

## Solved Examples

### JEE Main/Boards

**Example 1:** Distinguish between the following pairs:

- (I)  $(\text{PhNH}_3)_2^+\text{SO}_4^{2-}$  and (II)  $\text{H}_3\text{N}^+\text{C}_6\text{H}_4\text{SO}_3^-$   
 a.  $(\text{PhNH}_3)_2^+\text{SO}_4^{2-}$  and  $\text{H}_3\text{N}^+\text{C}_6\text{H}_4\text{SO}_3^-$   
 b.  $\text{Me}_4\text{N}^+\text{Cl}^-$  and  $[\text{Me}_3\text{NH}^+]\text{Cl}^-$

**Sol:** First two compound can be differentiated by using  $\text{BaCl}_2$  solution as barium will form a ppt with sulphate ion. Other two compound as can be distinguished by treated with  $\text{NaOH}$ .

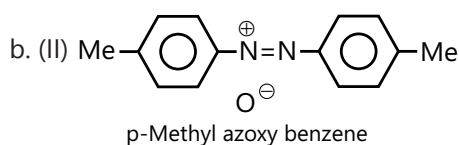
a. Add  $\text{BaCl}_2$  solution. (I) is a sulphate salt and will give a white precipitate of  $\text{BaSO}_4$ , (II) is a sulphonate (sulphonic acid salt) and will not give any precipitate.

b. Add concentrated  $\text{NaOH}$  and heat the mixture. (II will change to a volatile free base  $\text{Me}_3\text{N}$ , which has typical  $\text{NH}_3$  odour. Compound (I) will not react.

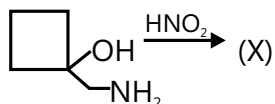
**Example 2:** Complete the following reactions:

- a.  $\text{PhNO}_2 \xrightarrow{\text{Zn+aq. NH}_4\text{Cl}}$  (I)  
 b.  $p\text{-Me-C}_6\text{H}_4\text{NO}_2 \xrightarrow{\text{Al}_2\text{O}_3/\text{aq. NaOH}}$  (II)

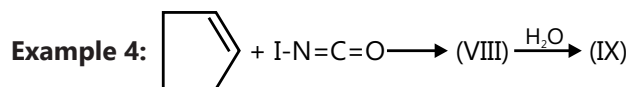
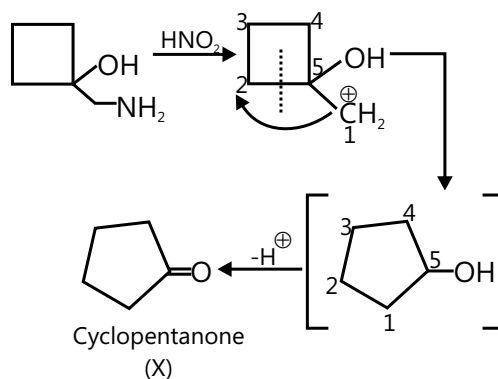
**Sol:** a. (I)  $\text{PhNHOH}$  (N-Phenyl hydroxylamine)



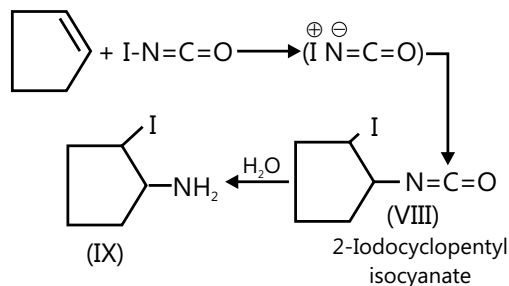
**Example 3:**



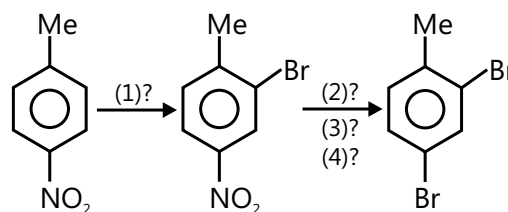
**Sol:** It is an example of pinacole-pinacolone type ring expansion which takes place via carbocation.



**Sol:** First step will lead to formation of an isocyanate. On treatment with water it yields primary amine.

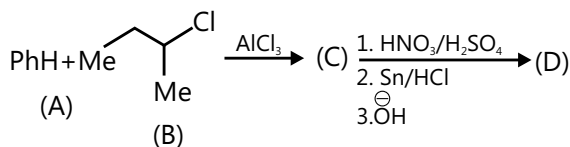


**Example 5:** Give the reagents in the following reactions:

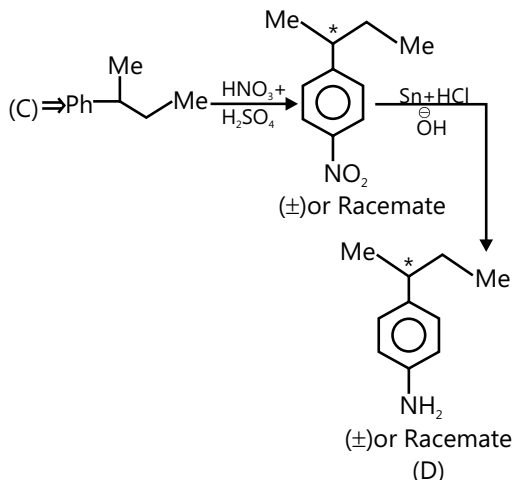


- Sol:** 1.  $\text{Br}_2 + \text{Fe}$       2.  $\text{Sn} + \text{HCl}; \text{OH}^-$   
 3.  $\text{HNO}_2 + 0-5^\circ\text{C}$       4.  $\text{CuBr}$

**Example 6:**

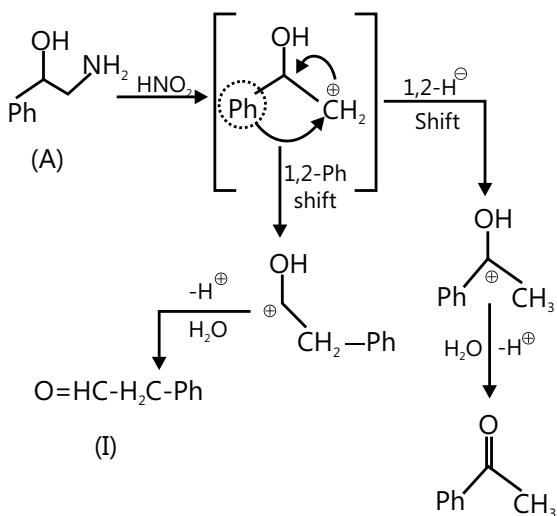


**Sol:** First step is Friedal craft alkylation. This step produces a new chiral centre on the product but it is optically inactive. The alkylated product is subjected to nitration to introduce nitro group at para position on treatment with reducing agents like Sn+HCl, nitro group gets reduced to amino group.

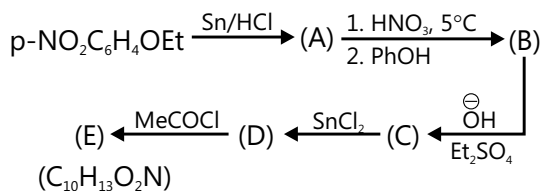


**Example 7:** Explain the formation of the mixture  $PhCH_2CHO$  (I) and  $PhCOMe$  (II) when  $PhCH(OH)CH_2NH_2$  (A) is treated with  $HNO_2$ .

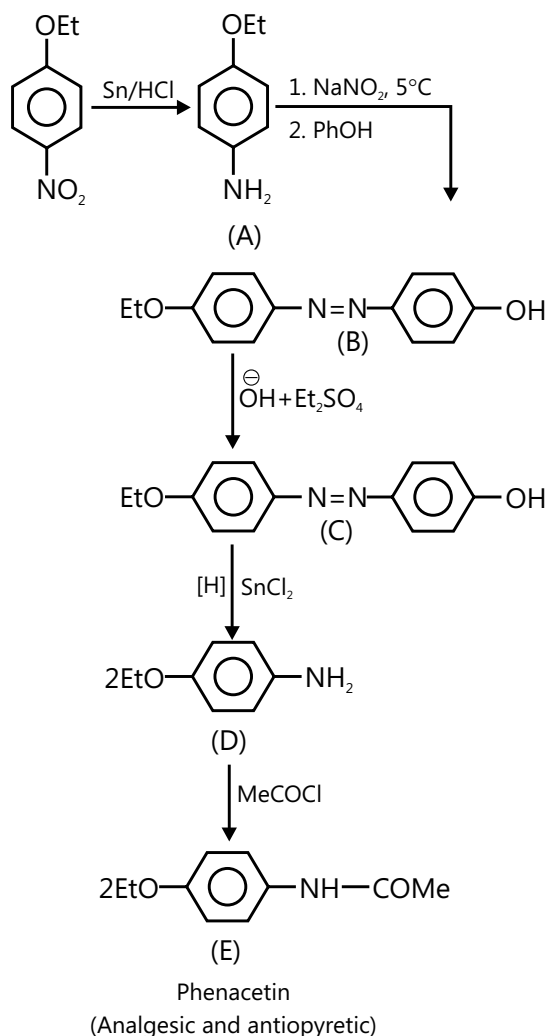
**Sol:** Attack of Nitrous acid produces primary carbocation which gets rearranged to secondary carbocation and tertiary carbocation. Due to formation of two different carbocation we get different product. With secondary carbocation we end up getting  $PhCH_2CHO$  and with tertiary carbocation we get  $PhCOMe$ .



**Example 8:** Identify compounds (A) to (E) in the following:

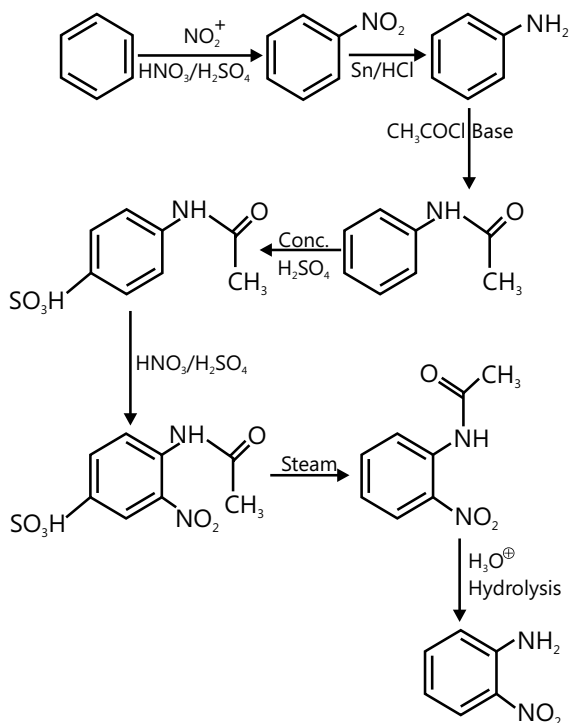


**Sol:**



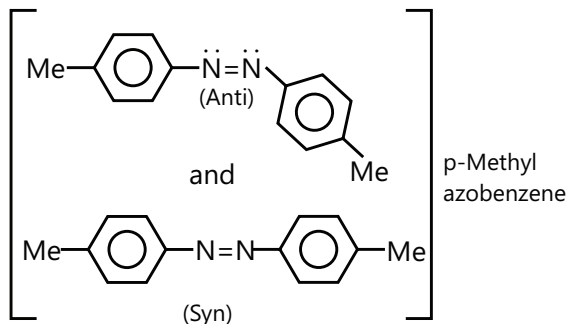
**Example 9:** Convert benzene to o-nitro aniline as the only product.

**Sol:**



**Example 10:**  $m\text{-Me-C}_6\text{H}_4\text{NO}_2 \xrightarrow{\text{LAH}} \text{(III)}$

**Sol:** (III) is

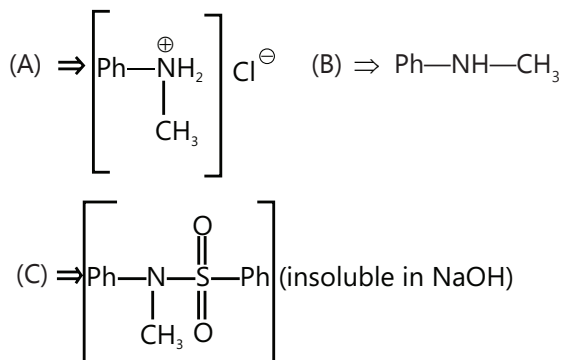


## JEE Advanced/Boards

**Example 1:** The aqueous solution of a nitrogen and chlorine containing organic compound (A) is acidic to litmus. (A) on treatment with aqueous NaOH, it gives a compound (B) containing nitrogen, but not chlorine. Compound (B) on treatment with  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$  in the presence of NaOH gives an insoluble product (C)  $\text{C}_{13}\text{H}_{13}\text{NO}_2\text{S}$ . Give the structures of (A) and (B).

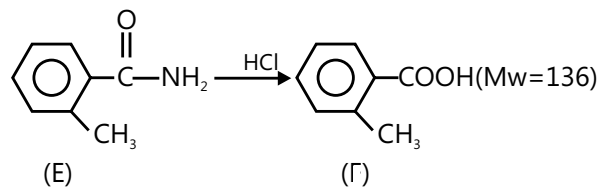
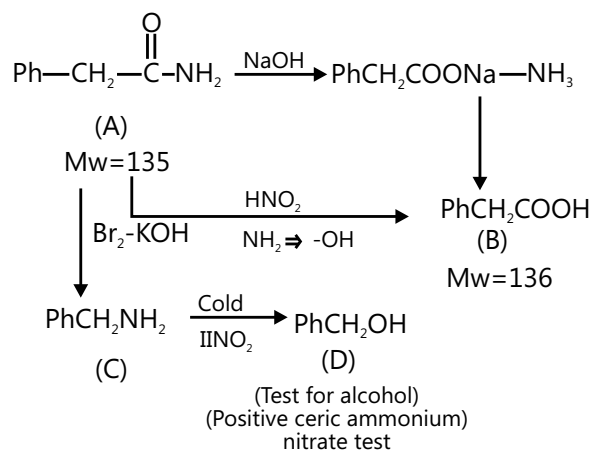
**Sol:** Quaternary ammonium salt on treatment with aqueous NaOH gives secondary amine. Secondary

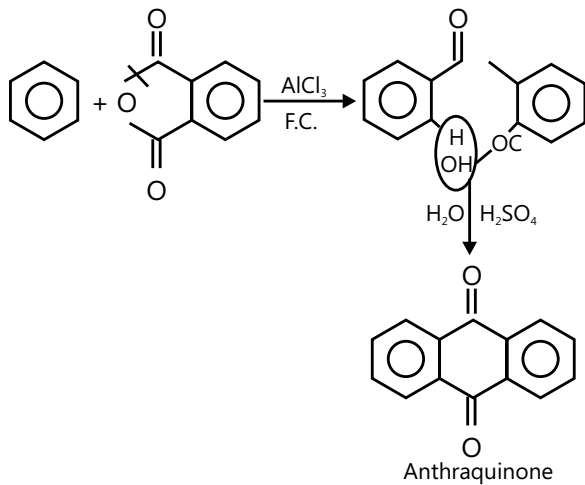
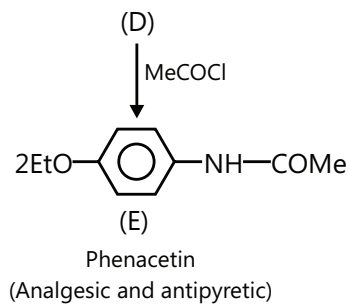
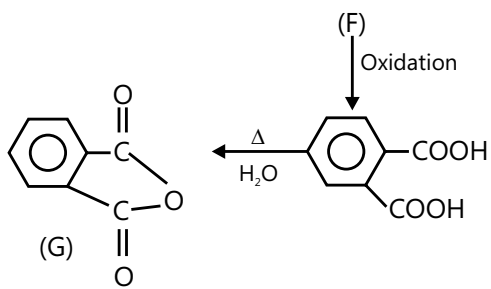
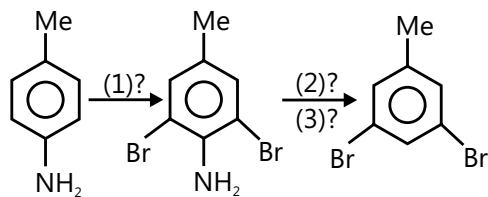
amine on treatment with benzene sulphonyl chloride its derivative.



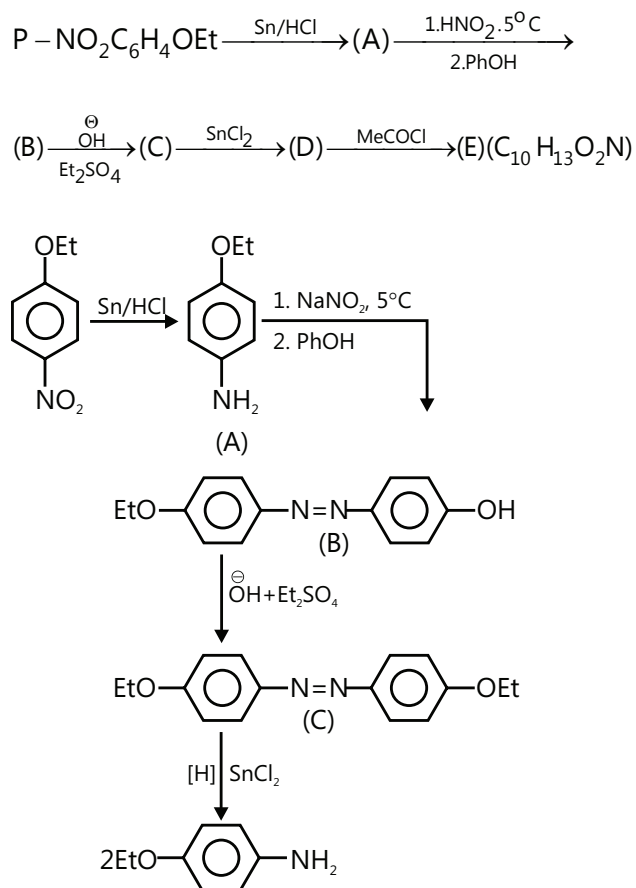
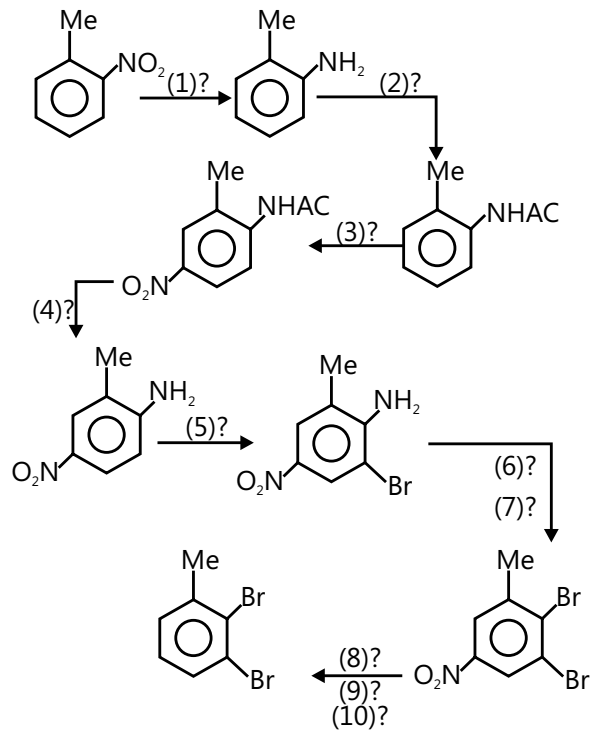
**Example 2:** An organic compound (A) of molecular weight 135 on boiling with NaOH evolves a gas which gives dense white fumes on bringing a rod dipped in HCl near it. The alkaline solution thus obtained on acidification gives the precipitate of a compound (B), having molecular weight 136. Treatment of (A) with  $\text{HNO}_2$  also yields (B), whereas its treatment with  $\text{Br}_2/\text{KOH}$  gives (C). Compound (C) reacts with cold  $\text{HNO}_2$  to give (D) which gives red colour with ceric ammonium nitrate. On the other hand, (E) an isomer of (A) on boiling with dilute HCl gives an acid (F), having molecular weight 136. On oxidation, followed by heating, (F) gives an anhydride (G) which condenses with benzene in the presence of  $\text{AlCl}_3$  to give anthraquinone, Give structures of (A) to (G) with proper reasoning.

