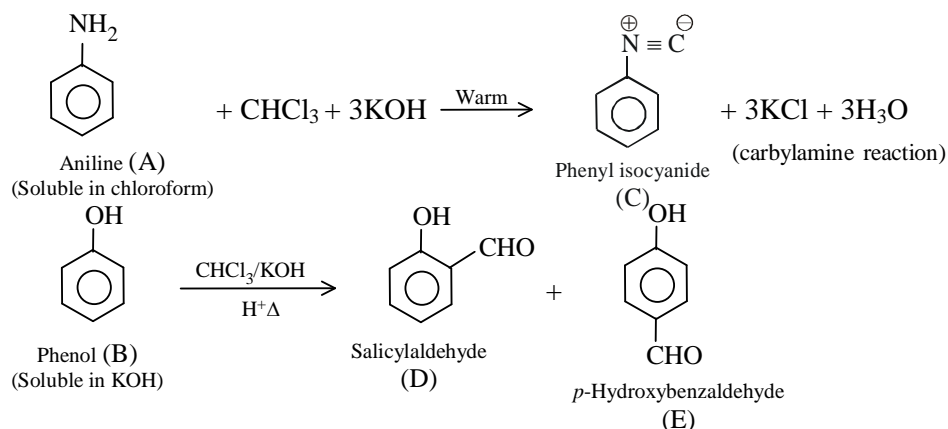


## SOLVED EXAMPLES

**Example 1 :** Mixture of two aromatic compounds (A) and (B) was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound (A), when heated with alcoholic solution of KOH produced a compound (C) ( $C_7H_5N$ ) associated with an unpleasant odour. The alkaline aqueous solution on the other hand, when heated with chloroform and then acidified give a mixture of two isomeric compounds (D) and (E) of molecular formula  $C_7H_6O_2$ . Identify the compounds (A), (B), (C), (D), (E) and write their structures.

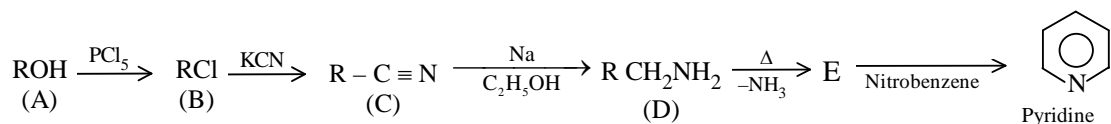
- Solution :**
- One of the compound A and B is soluble in aq.KOH and thus it must be acidic in nature whereas another compound is soluble in chloroform is either basic or neutral in nature.
  - The compound (A) on heating with alcoholic KOH solution (chloroform already present) produces compound (C) ( $C_7H_5N$ ) having unpleasant odour. The compound (C) is Phenylisocyanide and, therefore, compound (A) must be aniline which is soluble in chloroform but insoluble in aq.KOH.
  - The compound (B) must be phenol as it is soluble in aqueous KOH and produces isomers *o*-hydroxybenzaldehyde (D) and *p*-hydroxybenzaldehyde (E) on heating, with chloroform followed by acidification.

The reactions are as follows :

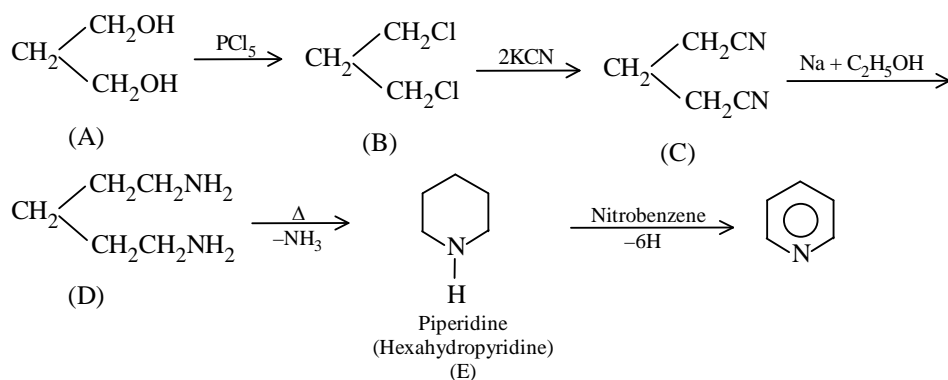


**Example 2 :** An organic compound (A) composed of C, H and O gives a characteristic colour with ceric ammonium nitrate. Treatment of (A) with  $\text{PCl}_5$  gives (B) which reacts with KCN to form (C). The reduction of (C) with Na and  $\text{C}_2\text{H}_5\text{OH}$  produces (D) which on heating gives (E) with evolution of  $\text{NH}_3$ . Pyridine is obtained on treatment of (E) with nitrobenzene. Give the structures of (A) to (E) with proper reasoning.

