHO}$

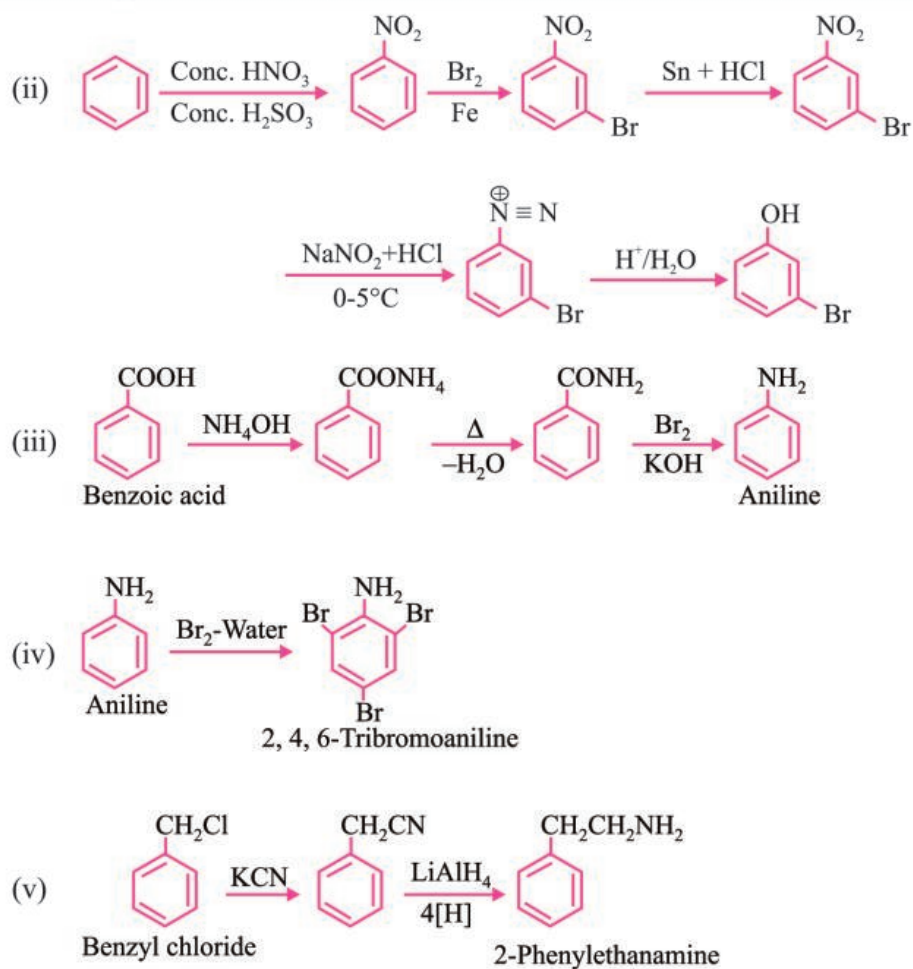


Q. 5. Write A, B and C in the given reactions :



Q. 6. Accomplish the following conversions :





Q. 7. Given reasons : (i) Acetylation of aniline reduces its activating effect.

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

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

Ans. (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