**Sol:**



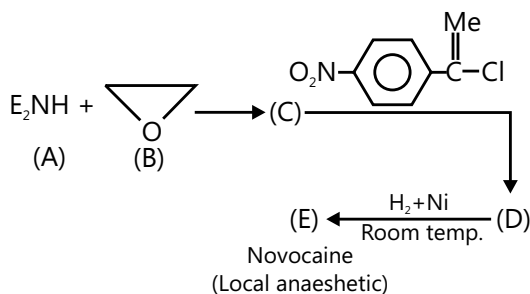
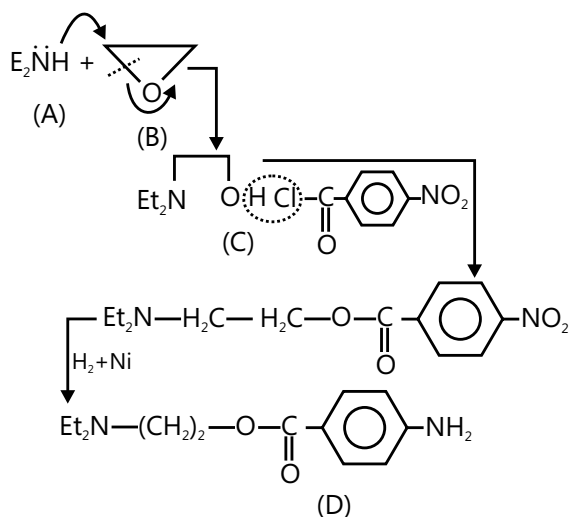

**Example 4:**

**Sol:**

1.  $\text{Br}_2 + \text{Fe}$
2.  $\text{HNO}_2, 0-5^\circ\text{C}$
3.  $\text{H}_3\text{PO}_2$

**Example 3:** Identify compounds (A) to (E) in the following:

**Example 5:**


- Sol:**
1.  $\text{Sn} + \text{HCl}$
  2.  $\text{Ac}_2\text{O}$
  3.  $\text{HNO}_3 + \text{H}_2\text{SO}_4$
  4.  $\text{OH}^-$

5.  $\text{Br}_2 + \text{Fe}$                       6.  $\text{HNO}_2, 0-5^\circ\text{C}$   
 7.  $\text{CuBr}$                                 8.  $\text{Sn} + \text{HCl}; \text{OH}^-$   
 9.  $\text{HNO}_2, 0-5^\circ\text{C}$                     10.  $\text{H}_3\text{PO}_2$

**Example 6:****Sol:**

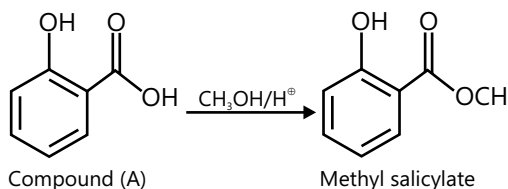
**Example 7:** A mixture of two organic compounds is added to cold water. After filtration, water-insoluble compound (A) burns with a smoky flame and it does not respond to Lassaigne's and Beilsteins test. When a small amount of this is added to  $\text{NaHCO}_3$  solution, a colourless gas is evolved with effervescence. When this compound is heated with  $\text{CH}_3\text{OH}$  in acidic medium, it gives the characteristic smell of the oil of wintergreen. Compound (B), which is water soluble, burns with a non-smoky flame and its sodium extract is prepared with cane sugar. It gives a Prussian blue colour with freshly prepared solution of  $\text{FeSO}_4 + 2-3$  drops  $\text{NaOH}$  and with few drops of  $\text{H}_2\text{SO}_4$ . When a small amount of this compound is heated in a dry test tube, a colourless gas is evolved that turns moist red litmus paper blue and a white residue is left. This white residue is dissolved in water and a drop of  $\text{CuSO}_4$  is added in the basic medium-a violet colour is obtained. Identify the compounds (A) and (B) with the help of the reactions involved.

**Sol:**

i. Compound (A) is insoluble in water and burns with a smoky flame; hence it should be an aromatic compound.

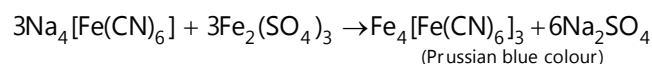
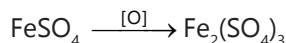
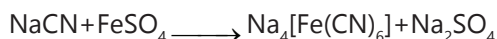
ii. It has no specific element such as N, S and halogens and gives a  $\text{CO}_2$  gas with  $\text{NaHCO}_3$  solution; hence it should contain  $(-\text{COOH})$  group.

iii. It gives the oil of wintergreen (methyl salicylate) with  $\text{CH}_3\text{OH}$  in acidic medium; hence it is salicylic acid.



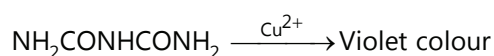
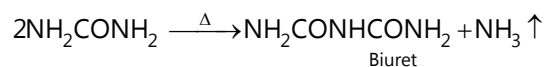
iv. Compound (B) is water soluble and burns with a non-smoky flame; hence it should be an aliphatic compound.

v. This compound has less carbon content because its sodium extract is prepared with sucrose and it gives a Prussian blue colour with the freshly prepared solution of  $\text{FeSO}_4 + 2-3$  drops of  $\text{NaOH}$  and a few drops of  $\text{H}_2\text{SO}_4$ ; hence it is a nitrogen-containing compound.



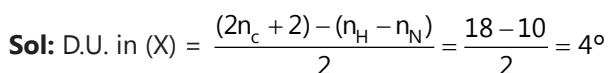
vi. On heating, it gives ammonia gas, which turns red litmus blue. Hence, it contains  $(-\text{CONH}_2)$  group.

vii. It also gives the biuret test.



Hence, this compound is urea ( $\text{NH}_2\text{CONH}_2$ ).

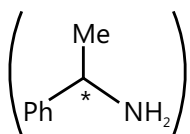
**Example 8:** Give the structural formula of a chiral compound  $\text{C}_8\text{H}_{11}\text{N}$  (X), which dissolves in dilute  $\text{HCl}$  and evolves  $\text{N}_2$  gas with  $\text{HNO}_2$ .



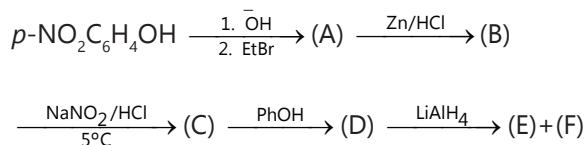
i. 4 D.U. is (X) suggests that it contains benzene ring.

ii. (X) is a  $1^\circ$  amine since it dissolves in  $\text{HCl}$  and gives  $\text{N}_2$  with  $\text{HNO}_2$ .

iii. The remaining C atom and the  $\text{NH}_2$  must form a chiral molecule. So, (X) is:

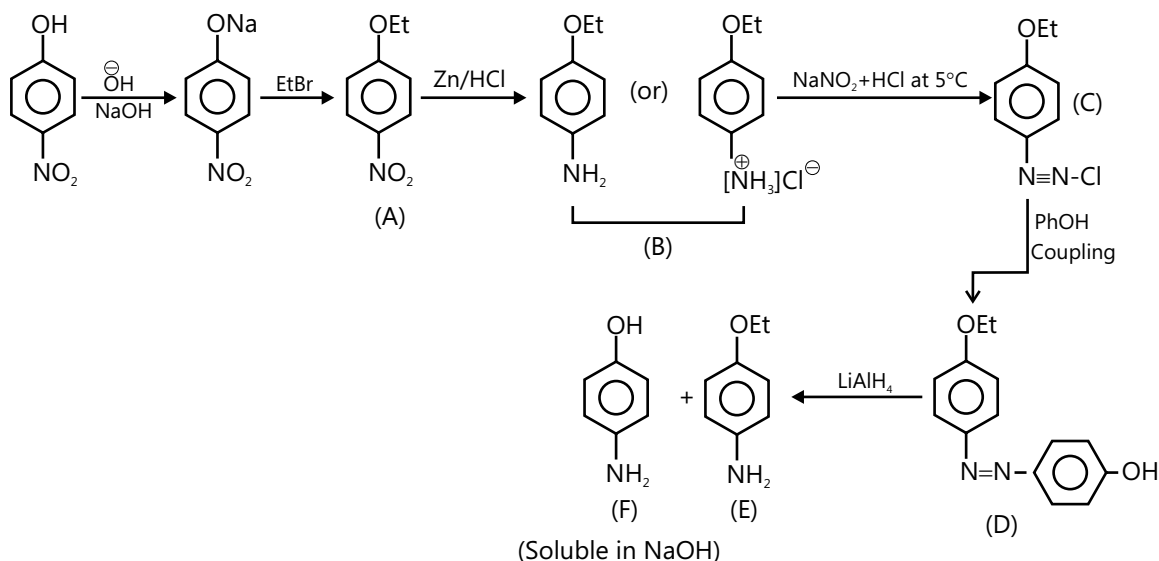


**Example 9:** Identify compounds (A) through (E) in the following:



(F) dissolves in NaOH.

**Sol:**

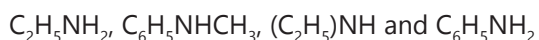


## JEE Main/Boards

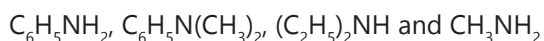
### Exercise 1

**Q.1** Arrange the following:

(i) In decreasing order of the  $\text{p}K_b$  values:



(ii) In increasing order of basic strength.



(iii) In increasing order of basic strength:

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

(b)  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{NHCH}_3$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ ,

**Q.2** Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.

**Q.3** Explain Hofmann Bromamide reaction with Mechanism.

**Q.4** Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis ?

**Q.5** Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

**Q.6** Write one chemical reaction each to illustrate the following

- (i) Hofmann Bromamide reaction.
- (ii) Gabriel Phthalimide reaction

**Q.7** Assign a reason for the following statements

- (a) Alkylamines are stronger bases than arylamines.
- (b) How would you convert methylamine into ethylamine?

**Q.8** Illustrate the following with an example of reaction in each case:

- (i) Sandmeyer reaction
- (ii) Coupling reaction

**Q.9** Write the chemical reaction equations for one example each of the following

- (i) A coupling reaction
- (ii) Hofmann's bromamide reaction
- (iii) Aryl cyanides cannot be formed by the reaction of aryl halides and sodium cyanide.

**Q.10** Account for the following:

- (i) Aniline is weaker base than methylamine.
- (ii) Aryl cyanides cannot be formed by the reaction of aryl halides and sodium cyanide.

**Q.11** Describe tests to distinguish between: Secondary amine and tertiary amine.

**Q.12** Account for the following observations:

- (i)  $pK_b$  for aniline is more than that for methylamine.
- (ii) Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.
- (iii) Aniline does not undergo Friedel Crafts reaction.

**Q.13** State the reactions and reaction conditions for the following conversion

- (i) Benzene diazonium chloride to nitrobenzene.
- (ii) Aniline to benzene diazonium chloride.
- (iii) Ethyl amide to methylamine.

**Q.14** Write the physical property of aniline

**Q.15** Write the method of formation of benzene diazonium chloride

**Q.16** Account for the following:

- (i) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
- (ii) Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

**Q.17** How will you convert:

- (i) Ethanoic acid into methanamine
- (ii) Hexanenitrile into 1-aminopentane
- (iii) Methanol to ethanoic acid
- (iv) Ethanamine into methanamine
- (v) Ethanoic acid into propanoic acid
- (vi) Methanamine into ethanamine
- (vii) Nitromethane into dimethylamine
- (viii) Propanoic acid into ethanoic acid?

**Q.18** Write short notes on the following:

- (i) Coupling reaction
- (ii) Ammonolysis
- (iii) Acetylation
- (iv) Gabriel phthalimide synthesis

**Q.19** Accomplish the following conversions

- (i) Nitrobenzene to benzoic acid
- (ii) Benzene to m-bromophenol
- (iii) Benzoic acid to aniline
- (iv) Aniline to 2,4,6-tribromofluorobenzene
- (v) Benzyl chloride to 2-phenylethanamine
- (vi) Chlorobenzene to p-chloroaniline
- (vii) Aniline to p-bromoaniline
- (viii) Benzamide to toluene
- (ix) Aniline to benzyl alcohol.

**Q.20** Write the equation of Curtius reaction with mechanism?

**Q.21** Complete the following reactions:

- (i)  $C_6H_5NH_2 + CHCl_3 + alc. KOH \rightarrow$

- (ii)  $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$   
 (iii)  $C_6H_5NH_2 + H_2SO_4 \text{ (conc.)} \rightarrow$   
 (iv)  $C_6H_5N_2Cl + C_2H_5OH \rightarrow$   
 (v)  $C_6H_5NH_2 + Br_2 \text{ (aq)} \rightarrow$   
 (vi)  $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$

**Q.22** Give possible 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.23** Write the reaction and conditions for the following conversions

- (i) Aniline to benzene  
 (ii) Methylamine to methyl cyanide  
 (iii) Propanenitrile to ethylamine  
 (iv) m-Bromoaniline to m-bromophenol  
 (v) Nitrobenzene to 2,4,6-tribromoaniline.

**Q.24** Write the method of formation of zwitter ion?

**Q.25** Explain nitration of aniline?

**Q.26** Why aniline does not give Friedel-Crafts reaction?

**Q.27** How will you convert 4-nitrotoluene to 2-Bromobenzoic acid?

**Q.28** Draw the structure of trimethylamine and tell the shape of the molecule. Show the angle between two methyl groups.

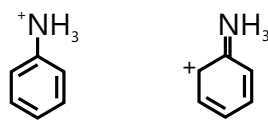
## Exercise 2

### Single Correct Choice Type

**Q.1** When aniline is treated with fuming sulphuric acid at 475K, it gives

- (A) Sulphanilic acid  
 (B) Aniline sulphate  
 (C) o-aminobenzenesulphonic acid  
 (D) m-aminobenzenesulphonic acid

**Q.2** Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below.



- (A) II is not an acceptable canonical structure, because carbonium ions are less stable than ammonium ions  
 (B) II is not an acceptable canonical structure, because it is non aromatic  
 (C) II is not an acceptable canonical structure, because the nitrogen has 10 valence electrons  
 (D) II is an acceptable canonical structure.

**Q.3** The correct order of basic strength in  $CCl_4$

- (1)  $NH_3$     (2)  $RNH_2$     (3)  $R_2NH$     (4)  $R_3N$   
 where R is  $CH_3$  group is

- (A)  $3 > 2 > 1 > 4$     (B)  $2 > 3 > 4 > 1$   
 (C)  $3 > 2 > 4 > 1$     (D) None of these

**Q.4** Place the following in the decreasing order of basicity.

- (1) Ethylamine    (2) 2-aminoethanol  
 (3) 3-aminopropan-1-ol  
 (A)  $1 > 3 > 2$     (B)  $1 > 2 > 3$   
 (C)  $2 > 1 > 3$     (D) None of these

**Q.5** Which of the following will give a positive carbylamine test?

- (A)  $H_3CNH_2$     (B)  $H_3C-NH-CH_3$   
 (C)  $(CH_3)_3N$     (D)  $C_6H_5NH_2$

**Q.6** Isopropylamine can be obtained by

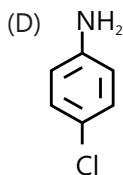
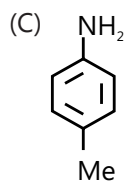
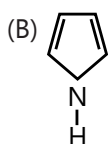
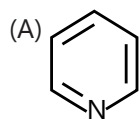
- (A)  $(CH_3)_2CHO + NH_2OH \xrightarrow{LiAlH_4} ?$   
 (B)  $(CH_3)_2CHO + NH_3 \xrightarrow[\Delta]{H_2/Ni} ?$   
 (C)  $CHOH + NH_3 \longrightarrow ?$   
 (D) All of these

**Q.7** The basic strength of amines (ethyl) and ammonia in  $H_2O$  is

- (A)  $NH_3 > p > s > t$     (B)  $P > s > t > NH_3$   
 (C)  $s > p > t > NH_3$     (D) None of these



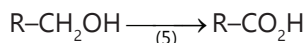
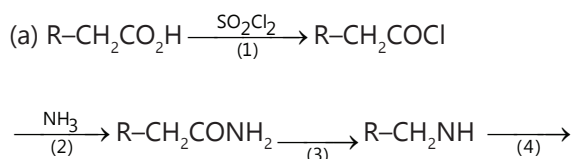
**Q.8** Which of the following will have highest  $K_b$  value?



**Q.9** The product not obtained in the following reaction,  $\text{CH}_3\text{-NO}_2 + \text{Cl}_2 + \text{NaOH} \longrightarrow$  is

- (A)  $\text{ClCH}_2\text{NO}_2$       (B)  $\text{Cl}_2\text{CHNO}_2$   
(C)  $\text{Cl}_3\text{CNO}_2$       (D)  $\text{CH}_3\text{NH}_2$

**Q.10** A sequential reaction may be performed as represented below:



The appropriate reagent for step (3) is

- (A) NaBr    (B) Bromine+alkali    (C) HBr    (D)  $\text{P}_2\text{C}_5$

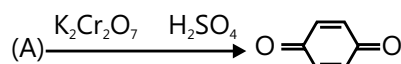
**Q.11** Which of the following amine form N-nitroso derivative when treated with  $\text{NaNO}_2$  and HCl?

- (A)    (B)   
(C)    (D)

**Q.12** The strongest base among the following is

- (A)    (B)   
(C)    (D)

**Q.13** Identify compound (A) in the following oxidation reaction.



- (A)    (B)   
(C)    (D) All of these

**Q.14** + phosgene  $\longrightarrow$  X. Here X is

- (A)    (B)   
(C)    (D) None of these

**Q.15** Ethylamine undergoes oxidation in the presence of  $\text{KMnO}_4$  to give

- (A)  $\text{CH}_3\text{COOH}$     (B)  $\text{CH}_3\text{CH}_2\text{OH}$   
(C)  $\text{CH}_3\text{CHO}$     (D) N-oxide

**Q.16** Baker Mulliken's test is used to detect the presence

- (A)  $-\text{COOH}$  gp    (B)  $-\text{NO}_2$   
(C)  $-\text{OH}$     (D)  $-\text{NH}_2$

**Q.17** t-amines with different alkyl group has a chiral nitrogen atom still it is optically inactive because

- (A) Chiral N-atoms cannot rotate plane polarized light  
(B) The lone pair prevents the rotation of plane polarized light  
(C) Both of these  
(D) None of these

**Q.18** In  $\text{CH}_3\text{NO}_2$  we can observe

- (A) H-bonding  
 (B)  $\alpha$ -halogenation reaction  
 (C) Tautomerism  
 (D) All of these

**Q.19** Match list I (condition of reaction of nitrobenzene) with list II (products formed) and select the correct answer the codes given below.