- Solution :** (A) is an alcohol which gives characteristic red colour with ceric ammonium nitrate.

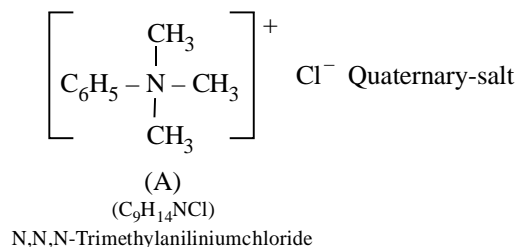


Start with propane-1, 3-diol



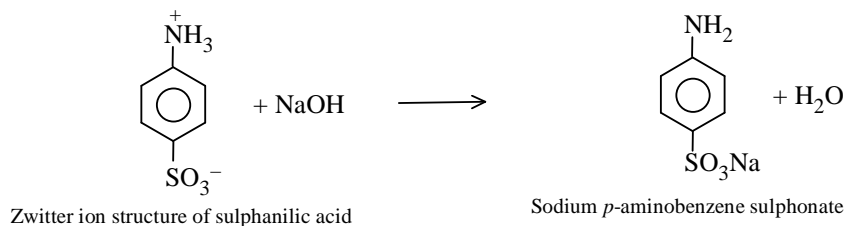
**Example 3 :** Compound (A) has molecular formula  $\text{C}_9\text{H}_{14}\text{NCl}$ . (A) gives an immediate precipitate with  $\text{AgNO}_3$ . It is very resistance to bromination in either acid or alkaline solution. It is also resistance to heat, nitration and oxidation by  $\text{KMnO}_4$ . Suggest structure for (A).

**Solution :** Since (A) ( $\text{C}_9\text{H}_{14}\text{NCl}$ ) gives immediate precipitate with  $\text{AgNO}_3$ , it must be an ionic compound. Further, it is resistant to oxidation, heat, nitration etc, it must be a quaternary ammonium salt. Therefore, possible structure of (A) may be :



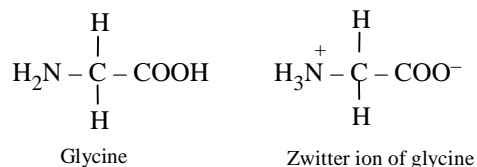
**Example 4 :** Sulphanilic acid is insoluble in water and acid but soluble in caustic alkali. Comment.

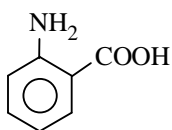
**Solution :** Sulphanilic acid exist as a Zwitter ion and exhibits strong dipole-dipole interactions. Therefore, it is insoluble in water. On adding acid,  $\text{SO}_3^-$  fails to accept  $\text{H}^+$  ion, thus sulphanilic acid is insoluble in acid. However, when alkali is added, strongly basic hydroxyl ion can abstract a proton from  $-\text{NH}_3^+$  to form soluble salt.



**Example 5 :** Glycine exists as a Zwitter ion but anthranilic acid does not. Comment.

**Solution :**  $-\text{COOH}$  group of glycine releases  $\text{H}^+$  ion which is accepted by  $-\text{NH}_2$  group. Thus glycine exist as a Zwitter ion.



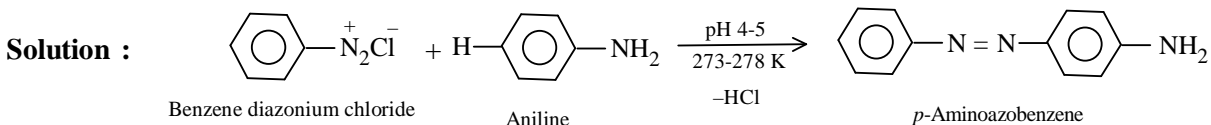


In anthranilic acid,

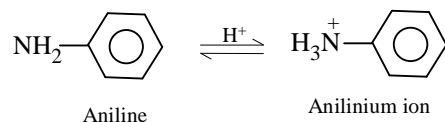
Anthranilic acid  
(2- Aminobenzoic acid)

Electron withdrawing  $-\text{COOH}$  and phenyl group reduces electron density of N of  $-\text{NH}_2$  group, therefore,  $-\text{NH}_2$  fails to accept a proton. Thus anthranilic acid can not form Zwitter ion.

**Example 6 :** A weakly acidic medium is provided for coupling of benzene diazonium chloride with aniline.  
Comment.



If high conc. of  $\text{H}^+$  ions are used during these reactions, then protonation of aniline takes place.



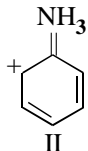
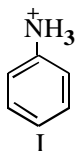
The positive charge on protonated amine exerts  $-I$  effect, thus coupling of amine with diazonium salt is not favoured, at low pH (or high acid strength). Also, we know high pH is not desirable for coupling reactions. Therefore, optimum pH for coupling reactions with amines is 4-5.

# OBJECTIVE QUESTIONS

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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.
2. When nitrobenzene is treated with Br<sub>2</sub> in presence of FeBr<sub>3</sub>, 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 Br<sup>+</sup> at the meta position is least destabilized  
(c) Loss of aromaticity, when Br<sup>+</sup> attacks at the ortho and para positions, and not at meta position  
(d) Easier loss of H<sup>+</sup> ion to regain aromaticity from the meta position than from the ortho and para positions.

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



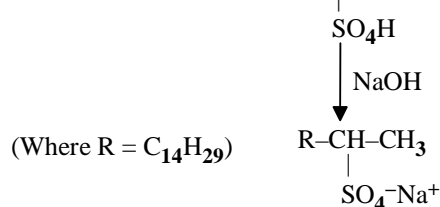
- (a) II is not an acceptable canonical structure, because carbonium ions are less stable than ammonium ions  
(b) II is not an acceptable canonical structure, because it is non aromatic  
(c) II is not an acceptable canonical structure, because the nitrogen has 10 valence electrons  
(d) II is an acceptable canonical structure.
4. The correct order of basic strength of the following amine in CCl<sub>4</sub>
- (1) NH<sub>3</sub> (2) RNH<sub>2</sub> (3) R<sub>2</sub>NH (4) R<sub>3</sub>N  
Where R is CH<sub>3</sub> group is:
- (a) 3 > 2 > 1 > 4 (b) 2 > 3 > 4 > 1 (c) 3 > 2 > 4 > 1 (d) None of these
5. 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
6. Which of the following will give a positive carbylamine test ?
1. H<sub>3</sub>CNH<sub>2</sub> 2. H<sub>3</sub>C-NH-CH<sub>3</sub> 3. (CH<sub>3</sub>)<sub>3</sub>N 4. C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>
- Select the correct answer using the codes given below.
- (a) 1 and 3 (b) 2 and 4 (c) 3 and 4 (d) 1 and 4.
-

7. 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.

Select the correct answer using the codes given below in the list .

- | <i>List I</i>          | <i>List II</i>   |
|------------------------|--|
| (A) Propyne            | 1. Reduces Fehling's solution  |
| (B) Ethyl benzoate     | 2. Forms a precipitate with $\text{AgNO}_3$ in ethanol                               |
| (C) Acetaldehyde       | 3. Insoluble in water, but dissolves in aqueous NaOH upon heating                    |
| (D) Aniline            | 4. Dissolves in dilute HCl in the cold and is precipitated by the addition of alkali |
| (a) A-3, B-2, C-1, D-4 | (b) A-2, B-3, C-1, D-4   |
| (c) A-2, B-3, C-4, D-1 | (d) A-1, B-3, C-2, D-4   |

8. In the following reaction sequence:  $\text{R-CH=CH}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{R-CH-CH}_3$  the end product would be useful



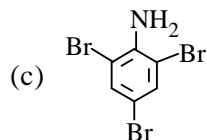
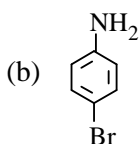
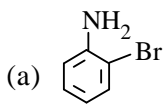
as

- (a) A fertilizer      (b) An explosive      (c) A detergent      (d) None of these
9. The basic strength of amines (ethyl) and ammonia in  $\text{H}_2\text{O}$  is
- (a)  $\text{NH}_3 > p > s > t$     (b)  $p > s > t > \text{NH}_3$     (c)  $s > p > t > \text{NH}_3$     (d) None of these
10. Which of the following will have the highest  $K_b$  value.