	List I		List II
(i)	Sn and HCl	(p)	Hydrazobenzene
(ii)	Zn and $\text{NH}_4\text{Cl}$	(q)	Azoxybenzene
(iii)	Methanolic NaOMe	(r)	Phenyl hydroxylamine
(iv)	Zn and KOH	(s)	Aniline

- (A) (i) - q, (ii) - p, (iii) - r, (iv) - s  
 (B) (i) - s, (ii) - r, (iii) - q, (iv) - p  
 (C) (i) - p, (ii) - s, (iii) - q, (iv) - r  
 (D) (i) - p, (ii) - r, (iii) - q, (iv) - s

**Q.20** The increasing order of basicity of  $\text{RCN}$ ,  $\text{RCH}=\text{NR}$  and  $\text{RNH}_2$  is

- (A)  $\text{RCN} < \text{RCH}=\text{NR} < \text{RNH}_2$   
 (B)  $\text{RNH}_2 < \text{RCN} < \text{RCH}=\text{NR}$   
 (C)  $\text{RCN} > \text{RCH}=\text{NR} < \text{RNH}_2$   
 (D) None of these

**Q.21** How many isomeric amines with that formula  $\text{C}_7\text{H}_9\text{N}$  contain a benzene ring?

- (A) Two      (B) Three      (C) Four      (D) Five

## Previous Years' Questions

**Q.1** Match the compounds given in list I with their characteristic reactions given in list II. Select the correct option **(2010)**

List I	List II
(i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	(p) Alkaline hydrolysis
(ii) $\text{CH}_3\text{C}\equiv\text{CH}$	(q) With KOH (alcohol) and $\text{CHCl}_3$ produces bad smell
(iii) $\text{CH}_3\text{CH}_2\text{COOCH}_3$	(r) Gives white ppt. with ammonical $\text{AgNO}_3$

List I	List II
(iv) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	(s) With Lucas reagent cloudiness appears after 5 minutes

- (A) (i) - q, (ii) - p, (iii) - s, (iv) - r  
 (B) (i) - r, (ii) - q, (iii) - p, (iv) - s  
 (C) (i) - q, (ii) - r, (iii) - p, (iv) - s  
 (D) (i) - s, (ii) - q, (iii) - r, (iv) - p

**Q.2** A primary amine is formed an amide by the treatment of bromine and alkali. The primary amine has **(2004)**

- (A) 1 carbon atom less than amide  
 (B) 1 carbon atom more than amide  
 (C) 1 hydrogen atom less than amide  
 (D) 1 hydrogen atom more than amide

**Q.3** Indicate which nitrogen compound amongst the following would undergo Hofmann's reaction (i.e. reaction with  $\text{Br}_2$  and strong KOH) to furnish the primary amine ( $\text{R}-\text{NH}_2$ ) **(1989)**

- (A)  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}\cdot\text{CH}_3$       (B)  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}\cdot\text{NH}_4$   
 (C)  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$       (D)  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHOH}$

**Q.4** The order of basic strength among the following amines in benzene solution is **(1991)**

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

**Q.5** The refluxing of  $(\text{CH}_3)_2\text{NCOCH}_3$  with acid gives **(1996)**

- (A)  $2\text{CH}_3\text{NH}_2 + \text{CH}_3\text{COOH}$   
 (B)  $2\text{CH}_3\text{OH} + \text{CH}_3\text{COOH}$   
 (C)  $(\text{CH}_3)_2\text{NH} + \text{CH}_3\text{COOH}$   
 (D)  $(\text{CH}_3)_2\text{NCOOH} + \text{CH}_4$

**Q.6** Order of basicity of ethyl amines is (1988)

- (A) Secondary > Primary > Tertiary  
 (B) Primary > Secondary > Tertiary  
 (C) Secondary > Tertiary > Primary  
 (D) Tertiary > Primary > Secondary

**Q.7** The following reaction is  $RX + KOH$  (solid)  $\xrightarrow{\text{heat}}$  (1988)

- (A) Nucleophilic substitution  
 (B) Electrophilic substitution  
 (C) Free radical substitution  
 (D) None of these

Read the assertion and reason carefully to mark the correct option out of the options given below:

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

**Q.8 Assertion:** Benzene diazonium chloride does not give tests for nitrogen.

**Reason:**  $N_2$  gas lost during heating (1999)

**Q.9 Assertion:** Amines are basic in nature.

**Reason:** Presence of lone pair of electron on nitrogen atom. (1999)

**Q.10 Assertion:** Alkyl isocyanides in acidified water give alkyl formamides.

**Reason:** In isocyanides, carbon first acts as a nucleophile then as an electrophile. (2005)

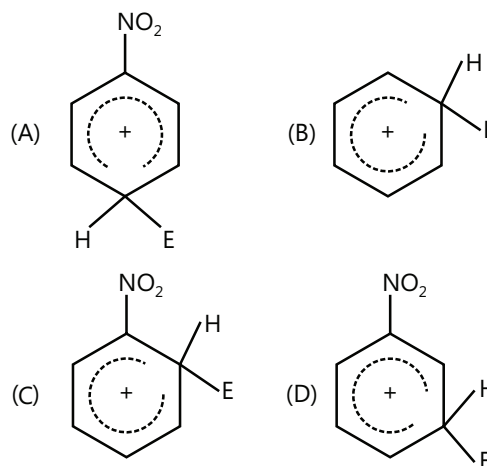
**Q.11 Assertion:** Amines are more basic than esters and ethers.

**Reason:** Nitrogen is less electronegative than oxygen. It is in better position to accommodate the positive charge on the proton. (2007)

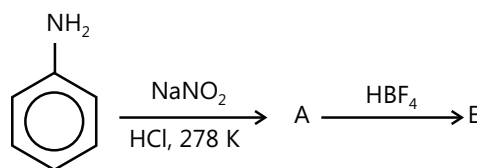
**Q.12 Assertion:** Nitrobenzene is used as a solvent in Friedel-Craft's reaction.

**Reason:** Fusion of nitrobenzene with solid KOH gives a low yield of a mixture of o- and p- nitro phenols. (2008)

**Q.13** The electrophile,  $E^+$  attacks the benzene ring to generate the intermediate  $\sigma$ -complex of the following, which  $\sigma$ -complex is of lowest energy? (2008)



**Q.14** In the chemical reactions the compounds 'A' and 'B' respectively are (2010)



- (A) Nitrobenzene and fluorobenzene  
 (B) Phenol and benzene  
 (C) Benzene diazonium chloride and fluorobenzene  
 (D) Nitrobenzene and chlorobenzene

**Q.15** Which of the following compounds can be detected by Molisch's test? (2012)

- (A) Nitro compounds (B) Sugars  
 (C) Amines (D) Primary alcohols

**Q.16** On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is: (2014)

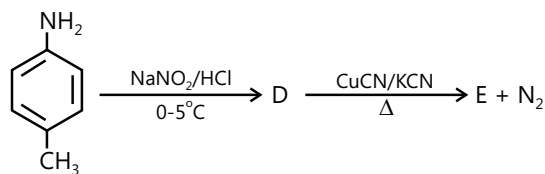
- (A) An alcohol (B) An alkanediol  
 (C) An alkyl cyanide (D) An alkyl isocyanide

**Q.17** Considering the basic strength of amines in aqueous solution, which one has the smallest  $pK_b$  value? (2014)

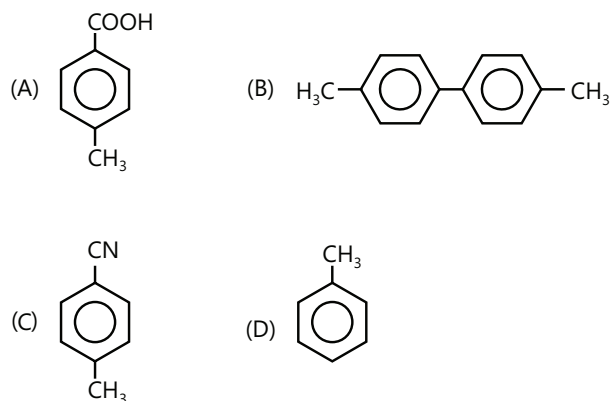
- (A)  $(CH_3)_2NH$  (B)  $CH_3NH_2$   
 (C)  $(CH_3)_3N$  (D)  $C_6H_5NH_2$

Q.18 In the reaction

(2015)



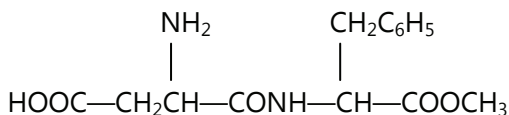
the E is: product



## JEE Advanced/Boards

### Exercise 1

Q.1 Aspartame, an artificial sweetener, is a peptide and has the following structures:



- (i) Identify the four functional groups.
- (ii) Write the zwitter ionic structure
- (iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.
- (iv) Which of the two amino acids is more hydrophobic?

Q.2 Compound of A (molecular formula C<sub>9</sub>H<sub>11</sub>NO) gives a positive Tollen's test and is soluble in dilute HCl. It gives no reaction with benzene sulphonyl chloride or with NaNO<sub>2</sub> and HCl at 0°C. (A), upon oxidation with KMnO<sub>4</sub> gives an acid (B). When (B) is heated with soda-lime, compound (C) is formed which reacts with NaNO<sub>2</sub> and HCl at 0–5°C. What is (A)?

Q.3 An organic compound A, when treated with nitrous acid yields an alcohol B, C<sub>4</sub>H<sub>10</sub>O with the evolution of N<sub>2</sub>. B on careful oxidation yields a substance C of vapour density 36 which forms oxime; B can react with NaHSO<sub>3</sub> but does not reduce Fehling solution. Identify compound A and write the structural formulae of the isomeric compounds that behave with HNO<sub>2</sub> in the same manner.

Q.4 An organic compound (A), C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>O<sub>4</sub>, is insoluble in both dilute acid and base and its dipole moment is zero. Deduce the structure of (A).

Q.5 Explain the following observations:

- (i) Aniline dissolves in aqueous HCl.
- (ii) The amino group in ethylamine is basic whereas that in acetamide it is not basic.
- (iii) Dimethylamine is a stronger base than trimethylamine.
- (iv) Sulphanilic acid although has acidic as well as basic group, it is soluble in alkali but insoluble in mineral acids.

Q.6 Explain, why?

- (i) Glycine exists as H<sub>3</sub>N<sup>+</sup>CH<sub>2</sub>COO<sup>-</sup> while anthranilic acid, p-NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-COOH does not exist as dipolar ion.
- (ii) Benzenesulphonic acid is a stronger acid than benzoic acid.
- (iii) A weakly basic solution favours coupling with phenol.
- (iv) It is difficult to prepare pure amines by ammonolysis of alkyl halides.

Q.7 Explain with reason?

- (i) Although trimethylamine and n-propylamine have same molecular weight, the former boils at a lower temperature (3°C) than the latter (49°C).

(ii) Dimethylamine is a stronger base than methylamine but trimethylamine is a weaker base than both dimethylamine and methylamine.

(iii) Silver chloride dissolves in aqueous solution of methylamine. Explain.

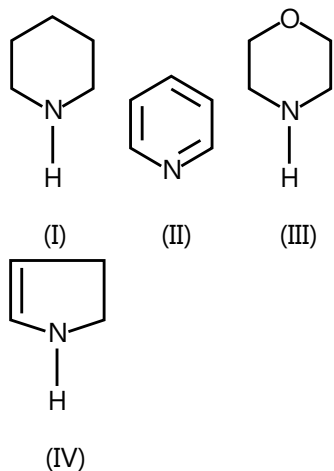
**Q.8** Explain it?

(i) An aqueous solution of ethylamine gives a red precipitate with ferric chloride. Explain.

(ii) Tertiary amines do not undergo acetylation. Comment

(iii) 2,6-Dimethyl-N,N-dimethylaniline, although has a free p-position, does not undergo coupling with benzene diazonium chloride. Comment.

(iv) In the following compounds:



The order of basicity is I > III > II > IV. Explain.

**Q.9** Explain it with reason.

(i) tert-Butylamine cannot be prepared by the action of  $\text{NH}_3$  on tert-butyl bromide.

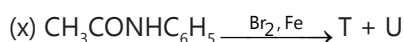
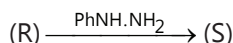
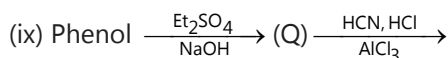
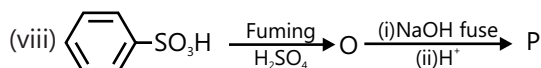
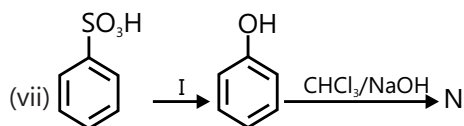
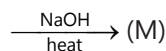
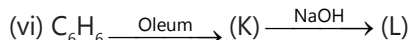
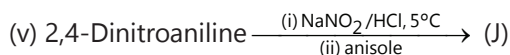
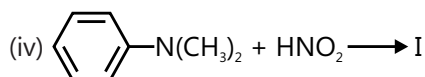
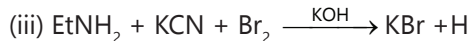
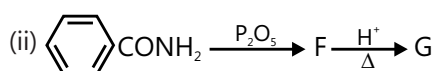
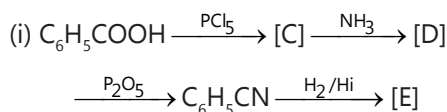
(ii) Isocyanides are hydrolysed by dilute acids but not by alkalis to form amine and formic acid.

(iii) How will you explain the acidic nature of 1° and 2° nitroalkanes?

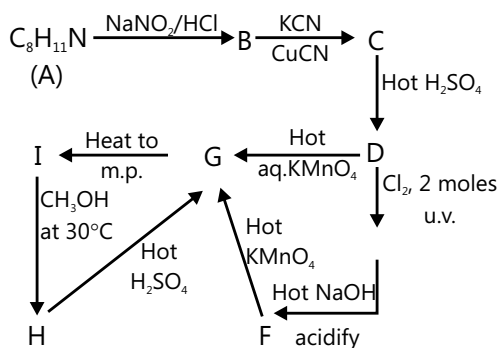
(iv) Aniline does not undergo Friedel Craft's reaction?

(v) Although boron trifluoride adds on trimethylamine, it does not add on triphenylamine. Comment.

**Q.10** Complete the following reactions:



**Q.11** Give structures for the compounds (A) to (I):



**Q.12** When 2.25 g of an unknown amine was treated with nitrous acid, the evolved nitrogen, corrected to S.T.P. measured 560 ml. The alcohol isolated from the reaction mixture gave a positive iodoform reaction. What is the structural formula of the unknown amine?

**Q.13** The aqueous solution of a nitrogen and chlorine containing organic compound (A) is acidic towards litmus. (A) on treatment with aqueous NaOH gives a compound (B), containing nitrogen, but not chlorine. Compound (B)

on treatment with  $C_6H_5SO_2Cl$  in the presence of NaOH gives an insoluble product (C),  $C_{13}H_{13}NO_2S$ . Give the structures of compounds (A) and (B).

**Q.14** An organic compound (A) composed of C, H and O gives characteristic colour with ceric ammonium nitrate. Treatment of (A) with  $PCl_5$  gives (B), which reacts with KCN to form (C). The reduction of (C) with warm  $Na/C_2H_5OH$  products (D), which on heating gives (E) with evolution of ammonia. Pyridine is obtained on treatment of (E) with nitrobenzene. Give structure of compounds (A) to (E) with proper reasoning.

**Q.15** One mole of bromo derivative (A) and mole of  $NH_3$  react to give one mole of an organic compound (B). (B) reacts with  $CH_3I$  to give (C). Both (B) and (C) react with  $HNO_2$  to give compounds (D) and (E) respectively. (D) on oxidation and subsequent decarboxylation gives 2-methoxy-2-methyl propane. Give structures of compounds (A) to (E) with proper reasoning.

**Q.16** What happens when cyclopentanone reacts with

- (i)  $CH_3CH_2NH_2$  ( $1^\circ$  amine)
- (ii)  $(CH_3CH_2)_2NH$  ( $2^\circ$  amine)

**Q.17** Cyclohexyl amine is a stronger base than aniline. Why?

**Q.18** How does the formation of  $2^\circ$  and  $3^\circ$  amines can be avoided during the preparation of  $1^\circ$  amines by alkylation?

**Q.19** It is necessary to acetylate aniline first for preparing bromoaniline. Why?

**Q.20** Dimethyl amine is a stronger base than methylamine but trimethylamine is a weaker base than both dimethyl amine and methylamine. Why?

**Q.21** From analysis and molecular weight determination, the molecular formula of (A) is  $C_3H_7NO$ . The compound gave following reactions.

- (i) On hydrolysis, it gives an amine (B) and a carboxylic acid (C)
- (ii) Amine (B) reacts with benzene sulphonyl chloride and gives a product which is insoluble in aqueous sodium hydroxide solution.
- (iii) Acid (C) on reaction with Tollen's reagent gives a silver mirror when are A, B and C. Explain the reactions.

**Q.22** An optically active amine (A) is subjected to exhaustive methylation and Hofmann elimination to yield an alkene (B). (B) on ozonolysis gives an equimolar mixture of formaldehyde and butanal. Deduce the structures of (A) and (B). Is there any structural isomer to (A), if yes draw its structure.

**Q.23** An aromatic compound (a) having molecular formula  $C_7H_7NO_2$  dissolves in  $NaHCO_3$  to evolve  $CO_2$  and when reacted with  $NaNO_2/HCl$  forms (b),  $C_7H_6O_3$ . (B) dissolves in  $NaHCO_3$  and gives colour reaction with  $FeCl_3$  and can be prepared by the action of  $CCl_4$  and NaOH on phenol. When (B) is reacted with excess  $HNO_3$ , it forms (C),  $C_6H_3N_3O_7$ . (C) undergoes acetylation and decomposes  $NaHCO_3$  to evolve  $CO_2$ . On reaction with  $PCl_5$  (C) is converted to (D),  $C_6H_5N_3O_6Cl$  which when reacted with water gives back (C). Identify compounds (A) to (D).

**Q.24** Compound (A) having M.F.  $C_8H_8O$  on treatment with  $NH_2OH.HCl$  gives (B) and (C). (B) and (C) rearrange to give (D) and (E), respectively on treatment with acid. Compounds (B), (C), (D) and (E) are all isomers of molecular formula  $C_8H_9NO$ . When (D) is boiled with alcoholic KOH, and oil (F)  $C_6H_7N$  separated out. (F) reacts rapidly with  $CH_3COCl$  to give back (D). On the other hand (E) on boiling with alkali followed by acidification gives a white solid (G),  $C_7H_6O_2$ . Identify the compounds (A) to (G).

**Q.25** An aromatic compound (A), having M.F.  $C_7H_5NO_2Cl_2$  on reduction with  $Sn/HCl$  gives (B), which on reaction with  $NaNO_2/HCl$  gives (C). Compound (B) is unable to form a dye with  $\beta$ -naphthol. However, (C) gives red colour with ceric ammonium nitrate and on oxidation gives an acid (D), having equivalent weight 191. Decarboxylation of (D) gives (e) which forms a single mononitro derivative (F), on nitration. Give the structures of (A) to (F) with proper reasoning.

**Q.26** An organic compound (A) of molecular weight 135, on boiling with NaOH evolves a gas which gives white dense fumes on bringing a rod dipped in HCl near it. The alkaline solution thus obtained on acidification gives the precipitate of a compound (B) having molecular weight 136. Treatment of (A) with  $HNO_2$  also yields (B), whereas its treatment with  $Br_2/KOH$  gives (C). Compound (C) reacts with cold  $HNO_2$  to gives (D), which give red colour with ceric ammonium nitrate. On the other hand, (E) an isomer of (A) on boiling with dilute HCl gives an acid (F), having molecular weight 136. On oxidation followed by heating, (F) gives an anhydride (G), which condenses with benzene in the presence of anhydrous  $AlCl_3$  to give anthraquinone. Give the structures of (A) to (G) with proper reasoning.

**Q.27** An organic compound (A) having M.F  $C_7H_9N$  on treatment with  $NaNO_2$  and  $HCl$  at room temperature forms another compound (B),  $C_7H_8O$ . When (A) or (B) is treated with bromine water, they form dibromo derivatives, When (A) is reacted with chloroform and alkali, it forms (C) having the molecular formula  $C_8H_7N$ . Hydrolysis of (C) followed by reaction with  $NaNO_2$  and  $HCl$  at low temperature and subsequent reaction with  $HCN$  in the presence of  $Cu$  (D), which is isomeric to (C). (D) on hydrolysis followed by oxidation gives a dibasic acid which on halogenation forms only one monohaloderivative. Identify the compounds (A) to (E).

**Q.28** An optically active compound (A),  $C_3H_7O_2N$  forms a hydrochloride but dissolves in water to give a neutral solution. On heating with soda lime (A) yields (B)  $C_2H_7N$ . Both (A) react with  $NaNO_2$  and  $HCl$  the former yielding a compound (C)  $C_3H_6O$ , which on heating is converted to (D),  $C_6H_8O_4$  while the latter yields (E),  $C_2H_6O$ . Account for the above reactions and suggest how (A) may be synthesized.

**Q.29** An optically inactive acid (A),  $C_5H_8O_5$ , on being heated lost  $CO_2$  to give an acid (B),  $C_4H_8O_3$  capable of being resolved. On action of sulphuric acid, B gave an acid C whose ethyl ester gave (D) on the action of hydrogen and platinum. (D) with conc.  $NH_3$  gave E,  $C_4H_9OH$  which with  $Br_2$  and  $KOH$  solution gave (F),  $C_3H_9N$ . F with  $HNO_2$  gave G (G) on mild oxidation gave H. Both A and H gave the iodoform reaction. Elucidate the reaction mechanism and suggest a synthesis of (C).