11. Aniline is a weaker base than ethyl amine because
- (a) Phenyl group in aniline is a +R group  
 (b) Ethyl group 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
12. 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
13. 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

14. Bromine in CS<sub>2</sub> reacts with aniline to give



(d) Both (a) and (b)

15. RNC cannot undergo

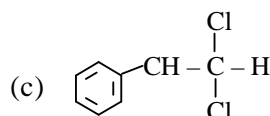
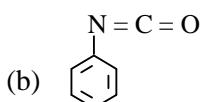
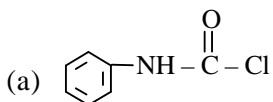
(a) Acidic hydrolysis

(b) Electrophilic, nucleophilic, addition on carbon

(c) Base hydrolysis

(d) Both (b) & (c)

16. + phosgene  $\longrightarrow$  X. Here X is



(d) None of these

17. Ethylamine undergoes oxidation in the presence of KMnO<sub>4</sub>/H<sup>+</sup>, H<sub>2</sub>O to give

(a) CH<sub>3</sub>COOH

(b) CH<sub>3</sub>CH<sub>2</sub>OH

(c) CH<sub>3</sub>CHO

(d) N-oxide

18. Baker Mulliken's test is used to detect the presence of

(a) -COOH group

(b) -NO<sub>2</sub>

(c) -OH

(d) -NH<sub>2</sub>

19. tert-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

20. In CH<sub>3</sub>NO<sub>2</sub> we can observe

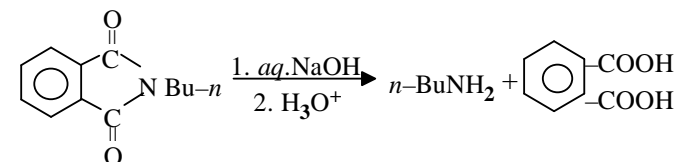
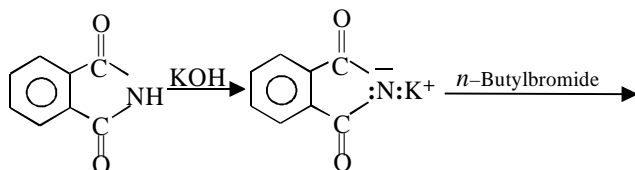
(a) H-bonding

(b) α-Halogenation reaction

(c) Tautomerism

(d) All of these

21. The reaction:



is called as:

(a) Carbylamine reaction

(b) Hofmann reaction

(c) Gabriel phthalimide synthesis

(d) Cope reaction .

22. The conjugate acid of HO(CH<sub>2</sub>)<sub>3</sub> NH<sub>2</sub> is

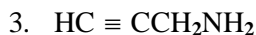
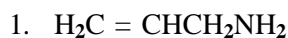
(a) H<sub>2</sub>O<sup>+</sup>(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>

(b) HO(CH<sub>2</sub>)<sub>3</sub>NH<sub>3</sub><sup>+</sup>

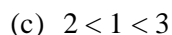
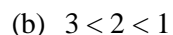
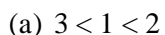
(c) O<sup>-</sup>(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>

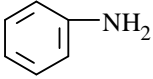
(d) HO(CH<sub>2</sub>)<sub>3</sub>NH<sup>+</sup>

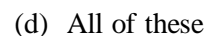
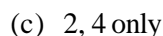
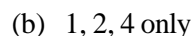
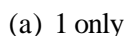
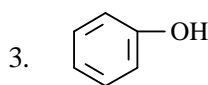
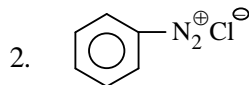
23. Consider the following compounds :



The increasing order of basicity is

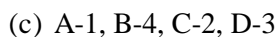
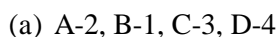
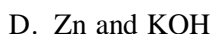
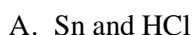


24. During the conversion of  with  $\text{HNO}_2$  at high temperature the following substances or intermediates are formed.

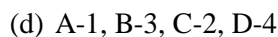
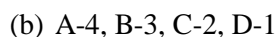
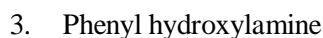


25. Match list I (condition of reaction of nitrobenzene) with list II (products formed) and select the correct answer using the codes given below.

**List I**

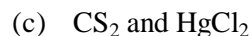
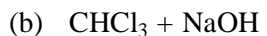


**List II**

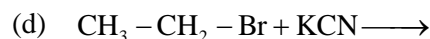
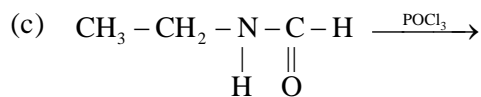
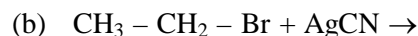
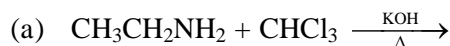