**Q.30** A neutral compound (A)  $C_8H_9OH$  on treatment with  $NaOBr$  forms an acid soluble substance  $C_7H_9N$ . On addition of aqueous  $NaNO_2$  to a solution of B in dilute  $HCl$  at  $0-5^\circ C$ , an ionic compound (C)  $C_7H_7N_2Cl$  is obtained. (C) yields a red dye with alkaline  $\beta$ -naphthol solution. When treated with potassium cuprocyanide (C) yields a neutral substance (D)  $C_8H_7N$ . ON hydrolysis (D) gives E ( $C_8H_6O_4$ ). (F) on nitration yields two isomeric mononitro derivatives (G and H) having molecular formula  $C_8H_5NO_6$ . Write the reactions involved in different steps.

## Exercise 2

### Single Correct Choice Type

**Q.1** Match the compounds in list I with the appropriate test that will be answered by each one of them in list II from the combinations shown.

Selects the correct answer using the codes given below the list.

List I	List II
(i) Propyne	(p) Reduces Fehling's solution
(ii) Ethyl benzoate	(q) Forms a precipitate with $AgNO_3 + C_2H_5OH$
(iii) Acetaldehyde	(r) Insoluble in water, but dissolves in aqueous $NaOH$ upon heating
(iv) Aniline	(s) Dissolves in dil. $HCl$ in the cold and is reprecipitated by the addition of alkali

(A) (i) - r, (ii) - q, (iii) - p, (iv) - s

(B) (i) - q, (ii) - r, (iii) - p, (iv) - s

(C) (i) - q, (ii) - r, (iii) - s, (iv) - p

(D) (i) - p, (ii) - r, (iii) - q, (iv) - s

**Q.2** Activation of benzene ring by  $-NH_2$  in aniline can be reduced by treating with

(A) Dilute  $HCl$  (B) Ethyl alcohol

(C) Acetic acid (D) Acetyl chloride

**Q.3** Dipolar ion structure for amino acid is

(A)  $H_2N-\underset{\substack{| \\ R}}{CH}-COOH$  (B)  $H_3N^+-\underset{\substack{| \\ R}}{CH}-COO^-$

(C)  $H_3^+N-\underset{\substack{| \\ R}}{CH}-COO^-$  (D) None of these

**Q.4**  $-NH_2$  group shows acidic nature while reacts with reagent.

(A)  $Na$  (B)  $CS_2$  (C)  $Br_2 + NaOH$  (D) Water

**Q.5** Which of the following does not give ethylamine on reduction

(A) Methyl cyanide (B) Ethyl nitrile

(C) Nitro ethane (D) Acetamide

**Q.6** Aniline is a weaker base than ethyl amine because

- (A) Phenyl gp in aniline is a +R gp  
 (B) Ethyl gp in ethyl amine decreases the electron density on nitrogen atom  
 (C) The lone pair of electron on nitrogen atom in aniline is delocalized over aniline.  
 (D) Aniline is less soluble in water than ethylamine

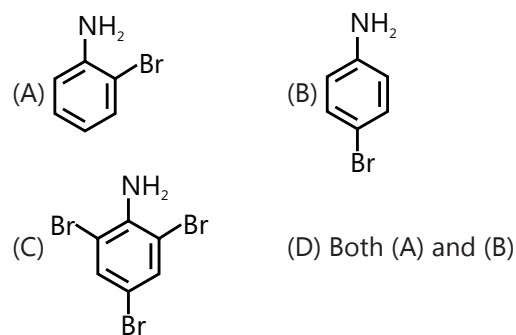
**Q.7** Diazonium coupling reaction with aniline should be carried out in

- (A) Weakly basic medium  
 (B) Weakly acidic medium  
 (C) Strongly basic medium  
 (D) Strongly acidic medium

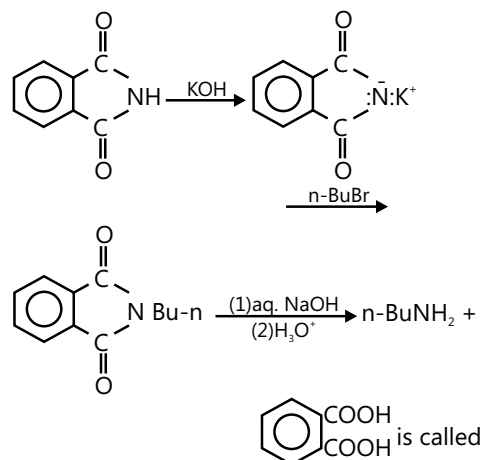
**Q.8** For  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{NO}_2$ ,  $\text{CH}_3\text{COOH}$

- (A) All have same chemical property  
 (B) All have one common chemical behaviour  
 (C) All are basic  
 (D) None of these

**Q.9** Bromine in  $\text{CS}_2$  reacts with aniline to give



**Q.10** The reaction:



- (A) Carbylamine reaction  
 (B) Hofmann reaction  
 (C) Gabriel phthalimide synthesis  
 (D) Cope reaction

**Q.11** The conjugate acid of  $\text{HO}(\text{CH}_2)_3\text{NH}_2$  is

- (A)  $\text{H}_2\text{O}^+(\text{CH}_2)_3\text{NH}_2$  (B)  $\text{HO}(\text{CH}_2)_3\text{NH}_3^+$   
 (C)  $\text{O}^-(\text{CH}_2)_3\text{NH}_2$  (D)  $\text{HO}(\text{CH}_2)_3\text{NH}^+$

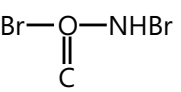
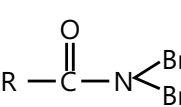
**Q.12** Consider the following compounds:

- $\text{H}_2\text{C}=\text{CHCH}_2\text{NH}_2$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
- $\text{HC}\equiv\text{CCH}_2\text{NH}_2$

The increasing order of basicity is

- (A)  $3 < 1 < 2$  (B)  $3 < 2 < 1$   
 (C)  $2 < 1 < 3$  (D) None of these

**Q.13** Reaction of  $\text{RCONH}_2$  with a mixture of  $\text{Br}_2$  and  $\text{KOH}$  gives  $\text{RNH}_2$  as the main product. The intermediate involved in the reaction is

- (A)  (B)  $\text{R-NHBr}$   
 (C)  (D)  $\text{R-C=N=O}$

**Q.14** Amines are highly soluble in:

- (A) Alcohol (B) Diethyl ether  
 (C) Benzene (D) Water

**Q.15** Which of the following reagents can convert benzene diazonium chloride into benzene?

- (A) Water  
 (B) Acid  
 (C) Hypophosphorous acid  
 (D)  $\text{HCl}$

**Q.16** The bromination of aniline produces

- (A) 2-bromoaniline (B) 4-bromoaniline  
 (C) 2,4,6-tribromoaniline (D) 2,6-dibromoaniline



**Q.17** The compound, which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosoamine is

- (A) Methylamine            (B) Ethylamine  
(C) Diethylamine        (D) Triethylamine

**Q.18** Carbylamine test is performed in alcoholic KOH by heating a mixture of

- (A) Chloroform and silver powder  
(B) Trihalogenated methane and a primary amine  
(C) An alkyl halide and a primary amine  
(D) An alkyl cyanide and a primary amine.

### Multiple Correct Choice Type

**Q.19** When nitrobenzene is treated with  $\text{Br}_2$  in presence of  $\text{FeBr}_3$ , the major product formed is m-bromonitrobenzene. Statements which are related to obtain m-isomer are:

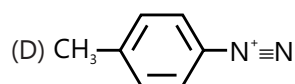
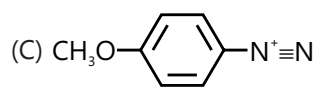
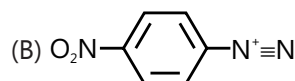
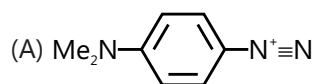
- (A) The electron-density on meta carbon is more than that on ortho and para positions  
(B) The intermediate carbonium ion formed after initial attack of  $\text{Br}^+$  at the meta position is least destabilized.  
(C) Loss of aromaticity, when  $\text{Br}^+$  attacks at the ortho and para positions, and not at meta position.  
(D) Easier loss of  $\text{H}^+$  to regain aromaticity from the meta position than from the ortho and para positions.

### Comprehension Type

Arene diazonium salts are more stable than alkanediazonium salts due to dispersal of the positive charge on the benzene ring. Obviously electron donating groups favour diazotisation by retarding the decomposition of diazonium salts to phenyl cation. The high reactivity of arenediazonium salts is due to the excellent leaving ability of the diazo group as  $\text{N}_2$  gas. Therefore, diazonium salts undergo a number of substitution reactions in which the diazo group is replaced by a monovalent atom/group such as H (by  $\text{H}_3\text{PO}_2$  in presence of  $\text{Cu}^+$  ions,  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{NaBH}_4$  etc), OH (by boiling in presence of mineral acids),  $\text{OCH}_3$  (by heating with  $\text{CH}_3\text{OH}$ ) Cl (by  $\text{CuCl}/\text{HCl}$  or  $\text{Cu}/\text{HCl}$ ), Br (by  $\text{CuBr}/\text{HBr}$  or  $\text{Cu}/\text{HBr}$ ) I (by KI in presence of  $\text{Cu}^+$  ions), F (by first converting into  $\text{N}_2\text{F}_4$  followed by heating), CN (by first neutralizing with  $\text{Na}_2\text{CO}_3$  and then reacting with  $\text{KCN}/\text{CuCN}$ ),  $\text{NO}_2$  (by first neutralizing with  $\text{Na}_2\text{CO}_3$  and then treating with  $\text{NaNO}_2$ ) phenyl or substituted phenyl (by treating with benzene or substituted benzene in presence of  $\text{NaOH}$ ) etc.

Diazonium salts also couple with phenols and aromatic amines to form coloured azo dyes. The reactivity of diazonium salts towards coupling reactions is favoured by presence of electron withdrawing groups; the reactivity of 2,4,6-trinitrobenzenediazonium chloride is so high that it even couples with reactive hydrocarbons such as mesitylene.

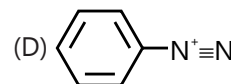
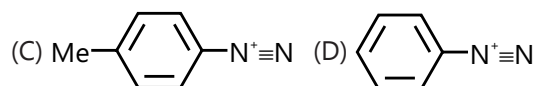
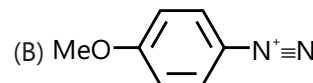
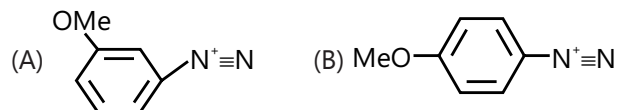
**Q.20** Consider the following ions:



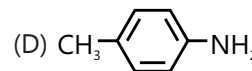
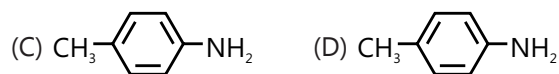
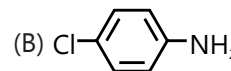
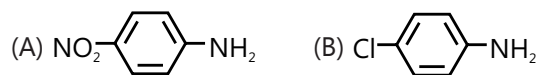
The reactivity of these ions towards azo coupling reactions under similar conditions is

- (A) I < IV < II < III                      (B) I < III < IV < II  
(C) III < I < II < IV                      (D) III < I < IV < II

**Q.21** Which of the following diazonium salts when boiled with dil.  $\text{H}_2\text{SO}_4$  gives the corresponding phenol most readily?



**Q.22** Which of the following arylamines undergoes diazotisation most readily?



**Q.23** The product formed when bromobenzene reacts with benzenediazonium chloride in presence of NaOH is

- (A) Diphenyl  
(B) p-Bromodiphenyl  
(C) p,p'-Dibromodiphenyl  
(D) p-Bromoazobenzene

### Assertion Reasoning Type

Each of the questions given below consists of two statements, an assertion (A) and reason (R). Select the number corresponding to the appropriate alternative as follows:

- (A) If both assertion and reason true and reason is the correct explanation of assertion, then mark (A)  
(B) If both assertion and reason are true but reason is not the correct explanation of assertion, then mark (B)  
(C) If assertion is true but reason is false, then mark (C)  
(D) If both assertion and reason false, then mark (D)

**Q.24 Assertion:** Benzyl amine is more basic than aniline.

**Reason:** Positive inductive effect of phenyl group creates high electron density around N atom.

**Q.25 Assertion:** White precipitate of silver chloride gets dissolved in  $\text{NH}_4\text{OH}$  solution.

**Reason:**  $\text{NH}_3$  reacts with  $\text{AgCl}$  to form a solution complex with formula  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ .

**Q.26 Assertion:** o-nitrophenol is more acidic than p-nitrophenol.

**Reason:** Nitro group has +M and -I effect.

**Q.27 Assertion:** 3° amine is proved to be less basic in aq. solution

**Reason:** Conjugate acid of 3° amine is poorly solvated in aq. solution.

**Q.28 Assertion:** In order to convert  $\text{R-Cl}$  to pure  $\text{R-NH}_2$ , Gabriel-phthalimide synthesis can be used.

**Reason:** With proper choice for alkyl halides, phthalimide synthesis can be used to prepare 1°, 2° and 3° amines.

**Q.29 Assertion:** 4-Nitrochlorobenzene undergoes nucleophilic substitution more readily than chlorobenzene.

**Reason:** Chlorobenzene undergoes nucleophilic substitution by elimination-addition mechanism while 4-nitrochlorobenzene undergoes nucleophilic substitution by addition-elimination mechanism.

**Q.30 Assertion:** 1° amides react with  $\text{Br}_2 + \text{NaOH}$  to give 1° amines with one carbon atom less than the parent amide.

**Reason:** The reaction occurs through intermediate formation of acyl nitrene.

**Q.31 Assertion:** Acetamide reacts with  $\text{Br}_2$  in presence of methanolic  $\text{CH}_3\text{ONa}$  to form methyl N-methylcarbonate.

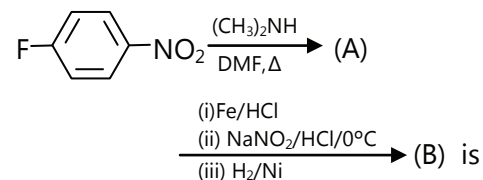
**Reason:** Methyl isocyanate is formed as an intermediate which reacts with methanol to form methyl N-methylcarbamate.

## Previous Years Questions

**Q.1** Benzene diazonium chloride on reaction with phenol in weakly basic medium gives **(1998)**

- (A) Diphenyl ether (B) p-hydroxy azobenzene  
(C) Chlorobenzene (D) Benzene

**Q.2** **(2007)**



- (A) (B) (C) (D)

**Q.3** Amongst the compounds given, the one that would form a brilliant coloured dye on treatment with  $\text{NaNO}_2$  in dil.  $\text{HCl}$  followed by addition to an alkaline solution of  $\beta$ -naphthol is **(2011)**

- (A) (B) (C) (D)

**Q.4 Match the Columns**

Match the compounds in column I with their characteristic test(s)/reaction(s) given in column II. (2010)

Column I	Column II
(A) $\text{H}_2\text{N}-\text{NH}_3^+\text{Cl}^-$	(p) Sodium fusion extract of the compound gives Prussian blue colour with $\text{FeSO}_4$
(B)	(q) Gives positive $\text{FeCl}_3$ test
(C)	(r) Gives white precipitate with $\text{AgNO}_3$
(D)	(s) Reacts with aldehydes to form the corresponding hydrazone derivative.

**Q.5** In an acidic medium, .....behaves as the strongest base. (nitrobenzene, aniline, phenol) (1981)

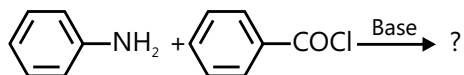
**Q.6** The high melting point and insolubility in organic solvents of sulphanilic acid are due to its ..... structure. (1994)

**Q.7** State the equation for the preparation of following compound. Chlorobenzene from aniline (in two steps) (1982)

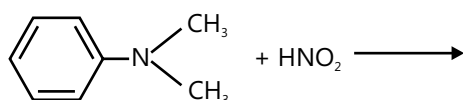
**Q.8** State the conditions under which the following preparation carried out.

"Aniline from benzene" (1983)

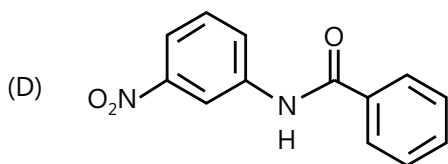
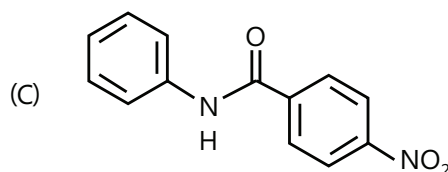
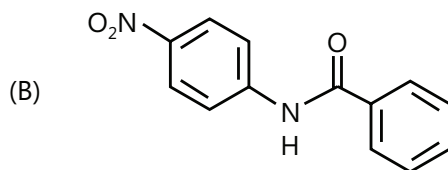
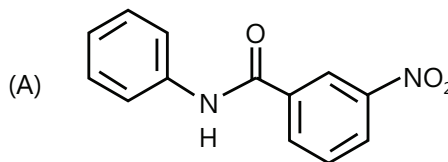
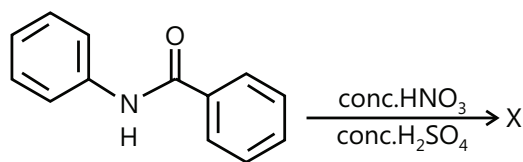
**Q.9** Complete the following with appropriate structures: (1986)



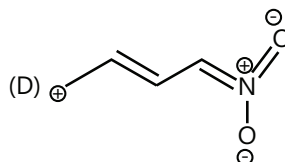
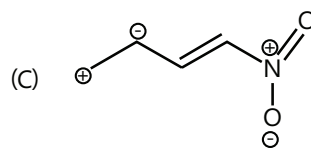
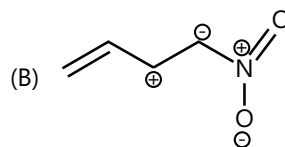
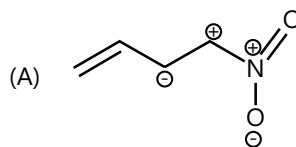
**Q.10** Write the structure of the major organic product expected from the following reaction. (1992)



**Q.11** In the following reaction the structure of the major product 'X' is: (2007)



**Q.12** Among the following, the least stable resonance structure is (2007)



**Q.13 Statement-I:** Aniline on reaction with  $\text{NaNO}_2/\text{HCl}$  at  $0^\circ\text{C}$  followed by coupling with  $\beta$ -naphthol gives a dark blue coloured precipitate.