**MORE THAN ONE CORRECT ANSWERS**

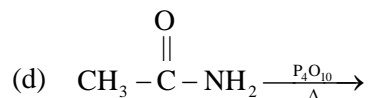
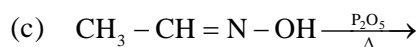
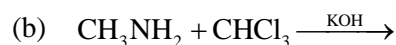
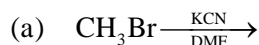
26. The presence of primary amine can be confirmed by its reaction with:



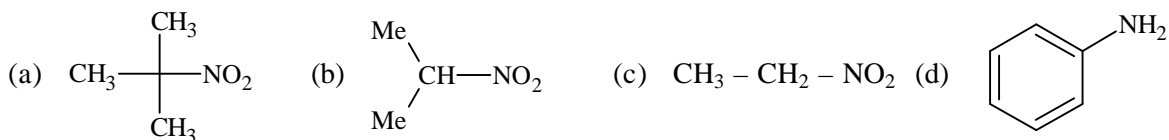
27. Which of the following reactions can be used to make ethyl isocyanide?



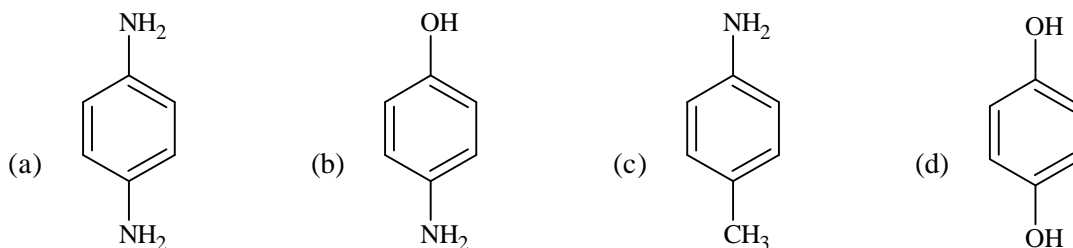
28. Which of the following reactions can be used to prepare methylcyanide?



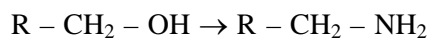
29. Which of the following compounds react with  $\text{HNO}_2$ ?



30. In the following reaction:  $\text{A} \xrightarrow[\text{H}^+]{\text{K}_2\text{C}_2\text{O}_7} \text{O}=\text{C}_6\text{H}_4=\text{C}=\text{O}$ . The reactant A can be

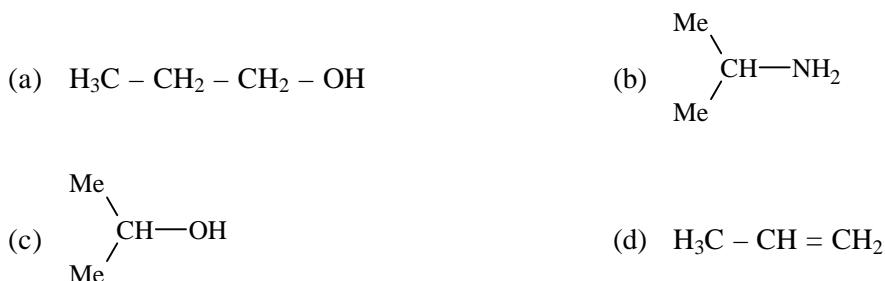


31. Which of the following sequence of reagent is the good means to give the conversion?

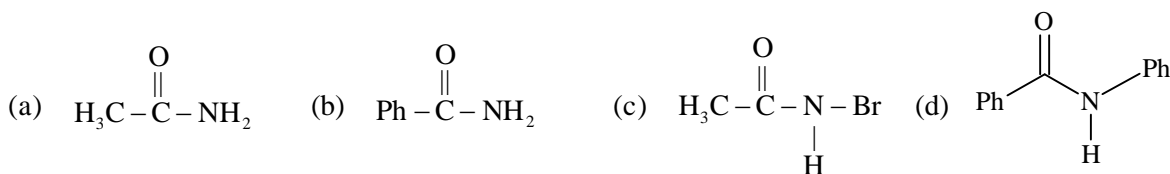


- (a)  $\text{KMnO}_4, \text{SOCl}_2, \text{NH}_3, \Delta, \text{NaOBr}$     (b)  $\text{SOCl}_2, \text{NaCN}, \text{H}_2/\text{Ni}$   
 (c)  $\text{CrO}_3$  in dilute acetone,  $\text{NH}_3, \text{H}_2/\text{Ni}$     (d)  $\text{Cu}$  at  $300^\circ, \text{NH}_3, \text{LiAlH}_4$

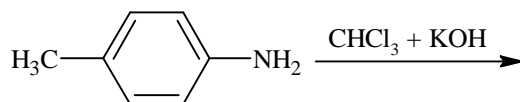
32. Which of the following products are formed when 1-Propanamine is treated with  $\text{NaNO}_2 + \text{HCl}$ ?



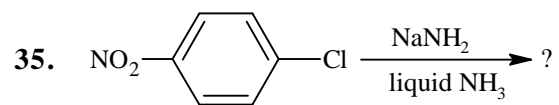
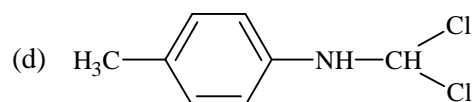
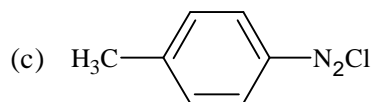
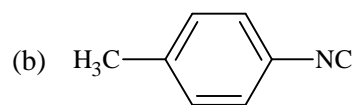
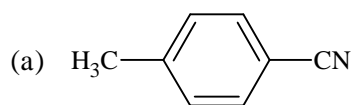
33. Which of the following will give Hofmann Bromamide degradation reaction?



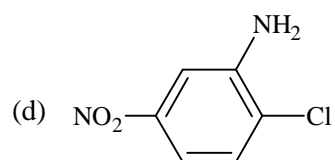
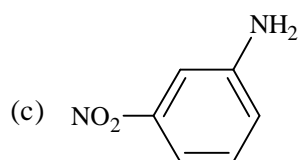
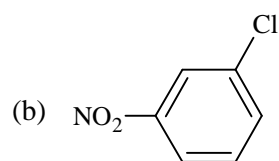
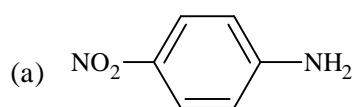
34. Which of the following products will not be formed by the following reaction?







The possible products are



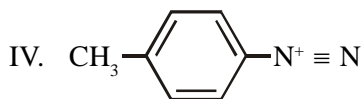
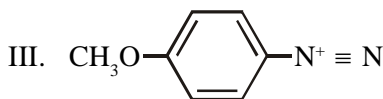
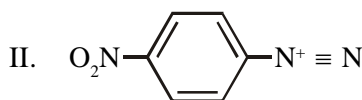
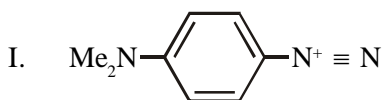
# MISCELLANEOUS ASSIGNMENT

## Comprehension-I

Arenediazonium 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  $N_2$  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  $H_3PO_2$  in presence of  $Cu^+$  ions,  $CH_3CH_2OH$ ,  $NaBH_4$  etc.),  $\bar{O}H$  (by boiling in presence of mineral acids),  $\bar{O}CH_3$  (by heating with  $CH_3OH$ )  $\bar{C}l$  (by  $CuCl/HCl$  or  $Cu/HCl$ ),  $\bar{B}r$  (by  $CuBr/HBr$  or  $Cu/HBr$ )  $\bar{I}$  (by  $KI$  in presence of  $Cu^+$  ions),  $\bar{F}$  (by first converting into  $N_2BF_4$  followed by heating),  $\bar{C}N$  (by first neutralizing with  $Na_2CO_3$  and then reacting with  $KCN/CuCN$ ),  $\bar{N}O_2$  (by first neutralizing with  $Na_2CO_3$  and then treating with  $NaNO_2$ ) phenyl or substituted phenyl (by treating with benzene or substituted benzene in presence of  $NaOH$ ) 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.

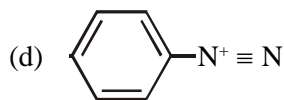
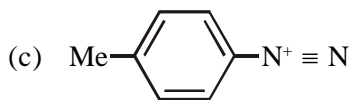
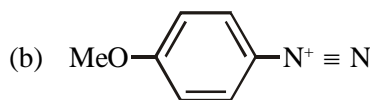
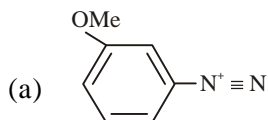
1. Consider the following ions:



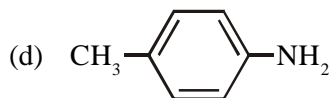
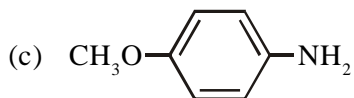
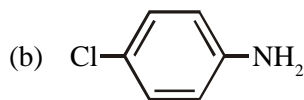
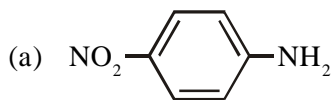
The reactivity of these ions towards azo coupling reactions under similar conditions is