**Statement-II:** The colour of the compound formed in the reaction of aniline with  $\text{NaNO}_2/\text{HCl}$  at  $0^\circ\text{C}$  followed by coupling with  $\beta$ -naphthol is due to the extended conjugation. **(2008)**

(A) Statement-I-I is True, statement-II is True; statement-II is correct explanation for statement-I

(B) Statement-I is True, statement-II is True; statement-II is NOT a correct explanation for statement-I

(C) Statement-I is True, statement-II is False

(D) Statement-I is False, statement-II is True

**Q.14** Match the compounds in column I with their characteristic test(s)/ reaction(s) given in column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix gives in the ORS **(2008)**

Column I	Column II
(A) $\text{H}_2\text{N}-\overset{\oplus}{\text{N}}\text{H}_3\text{Cl}^-$	(p) sodium fusion extract of the compound gives Prussian blue colour with $\text{FeSO}_4$
(B)	(q) gives positive $\text{FeCl}_3$ test
(C)	(r) gives white precipitate with $\text{AgNO}_3$
(D)	(s) reacts with aldehydes to form the corresponding hydrazone derivative

**Q.15** Match the four starting materials (P, Q, R, S) given in list I with the corresponding reaction schemes (I, II, III, IV) provided in list II and select the correct answer using the code given below the lists. **(2014)**

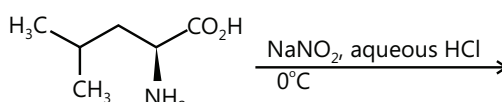
List I	List II
(i) $\text{H}\equiv\text{H}$	(p) Scheme I (i) $\text{KMnO}_4, \text{HO}^-$ , heat (ii) $\text{H}_2\text{O}$ ? $\xrightarrow{\text{(ii) SOCl}_2 \text{ (iv) NH}_3}$ $\text{C}_7\text{H}_6\text{N}_2\text{O}_3$
(ii)	(q) Scheme II (i) $\text{Sn/HCl}$ (ii) $\text{CH}_3\text{COCl}$ (iii) conc $\text{H}_2\text{SO}_4$ ? $\xrightarrow{\text{(ii) NHO}_3 \text{ (v) dil. H}_2\text{SO}_4, \text{ heat (vi) HO}^-}$ $\text{C}_6\text{H}_6\text{N}_2\text{O}_2$

(iii)	(r) Scheme III (i) red hot iron, 873 (ii) fuming $\text{HNO}_3, \text{H}_2\text{SO}_4$ , heat ? $\xrightarrow{\text{(ii) H}_2\text{S.NH}_3 \text{ (iv) NaNO}_2, \text{H}_2\text{SO}_4 \text{ (v) hydrolysis}}$ $\text{C}_6\text{H}_5\text{NO}_3$
(iv)	(s) Scheme IV (i) conc. $\text{H}_2\text{SO}_4, 60^\circ\text{C}$ ? $\xrightarrow{\text{(ii) conc. HNO}_3, \text{ conc. H}_2\text{SO}_4 \text{ (iii) dil. H}_2\text{SO}_4 \cdot \text{heat}}$ $\text{C}_6\text{H}_5\text{NO}_4$

Code:

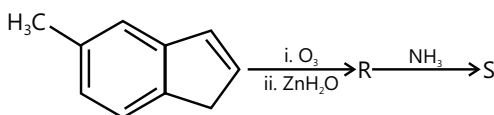
- (i) (ii) (iii) (iv)  
 (A) p s q r  
 (B) r p s q  
 (C) r s q p  
 (D) s p r q

**Q.16** The major product of the reaction is **(2015)**



- (A)   
 (B)   
 (C)   
 (D)

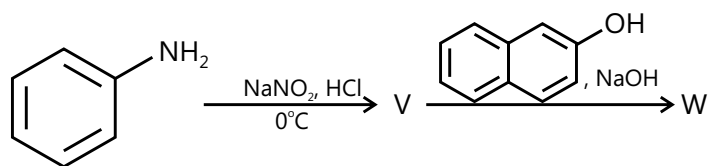
**Q.17** In the following reactions, the product S is **(2015)**



- (A)   
 (B)   
 (C)   
 (D)

**Q.18** In the following reactions, the major product W is

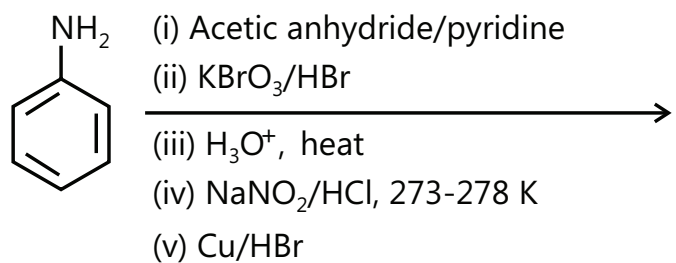
(2015)



- (A)
- (B)
- (C)
- (D)

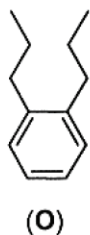
**Q.19** The product (s) of the following reaction sequence is (are)

(2016)



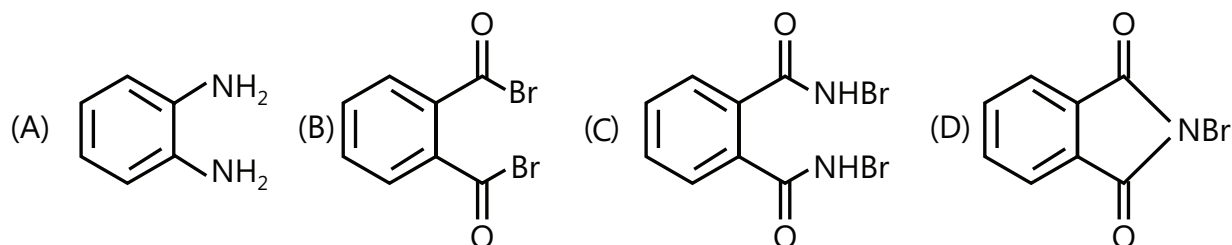
- (A)
- (B)
- (C)
- (D)

**Paragraph:** Treatment of compound O with  $\text{KMnO}_4/\text{H}^+$  gave P, which on heating with ammonia gave Q. The compound Q on treatment with  $\text{Br}_2/\text{NaOH}$  produced R. On strong heating, Q gave S, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound T



**Q.20** The compound R is

(2016)



**Q.21** The compound T is

(2016)

(A) Glycine

(B) Alanine

(C) Valine

(D) Serine

## MASTERJEE Essential Questions

### JEE Main/Boards

#### Exercise 1

Q.1 (iii)    Q.3    Q.12 (iii)

Q.17 (ii, vi)    Q.19 (iv)    Q.22 (ii)

Q.27

#### Exercise 2

Q.10    Q.14    Q.19

#### Previous Years' Questions

Q.1    Q.5    Q.10

### JEE Advanced/Boards

#### Exercise 1

Q.2    Q.6 (4)    Q.7 (4)

Q.14    Q.23    Q.29

#### Exercise 2

Q.8    Q.19    Q.20

Q.22    Q.28

#### Previous Years' Questions

Q.2    Q.4

## Answer Key

### JEE Main/Boards

#### Exercise 2

##### Single Correct Choice Type

Q.1 A	Q.2 C	Q.3 D	Q.4 B	Q.5 D	Q.6 C
Q.7 D	Q.8 A	Q.9 D	Q.10 B	Q.11 D	Q.12 A
Q.13 D	Q.14 B	Q.15 D	Q.16 B	Q.17 D	Q.18 D
Q.19 B	Q.20 A	Q.21 B	Q.22 A		

#### Previous Years' Questions

Q.1 C	Q.2 A	Q.3 C	Q.4 B	Q.5 C	Q.6 C
Q.7 A	Q.8 A	Q.9 A	Q.10 A	Q.11 A	Q.12 B
Q.13 B	Q.14 C	Q.15 B	Q.16 D	Q.17 A	Q.18 C

### JEE Advanced/Boards

#### Exercise 2

##### Single Correct Choice Type

Q.1 B	Q.2 D	Q.3 C	Q.4 C	Q.5 B	Q.6 C
Q.7 B	Q.8 B	Q.9 C	Q.10 C	Q.11 B	Q.12 A
Q.13 A	Q.14 D	Q.15 C	Q.16 C	Q.17 C	Q.18 B

##### Multiple Correct Choice Type

Q.19 A, B

##### Comprehension Type

Q.20 B	Q.21 A	Q.22 C	Q.23 B
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##### Assertion Reasoning Type

Q.24 C	Q.25 A	Q.26 D	Q.27 A	Q.28 C	Q.29 B
Q.30 A	Q.31 A				

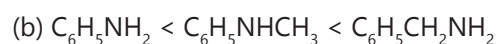
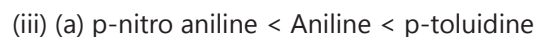
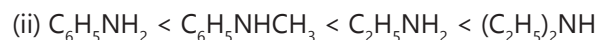
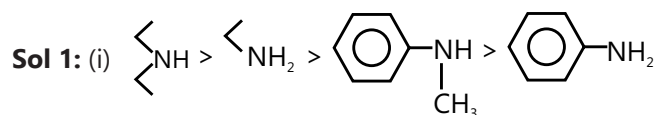
#### Previous Years Questions

Q.1 B	Q.2 A	Q.3 C	Q.4 A $\rightarrow$ p; B $\rightarrow$ q; C $\rightarrow$ r; D $\rightarrow$ s	Q.11 B	
Q.12 A	Q.13 D	Q.14 A $\rightarrow$ r, s; B $\rightarrow$ p, q; C $\rightarrow$ p, q, r; D $\rightarrow$ p, s		Q.15 C	
Q.16 C	Q.17 A	Q.18 A	Q.19 B	Q.20 A	Q.21 B

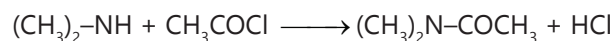
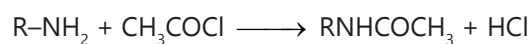
## Solutions

### JEE Mains/Boards

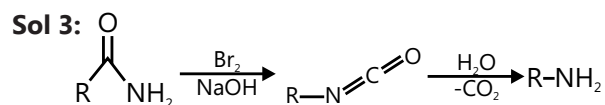
#### Exercise 1



**Sol 2:** 1° and 2° amines react with acetyl chloride to form acetyl derivatives.



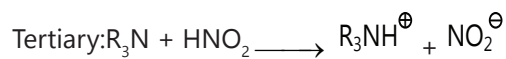
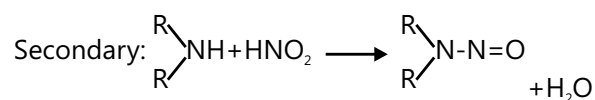
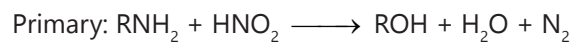
Tertiary amine do not undergo this reaction.



Reaction of a primary amide to form primary amine with one fewer carbon atom.

**Sol 4:** +ve charge or secondary carbon is not stable

**Sol 5:** Aliphatic amines

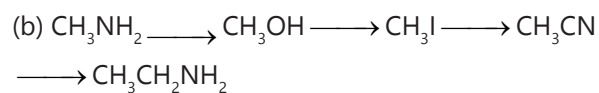


Aromatic Amines forms diazonium ions.

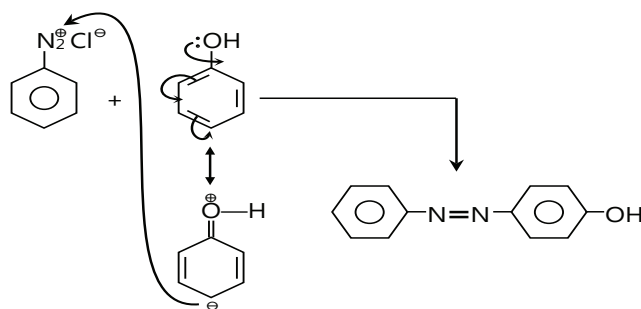
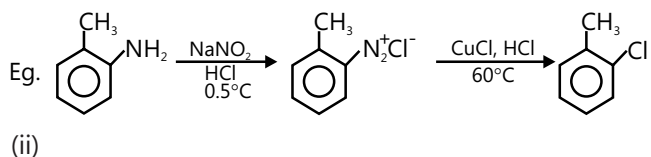
**Sol 6:** (i) Refer Sol.3

(ii) Refer Gabriel Pthalimide synthesis

**Sol 7:** (a) Lone pair delocalised in aryl amines.

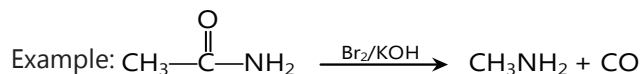


**Sol 8:** (i) Sandmeyer Reaction is used to synthesize aryl-halides from aryl amines.

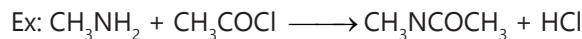


**Sol 9:** (i) Refer to Sol.8 (ii)

(ii) The reaction involves the conversion of an amide into one carbon loss, by action of hypoactive NaOH solution + Br<sub>2</sub>.

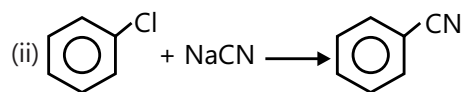


(iii) Acetylation - 1° or 2° amines react will acetyl chloride acetic anhydride to form acetyl derivatives.



**Sol 10:** (i) Aniline is a weaker base than methyl compound

In case of aniline, the lone pair is delocalised on the ring and hence it is less basic.



Cl<sup>-</sup> is a stronger base than CN<sup>-</sup> hence the reaction can take place, + there is not sufficient + ve on the for nucleophilic substitute to take place.

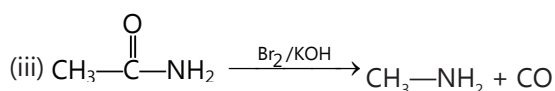
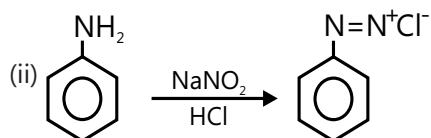
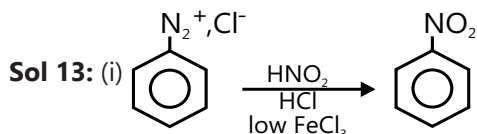
**Sol 11:** Refer to sol. 2

**Sol 12:** (i) Aniline is a weaker base as compared to methyl amine as lone pair of NH<sub>2</sub> is delocalised on the ring. Hence pK<sub>b</sub> aniline > pK<sub>b</sub> methyl amine.

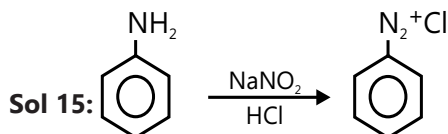


(ii)  $\text{MeNH}_2$  is a good base in water, it reacts with  $\text{FeCl}_3$  to form  $\text{Fe}(\text{OH})_3 + \text{MeNH}_4^+\text{Cl}^-$

(iii) Due to  $\text{NH}_2$  group on aniline, there is extra  $e^-$  density on benzene ring. Hence, nucleophilic substitution does not take place.



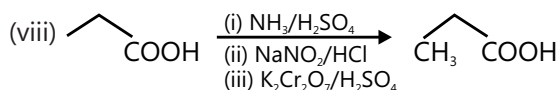
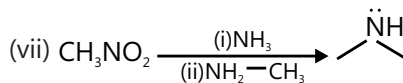
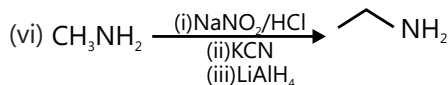
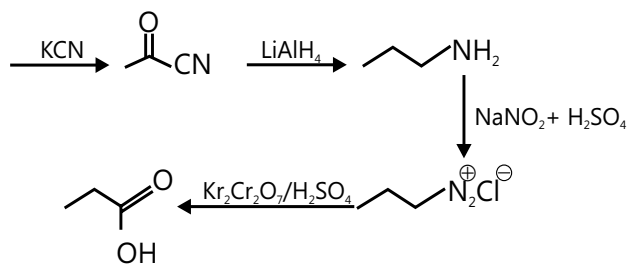
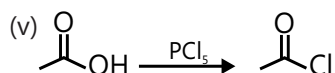
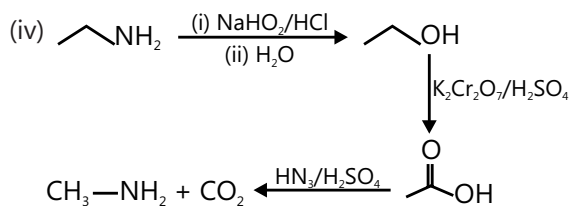
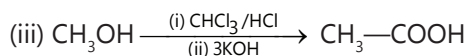
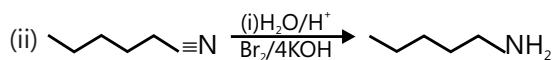
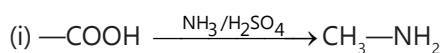
**Sol 14:** Factual



**Sol 16:** (i) In aromatic amines, the  $\oplus$  charge is delocalised on the less electron -ve ring C- due to good resonance.

(ii) Due to the smaller size of  $1^\circ$  amine it is easier to attack and hence, phthalimide synthesis is preferred for any amine.

**Sol 17:**



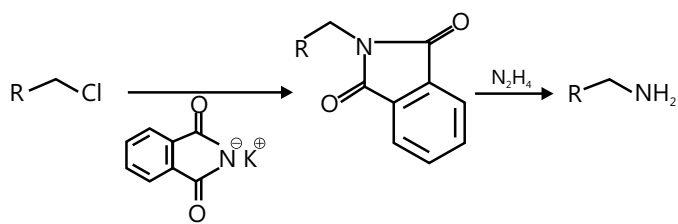
**Sol 18:** (i) Any reactions which involve two or more equivalent of reactions for proceeding reaction are known as coupling reaction

Exp. Wurtz, Pinacol-pinacolone etc.

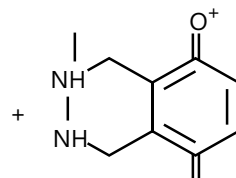
(ii) Addition of ammonia  $\longrightarrow$  Ammonolysis

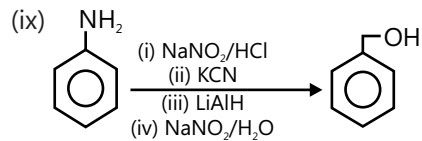
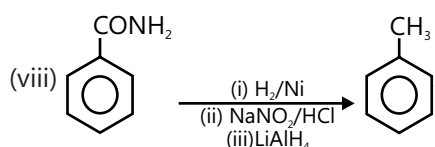
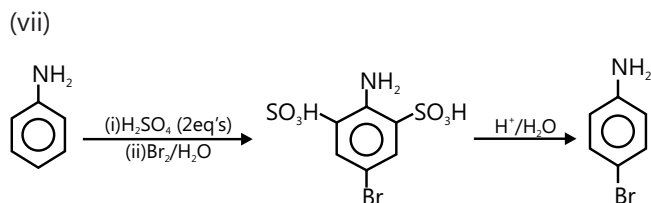
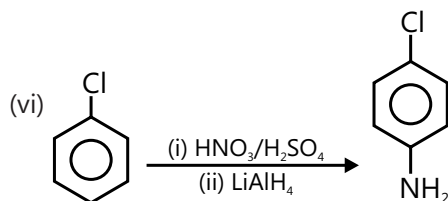
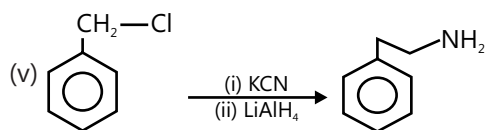
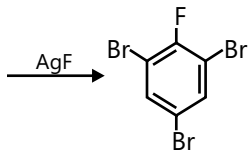
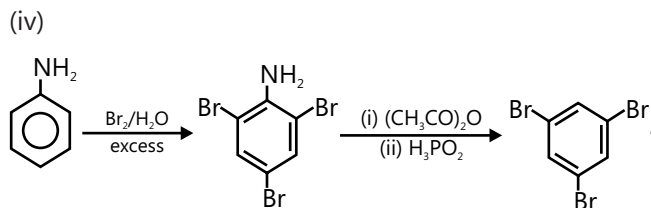
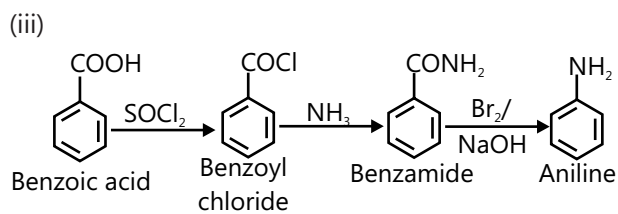
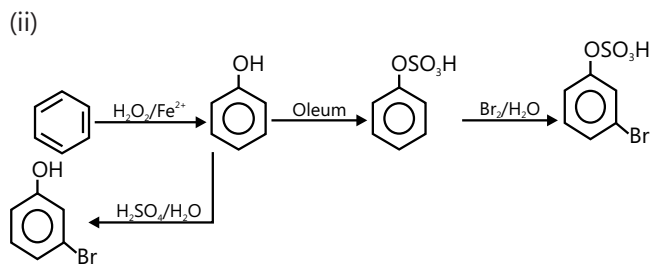
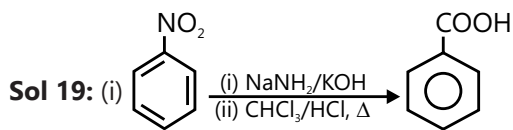
(iii) Addition of acetyl group  $\left(\text{CH}_3\text{C}(=\text{O})\right)$  acetylation

(iv) Gabriel Synthesis:



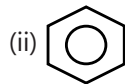
Test for  $1^\circ$  amines





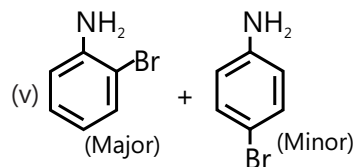
**Sol 20:** Refer Text for Curtius mechanism.

**Sol 21:** (i)  $\text{ph}-\text{N} \equiv \text{C}$



(iii) Acid-base reaction  $\text{ph}-\text{NH}_3^+ + \text{H}_2\text{SO}_4^-$

(iv)  $\text{phOEt}$



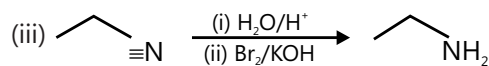
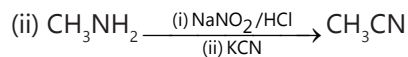
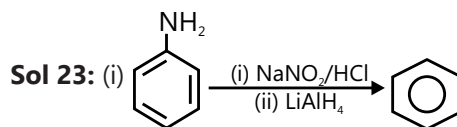
(vi) Acetophenone

(vii) Nitrobenzene

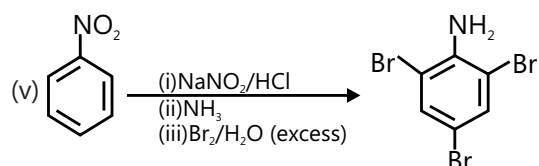
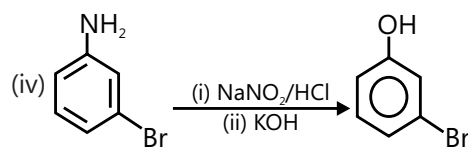
**Sol 22:** (i) Electronegativity of 'O' > 'N'

(ii) More surface area  $\Rightarrow$  more interaction b/w molecular  $\Rightarrow$  higher B.P.

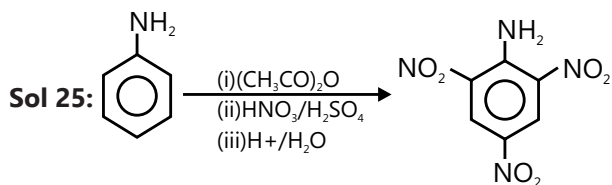
(iii) In aromatic amines, they have lone pair of N in conjugation with ring  $\Rightarrow$  less basic



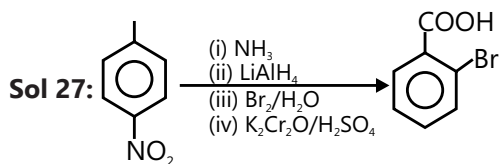
Schmidt reaction

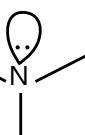


**Sol 24:** Intramolecular acid-base reactions of molecule (like some amine + carboxylic acid in same molecule)



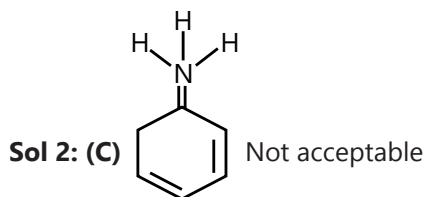
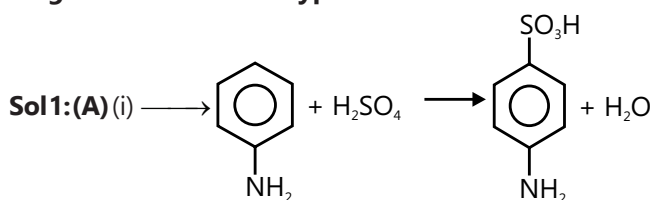
**Sol 26:** because carbocation intermediate in Friedel craft alkylation reach with l.p. of N in aniline



**Sol 28:**  due to flipping it is considered as planar molecule.

## Exercise 2

### Single Correct Choice Type



Nitrogen can't form 5 bonds

**Sol 3: (D)** Order of basic strength  
 $4 > 3 > 2 > 1$  Basic strength  $\propto$  +I effect

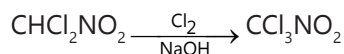
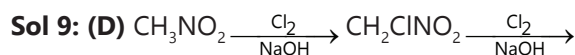
**Sol 4: (B)**  $1 > 2 > 3$

**Sol 5: (D)** Primary amines gives carbylamine test.

**Sol 6: (C)** End product has a hydrophobic and a hydrophilic part.

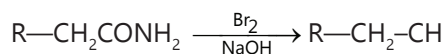
**Sol 7: (D)**  $s > t > p > \text{NH}_3$

**Sol 8: (A)**

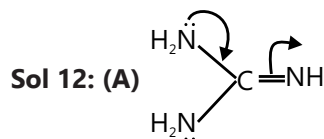
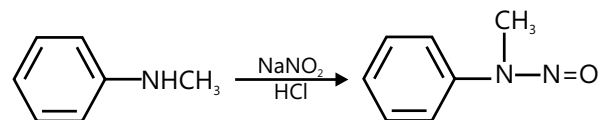


$\text{CH}_3\text{NH}_2$  is not formed

**Sol 10: (B)**  $\text{Br}_2/\text{NaOH}$



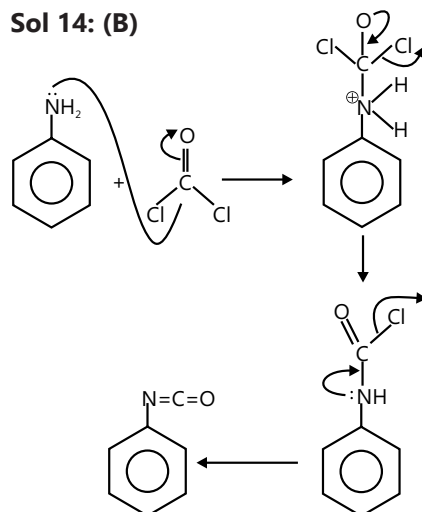
**Sol 11: (D)**



**Sol 13: (D)** All of these

$\text{K}_2\text{Cr}_2\text{O}_7$  is a strong oxidising agent.

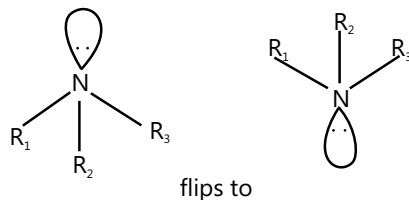
**Sol 14: (B)**



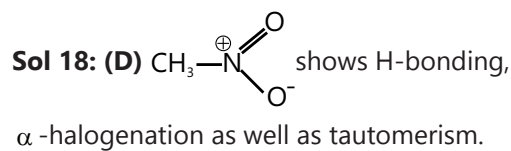


**Sol 16: (B)** Baker-Mulliken's Test is a test for nitrocompounds.

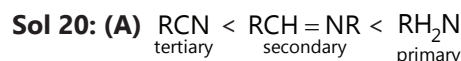
**Sol 17: (D)**



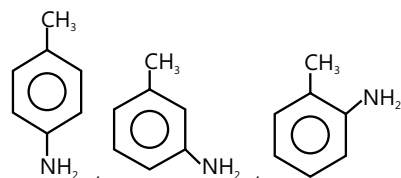
Due to flipping, tertiary amine is a racemic mixture.



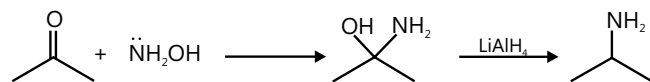
**Sol 19: (B)** Nitrobenzene on reduction with Sn/HCl gives aniline. With Zn it gives phenyl hydroxylamine. With methanolic NaOMe nitrobenzene gives Azoxybenzene. On reaction with Zn and strong base it gives Hydrazobenzene.



**Sol 21: (B)**

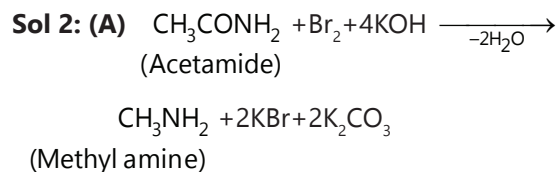


**Sol 22: (A)**

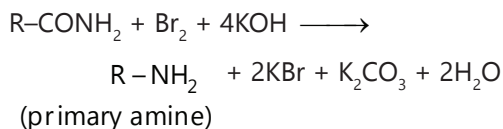


## Previous Years' Questions

**Sol 1: (C)** Self-explanatory

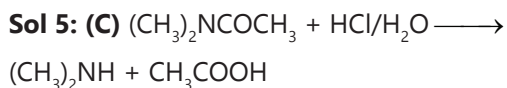


**Sol 3: (C)** Hofmann degradation of amide



**Sol 4: (B)**  $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N}$

$$K_b = 5.4 \times 10^{-4}, 4.5 \times 10^{-4}, 0.6 \times 10^{-4}$$



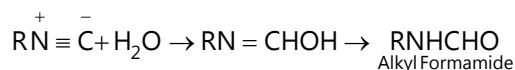
**Sol 6: (C)** Secondary > tertiary > primary

**Sol 7: (A)** Because  $\text{OH}^-$  is nucleophile.

**Sol 8: (A)** It is true that benzene diazonium chloride does not respond Lassaigne test of nitrogen because benzene diazonium chloride loses  $\text{N}_2$  on slight heat and thus it can't react with sodium metal.

**Sol 9: (A)** Amines are basic due to the presence of a lone pair of electrons on nitrogen atom. The lone pair can be easily donated.

**Sol 10: (A)** In an isocyanide, first an electrophile and then a nucleophile add at the carbon to form a species which usually undergoes further transformations.

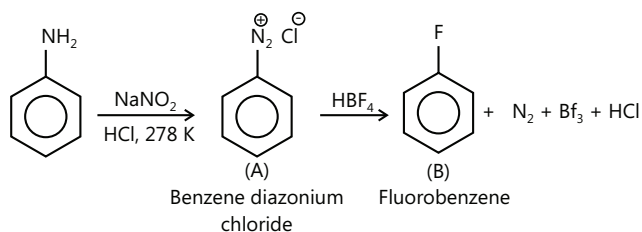


**Sol 11: (A)** self-explanatory

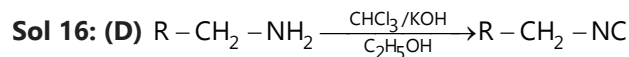
**Sol 12: (B)** Due to strong deactivation of benzene ring by  $-\text{NO}_2$  group, nitrobenzene is often used as a solvent in Friedel-Craft's reaction.

**Sol 13: (B)**  $-\text{NO}_2$  is electron withdrawing which will destabilize  $\sigma$ -complex.

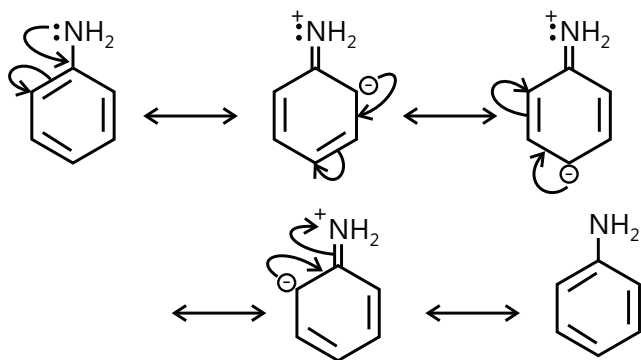
**Sol 14: (C)**



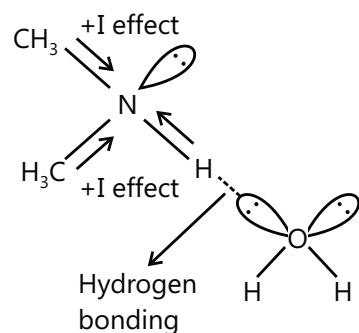
**Sol 15: (B)** Molisch's Test: when a drop or two of alcoholic solution of  $\alpha$ -naphthol is added to sugar solution and then conc.  $H_2SO_4$  is added along the sides of test tube, formation of violet ring takes place at the junction of two liquids.



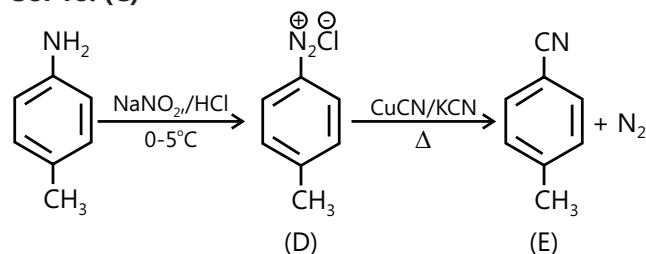
**Sol 17: (A)** Among  $C_6H_5NH_2$ ,  $CH_3NH_2$ ,  $(CH_3)_2NH$ ,  $(CH_3)_3N$ .  $C_6H_5NH_2$  is least basic due to resonance.



Out of  $(CH_3)_3N$ ,  $CH_3NH_2$ ,  $(CH_3)_2NH$ .  $(CH_3)_2NH$  is most basic due to +I effect and hydrogen bonding with  $H_2O$ .



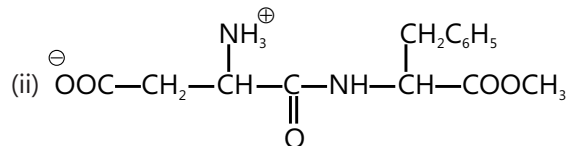
**Sol 18: (C)**



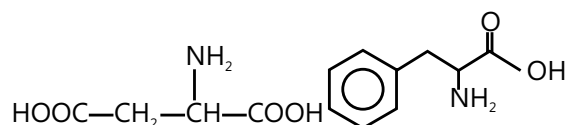
## JEE Advanced /Boards

### Exercise 1

**Sol 1:** (i) Carboxylic acid, amine, ester

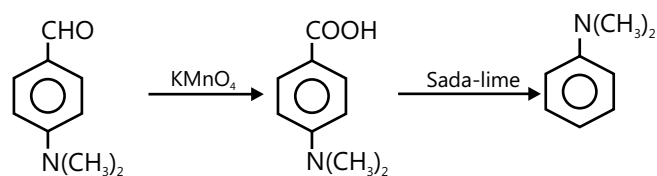


(iii) Aspartic acid and phenylalanine

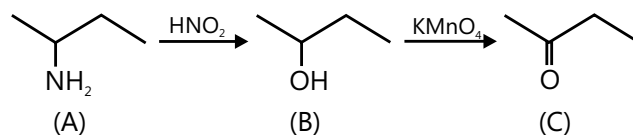


(iv) Phenylalanine is more hydrophobic because of the benzyl side chain.

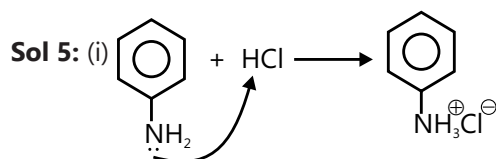
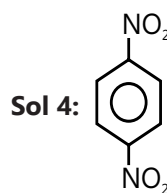
**Sol 2:**



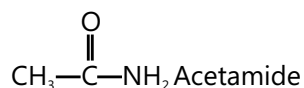
**Sol 3:**



Other isomers are primary amines.

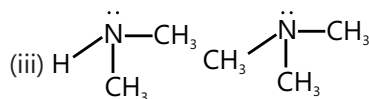


(ii)  $CH_3-CH_2-\ddot{N}H_2$  Ethylamine



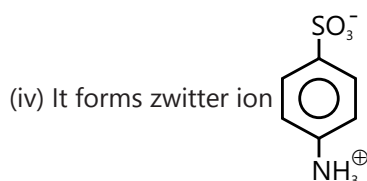
Ethylamine is basic due to the presence of localised lone pair.

Acetamide is acidic due to the presence of acidic hydrogen.



Dimethylamine Trimethylamine

More steric hinderance in Trimethylamine



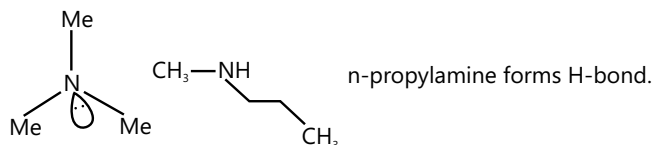
**Sol 6:** (i) Amine group in glycine is more basic.

(ii) More equivalent resonance structures

(iii) It stabilises the complex.

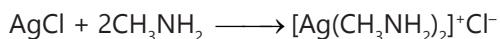
(iv) Because of side products

**Sol 7:** (i)



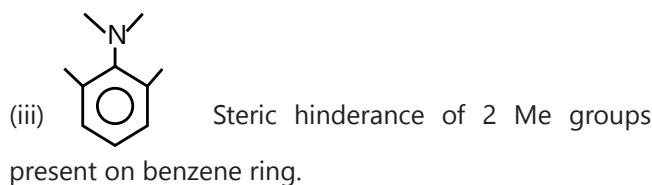
(ii) Steric hinderance in trimethylamine

(iii) Due of formation of a soluble complex salt



**Sol 8:** (i) Ethylamine in aqueous solution reacts with ferric chloride to precipitate hydrated ferric acid.

(ii) No N—H bond in tertiary amine.



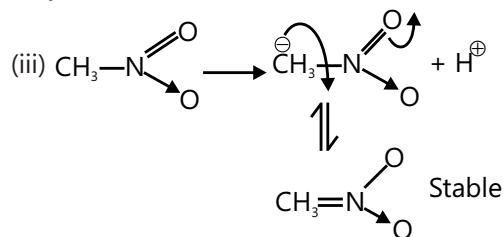
(iv) In (I) lone pair is localized, Inductive effect of 'O' in (III)

In IV the lone pair is delocalised

I > II > III > IV

**Sol 9:** (i) Steric hinderance

(ii) Isocyanides are stable in strong basic conditions, but they are sensitive of acids.



(iv) Aniline forms a salt with  $\text{AlCl}_3$ . Due to this nitrogen atom of aniline acquires a positive charge and hence acts as a strong deactivating group and doesn't allow the reaction to take place.

(v) The basicity of nitrogen in trimethylamine is greater.