- (a)  $I < IV < II < III$     (b)  $I < III < IV < II$     (c)  $III < I < II < IV$  (d)  $III < I < IV < II$

2. Which of the following diazonium salts when boiled with dil.  $H_2SO_4$  gives the corresponding phenol most readily?



3. Which of the following arylamines undergoes diazotisation most readily?



4. The product formed when bromobenzene reacts with benzenediazonium chloride in the presence of NaOH is

(a) Diphenyl

(b) *p*-Bromodiphenyl

(c) *p, p'*-Dibromodiphenyl

(d) *p*-Bromoazobenzene

5. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives:

(a) Diphenyl ether

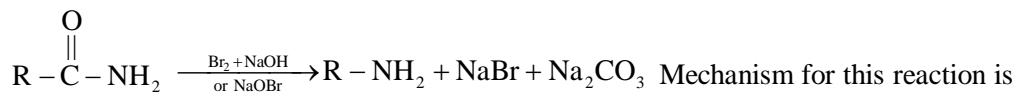
(b) *p*-Hydroxyazobenzene

(c) Chlorobenzene

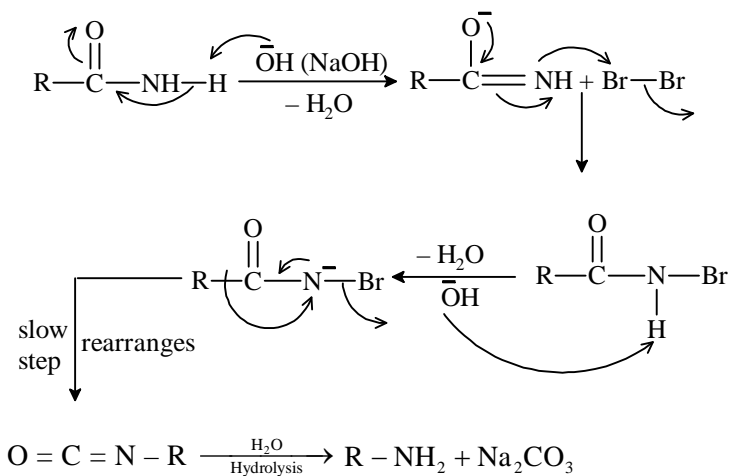
(d) Benzene

### Comprehension-II

The conversion of an amide by the action of NaOH and Br<sub>2</sub> to primary amine which has one carbon less than the starting amide is known as Hoffmann-Bromamide degradation reaction.



#### Mechanism:



N-Alkylcyanate.

Primary amine

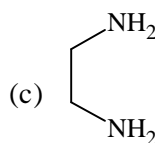
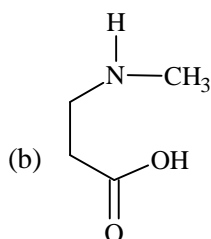
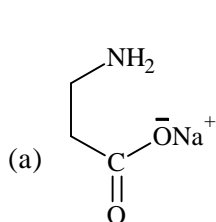
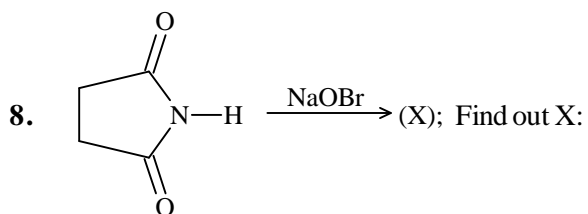
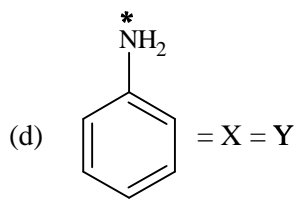
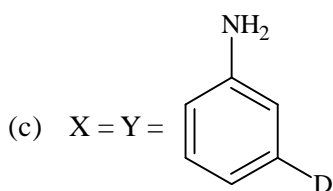
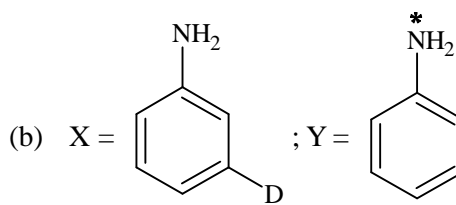
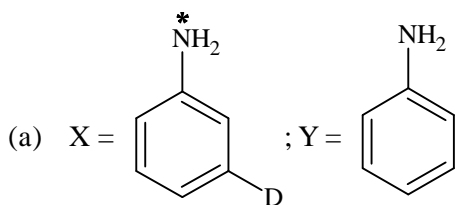
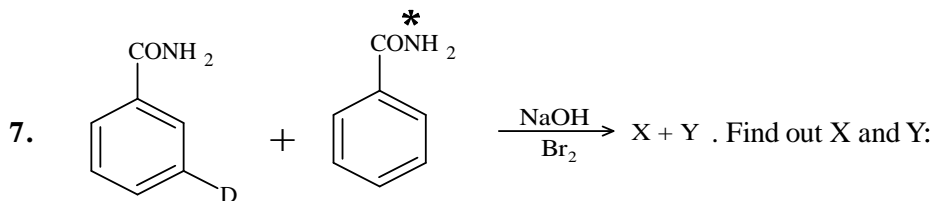
6. Number of moles of NaOH consumed in the above reaction is