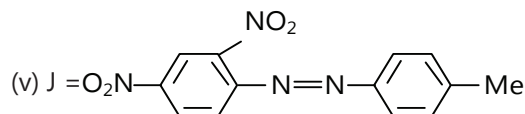
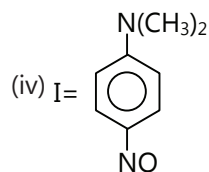
**Sol 10:**

(i) C =  $\text{C}_6\text{H}_5\text{COCl}$  D =  $\text{C}_6\text{H}_5\text{CONH}_2$

E =  $\text{C}_6\text{H}_5\text{CHNH}_2$

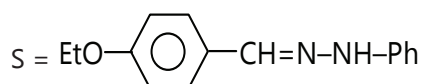
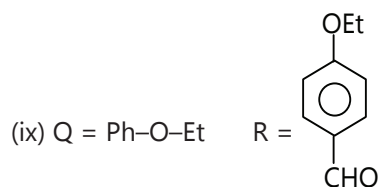
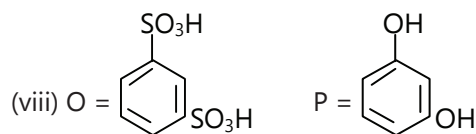
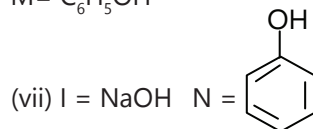
(ii) F =  $\text{C}_6\text{H}_5\text{CN}$ ; G =  $\text{C}_6\text{H}_5\text{COOH}$

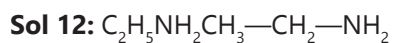
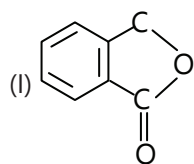
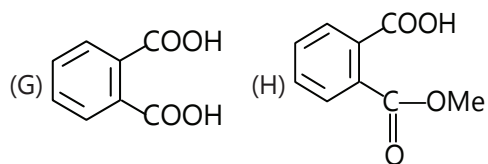
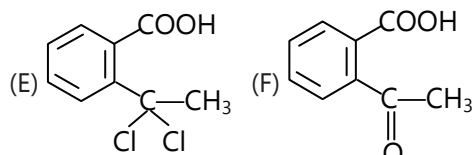
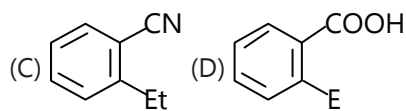
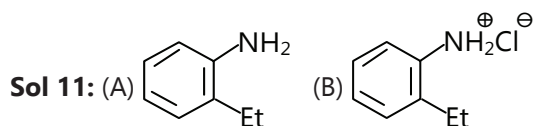
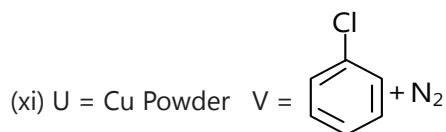
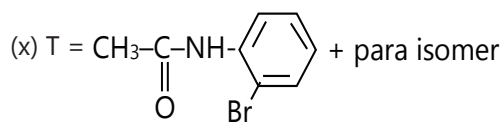
(iii) H =  $\text{EtNHBr}$



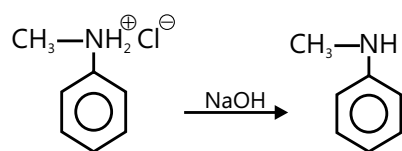
(vi) K =  $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ ; L =  $\text{C}_6\text{H}_5\text{SO}_3\text{Na}$

M =  $\text{C}_6\text{H}_5\text{OH}$

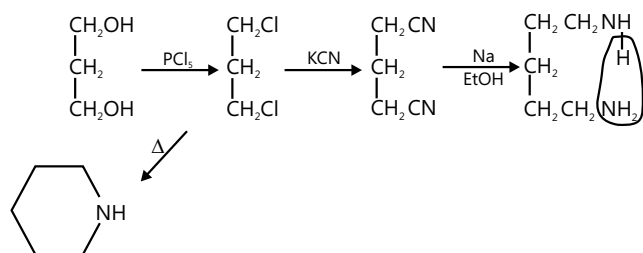




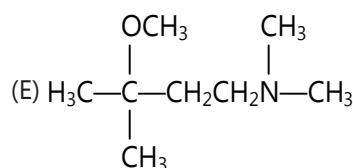
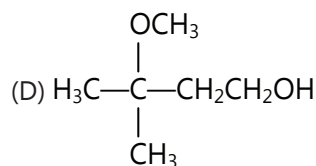
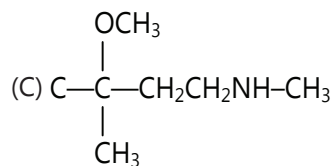
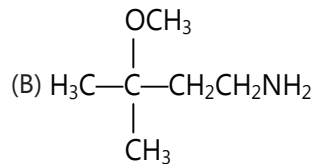
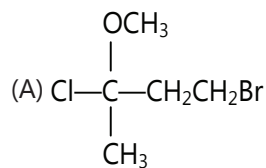
**Sol 13:**



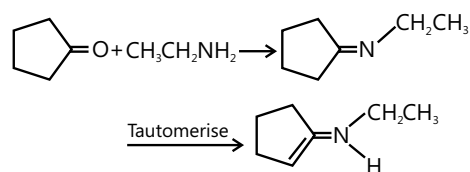
**Sol 14:**



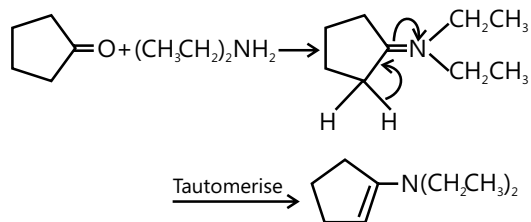
**Sol 15:**



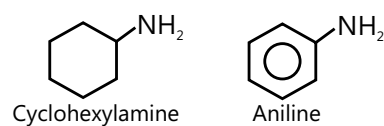
**Sol 16 (i)**



(ii)



**Sol 17:**



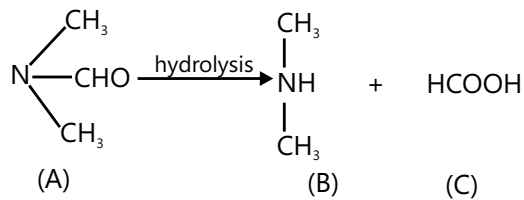
Lone pair of nitrogen in aniline is delocalized due to resonance.

**Sol 18:** Use excess of ammonia to reduce the chances of reaction of 1° amine with alkyl halide to form 2° and 3° amines.

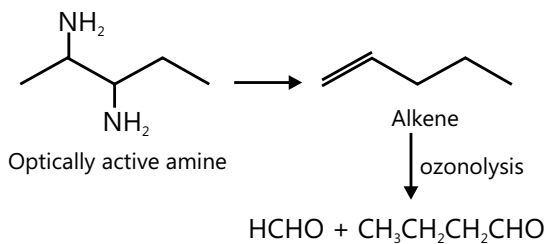
**Sol 19:** Amino group being activating group activates bromination of aniline and forms tribromoaniline.

**Sol 20:** Although inductive effect of alkyl groups is greater in trimethylamine but the alkyl groups crowd the nitrogen atom and reduces its basicity.

**Sol 21:**

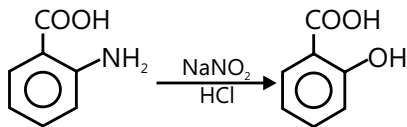


**Sol 22:**

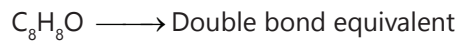
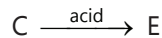
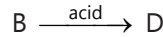
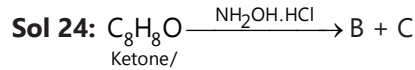
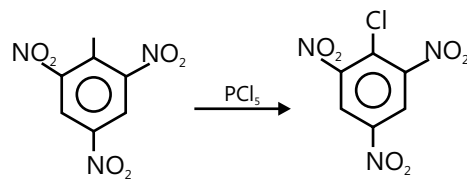
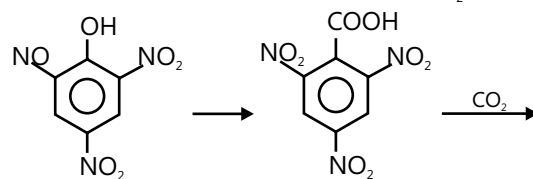
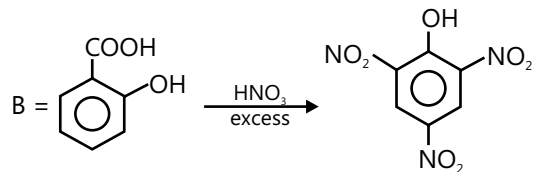
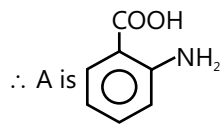


No, there is no structural isomer possible.

**Sol 23:**



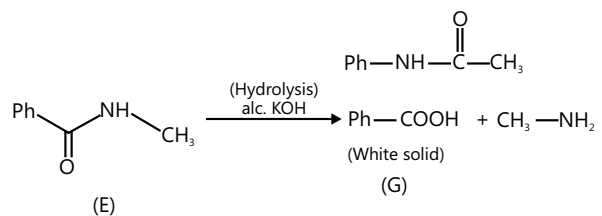
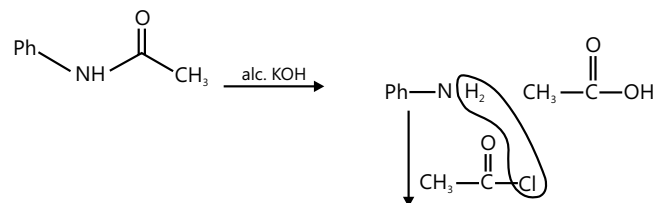
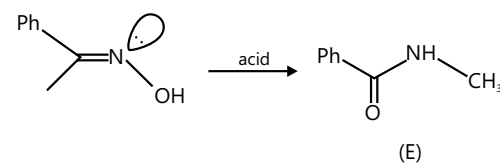
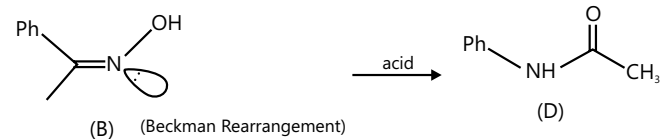
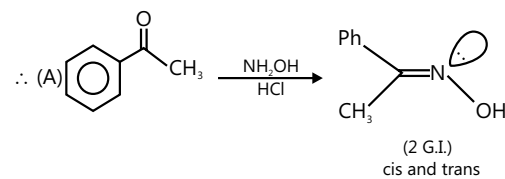
The compound gives +ve test for NH<sub>2</sub> and COOH



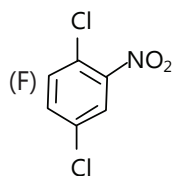
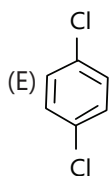
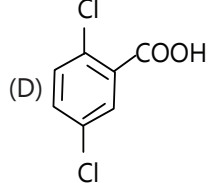
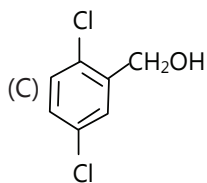
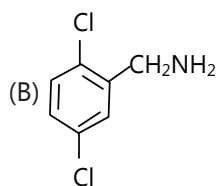
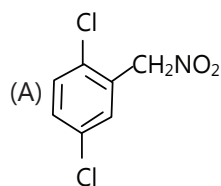
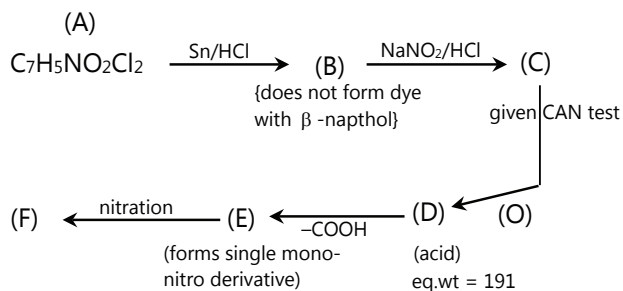
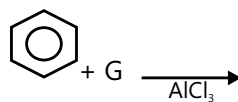
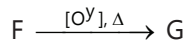
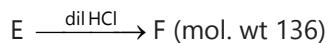
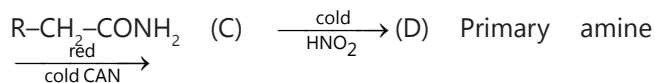
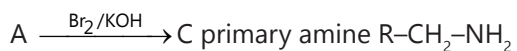
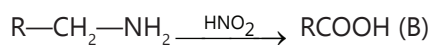
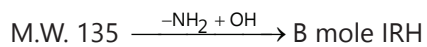
$\text{DBE} = \frac{1}{2}((16+2)-8) = 5 \longrightarrow \text{benzene ring and a } \pi \text{ bond outside.}$

∴ NH<sub>2</sub>OH/HCl  $\longrightarrow$  2 product (G.I.)

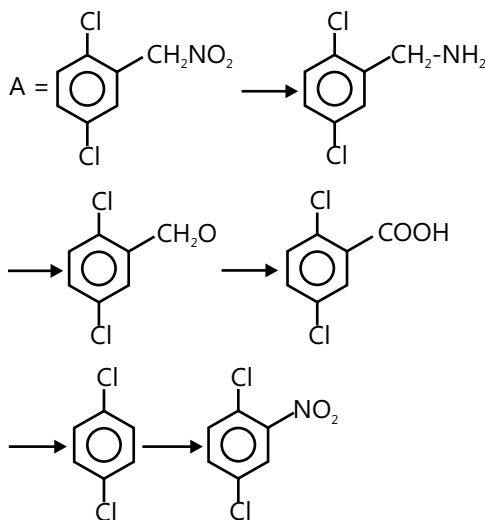
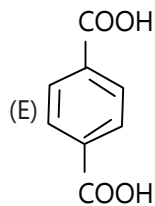
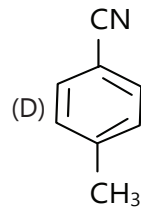
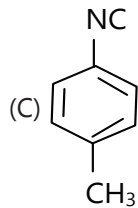
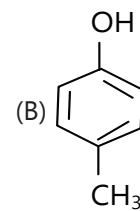
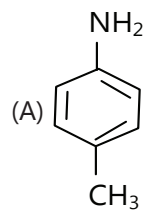
∴ It is a ketone.





**Sol 25:****Sol 26:**  $\therefore NH_4^+$ as gas is  $NH_3$ B =  $C_7H_5NH_2Cl_2$  does not give compound B-does not form a dye with  $\beta$ -naphthol $\therefore A$  is (C) is a primary alcohol.

as de-carboxylation gives single derivatives

 $\therefore Cl$  should be symmetrically oppositely placed.**Sol 27:**

**Sol 28:** Degree of unsaturation of A = 2 since A forms hydrochloride, it contains both a basic and acidic functional group. It's most likely to be an amino acid. On decarboxylation, it forms an amine B, Degree of unsaturation of B = 0

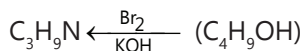
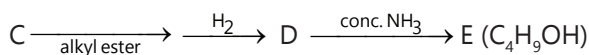
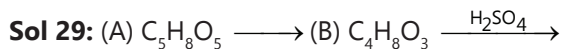
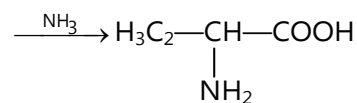
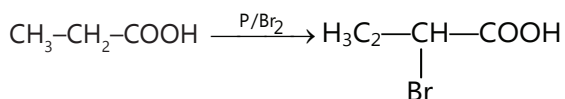
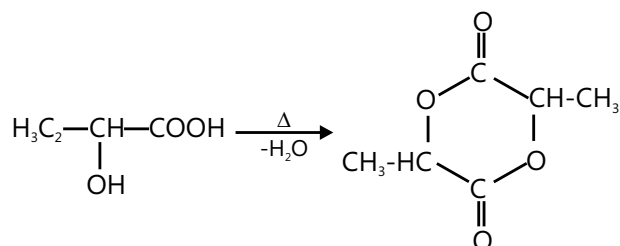
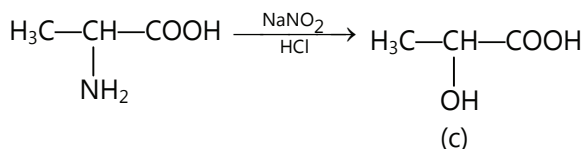
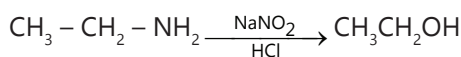
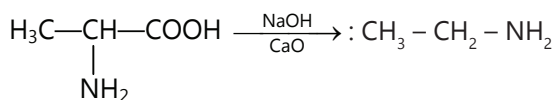
∴ B is saturated amine.

∴ B  $\xrightarrow[\text{HCl}]{\text{NaNO}_2}$  give  $\text{C}_2\text{H}_5\text{OH}$  (E)

∴ B is  $\text{CH}_3\text{CH}_2\text{NH}_2$

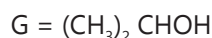
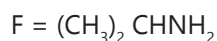
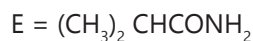
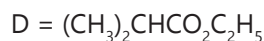
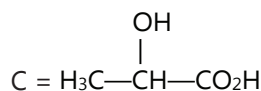
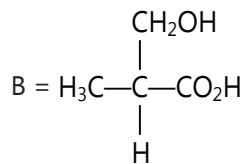
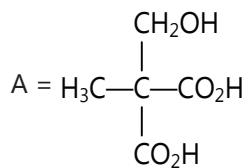
$\xrightarrow[\text{HCl}]{\text{NaNO}_2}$  C (a hydroxyl acid) Which yields cyclic diester on heating

∴ Reactions

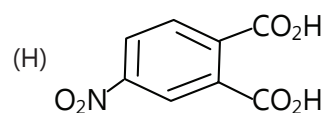
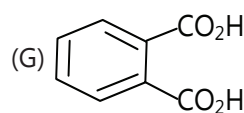
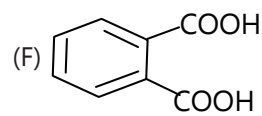
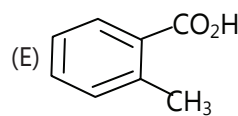
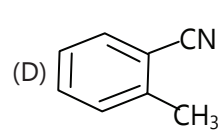
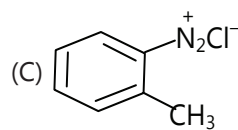
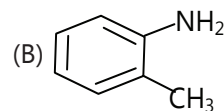
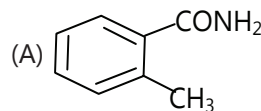


degree of unsaturation =  $2 \times 5 + 2 - 8$

$$= 4 - 2 = 2$$



**Sol 30:**



## Exercise 2

### Single Correct Choice Type

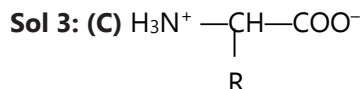
**Sol 1: (B)** Propyne - Forms a precipitate with  $\text{AgNO}_3$  in ethanol.

Ethyl Benzoate - Insoluble in water, but dissolves in aqueous  $\text{NaOH}$  upon heating

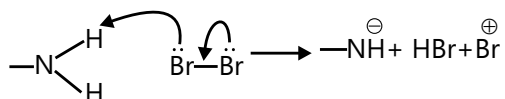
Acetaldehyde- Reduces Fehling's solution

Aniline- Dissolves in dilute HCl in the cold and is reprecipitated by the addition of alkali.

**Sol 2: (D)** Acetic acid



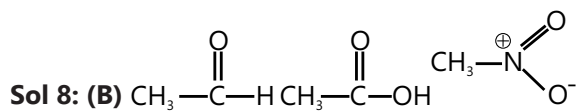
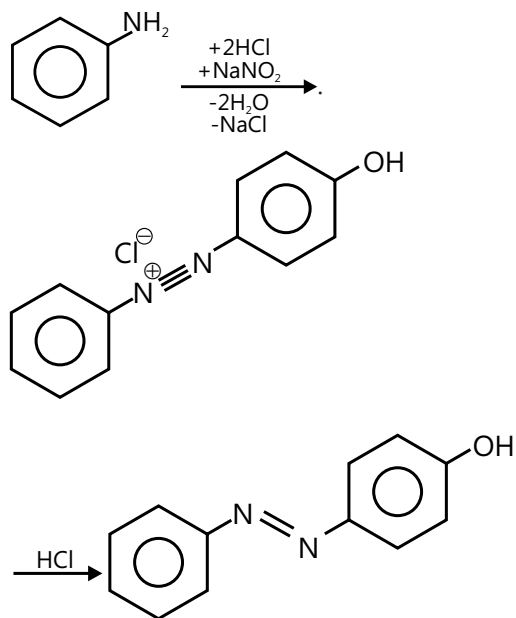
**Sol 4: (C)**



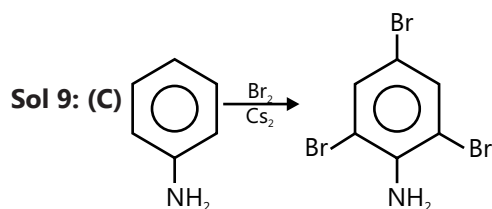
**Sol 5: (B)** Ethynitrile ( $\text{CH}_3\text{CN}$ )

**Sol 6: (C)** The lone pair of electron on nitrogen atom in aniline is delocalized over aniline.

**Sol 7: (B)**  $\text{R}-\ddot{\text{N}}\text{H}_2$  behave as a base in weakly acidic medium

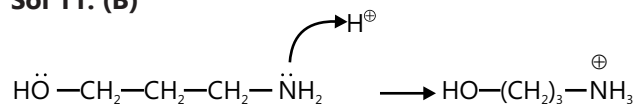


All three shows acidic behaviour.



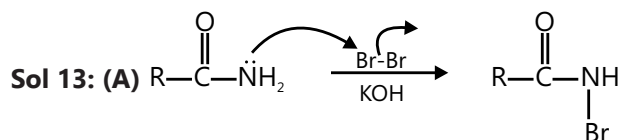
**Sol 10: (C)** Gabriel-phthalimide synthesis.

**Sol 11: (B)**



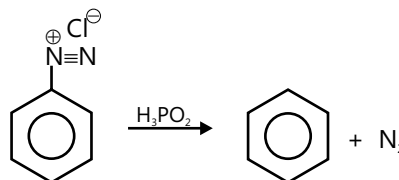
**Sol 12: (A)**  $2 > 1 > 3$

Consider inductive effect of primary, secondary and tertiary law.

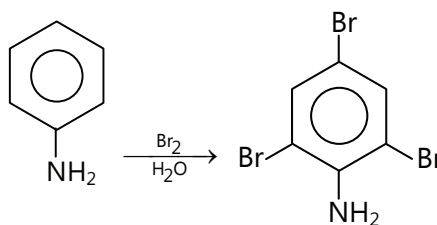


**Sol 14: (D)** Self-explanatory

**Sol 15: (C)**



**Sol 16: (C)**



**Sol 17: (C)** Secondary amine

**Sol 18: (B)** Trihalogenated amine and a primary amine

**Multiple Correct Choice Type**

**Sol 19: (A, B)** The electron density on meta carbon is more than that on ortho and para positions. The intermediate carbonium ion formed after initial attack of  $\text{Br}^+$  at the meta position is least destabilized due to no mesomeric effect.

**Comprehension Type**

**Sol 20: (B)**  $\text{NO}_2 \longrightarrow -M$  effect

$\text{CH}_3 \longrightarrow +Z$  effect

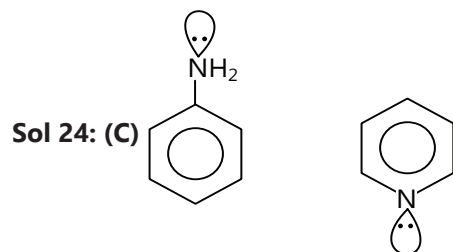
$\text{OCH}_3 \longrightarrow \text{mid } +M$  effect

$\text{NMe}_2 \longrightarrow \text{high } +M$  effect

**Sol 21: (A)**  $-I$  effect of  $-\text{OMe}$

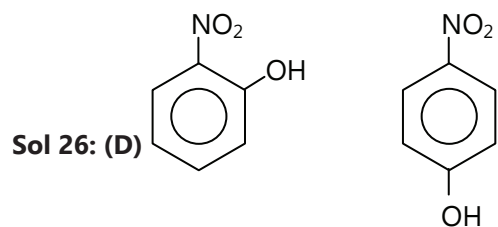
**Sol 22: (C)**  $+M$  effect of  $-\text{OMe}$  at para position

**Sol 23: (B)** The product formed when bromobenzene reacts with benzenediazonium chloride in presence of  $\text{NaOH}$  is p-Bromodiphenyl

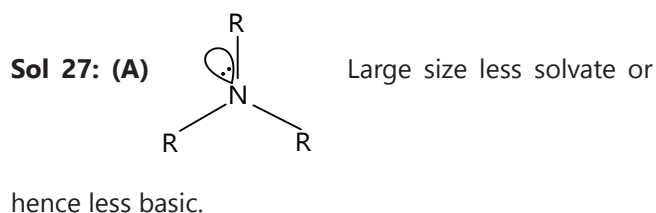
**Assertion Reasoning Type**

**Sol 25: (A)** False lone pair is delocalised of  $\text{Ph-NH}_2$  whereas its localised for aniline .

Self Explanatory

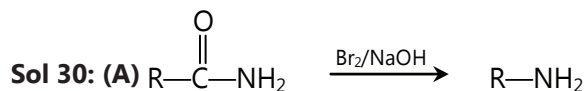


$\text{NO}_2$  has  $-M$  and  $-I$  effect. p-Nitro-phenol more acidic than ortho nitro phenol as o-nitro phenol intermolecular H-bonding where p-nitro phenol has inter molecular H-bond.



**Sol 28: (C)**  $3^\circ$  amine cannot be synthesised using Gabriel phthalimide

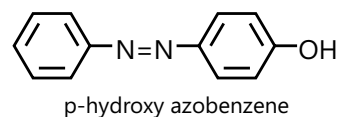
**Sol 29: (B)** Both statements are true but 4-nitrochlorobenzene goes nucleophilic substitutions more readily than benzene due to the  $M$ -effect of nitro group  $2^+$  +ve charge is created on C attaches to Cl Molecule



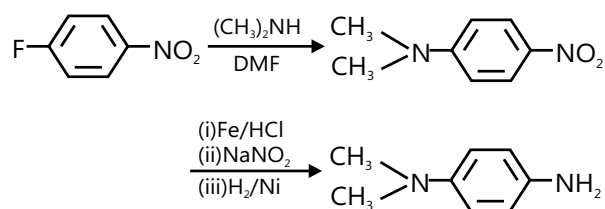
**Sol 31: (A)** Self explanatory (refer to theory of reaction)

**Previous Years' Questions**

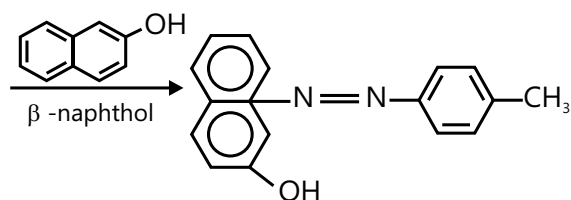
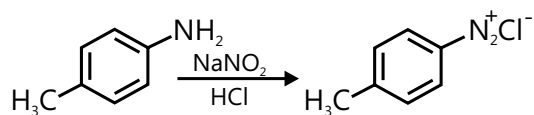
**Sol 1: (B)**  $\text{C}_6\text{H}_5\text{N}_2^+ \text{Cl}^- + \text{C}_6\text{H}_5\text{OH} \longrightarrow$



**Sol 2: (A)**



**Sol 3: (C)** As we know, benzenediazonium salt forms brilliant coloured dye with  $\beta$ -naphthol, the compound under consideration must be p-toluidine (c) as it is a primary aromatic amine. Primary aromatic amine, on treatment with  $\text{NaNO}_2$  in dil.  $\text{HCl}$  forms the corresponding diazonium chloride salt.

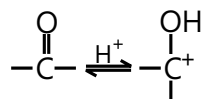


**Sol 4:** A → p; B → q; C → r; D → s

Sodium fusion extract gives Prussian blue colouration, nitrogen and carbon both present in the compound.

Phenolic group and salt of carboxylic acid gives  $\text{FeCl}_3$  test. Chloride salt gives white precipitate of  $\text{AgCl}$  on treatment with  $\text{AgNO}_3$ .

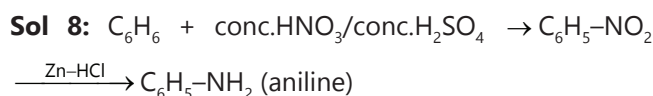
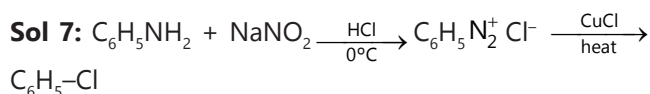
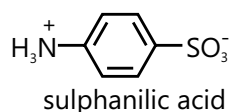
Hydrazone formation occur effectively at  $\text{pH} = 4.5$ . The reaction proceeds in that condition only when  $\text{H}^+$  concentration is just sufficient to activate the following enolization.



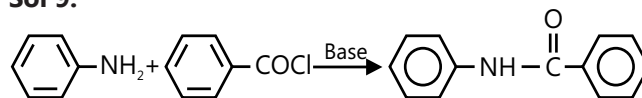
As  $\text{H}^+$  concentration rises sufficiently, a large number of molecules of hydrazine gets converted into hydrazone ion which is not nucleophilic and reaction becomes impossible. Further low concentration of  $\text{H}^+$  (in the case of 2,4-dinitrophenylhydrazinium bromide) is not effective to proceed elimination.

**Sol 5: Aniline:** It is a stronger base than either phenol or nitrobenzene.

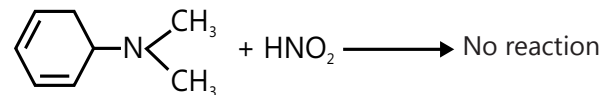
**Sol 6:** Zwitter ionic:



**Sol 9:**

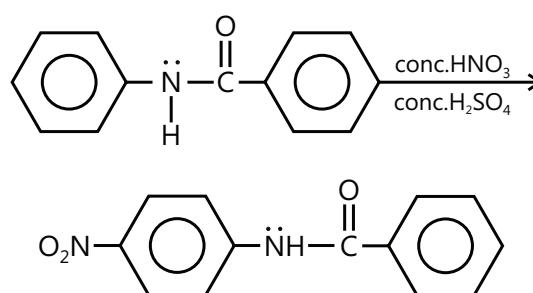


**Sol 10:**



Tertiary amine does not react with nitrous acid.

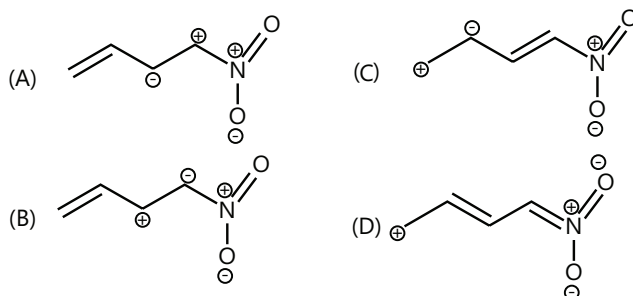
**Sol 11: (B)**



Due to presence of lone pair of electron on nitrogen atom, it will activate the ring and it will stabilize intermediate cation at o and p positions.

Hence (B) is correct

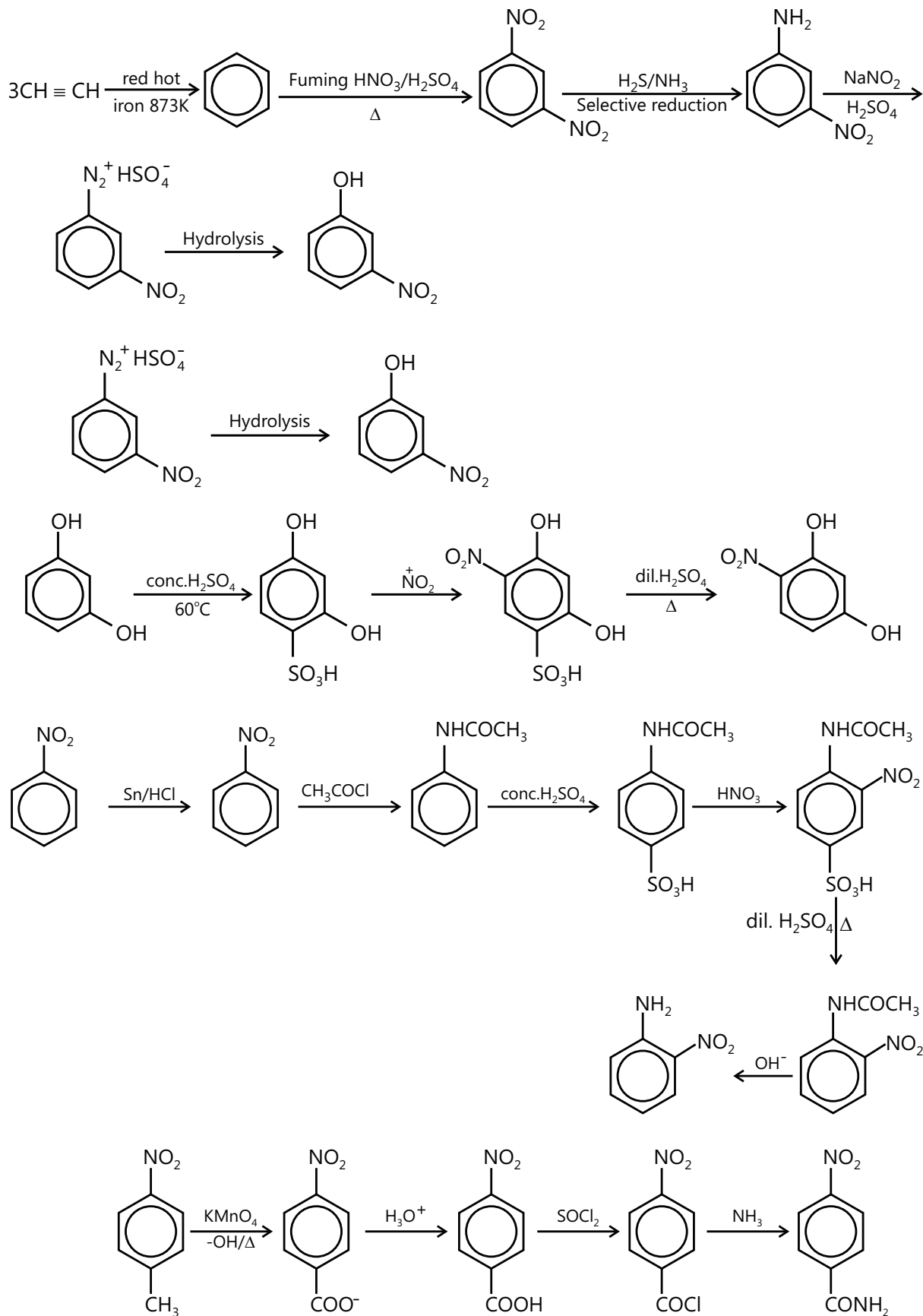
**Sol 12: (A)** Same charges are present at nearest position (Less stable)



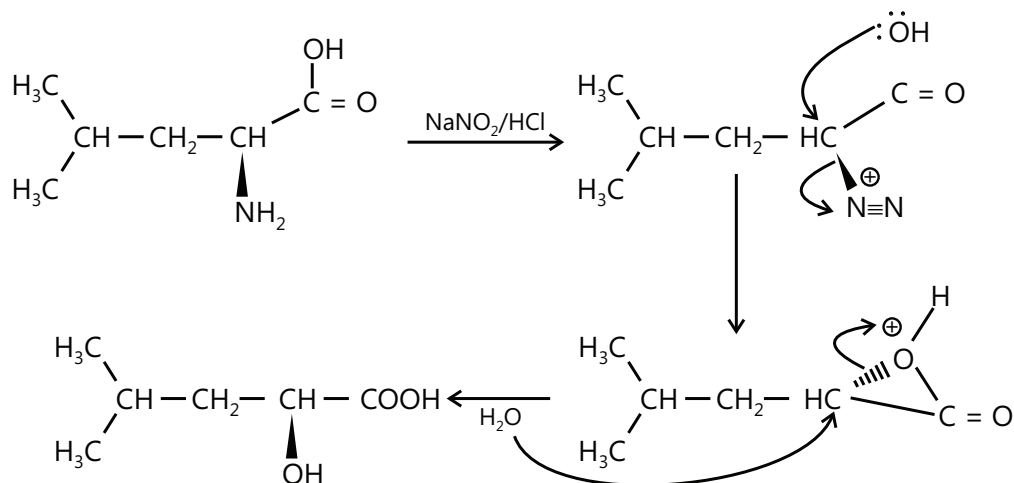
**Sol 13: (D)**  $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$  gives scarlet red coloured dye with  $\beta$ -naphthol

**Sol 14:** A → r; s B → p, q; C → p, q, r; D → p, s

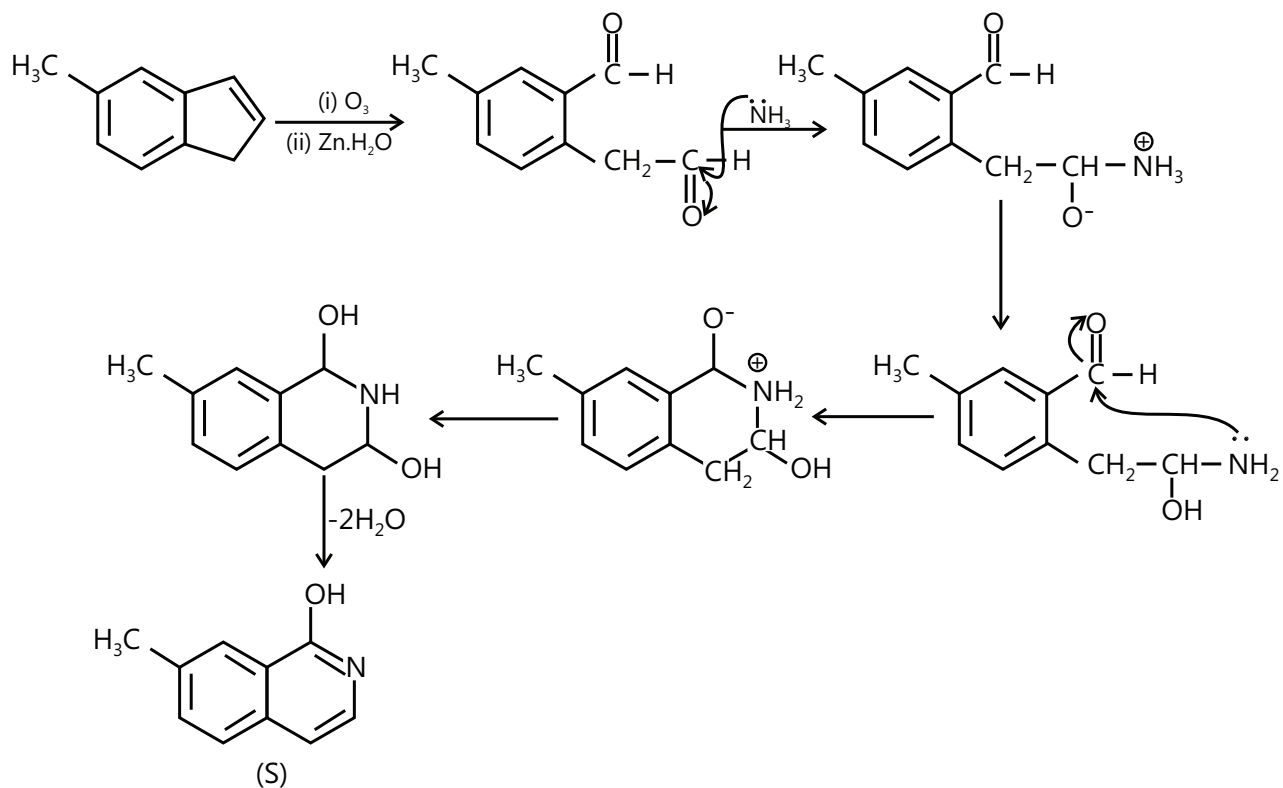
## Sol 15: (C)



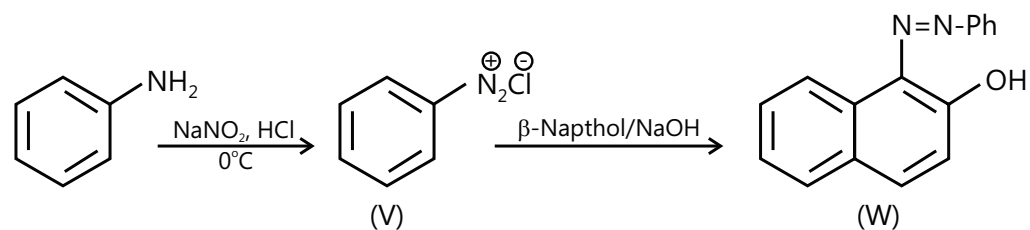
## Sol 16: (C)



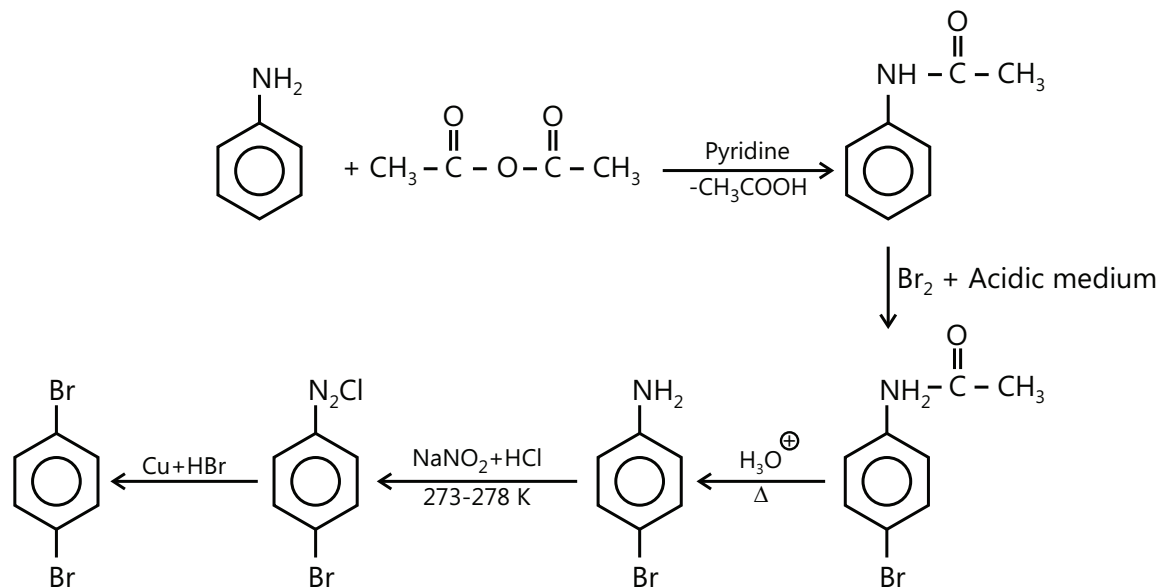
## Sol 17: (A)



## Sol 18: (A)



## Sol 19: (B)



## Sol 20 and 21 (A) and (B):