(a) 1

(b) 2

(c) 3

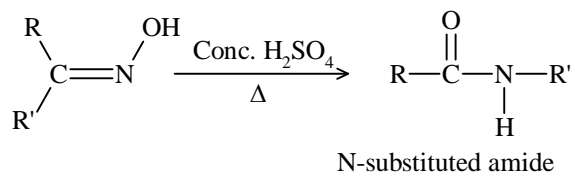
(d) 4



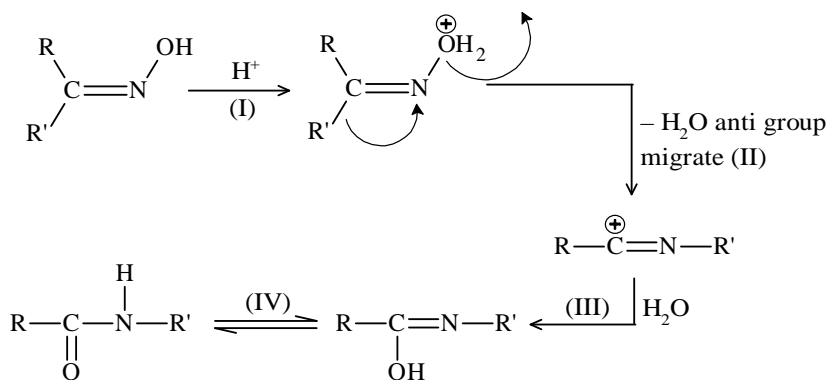
(d) all of these

### Comprehension-III

Ketoxime when heated with certain reagents undergoes rearrangement to form amides. This is known as Beckmann's rearrangement



## Mechanism



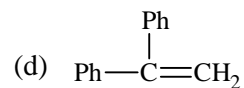
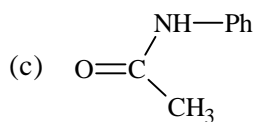
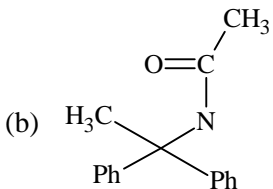
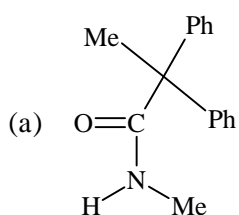
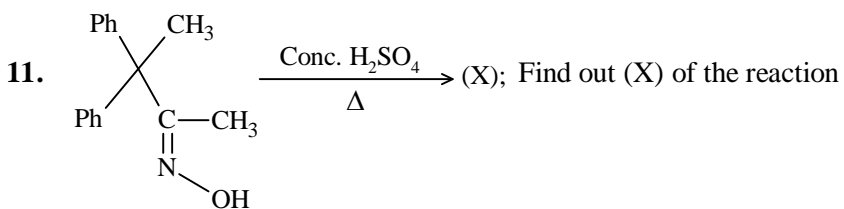
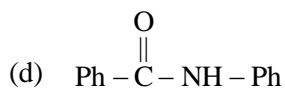
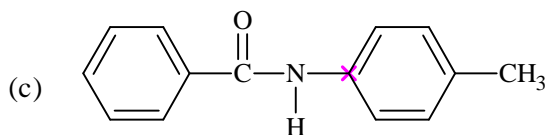
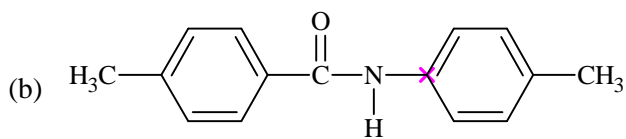
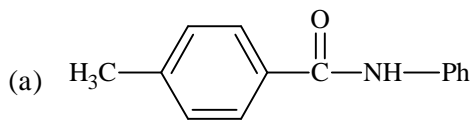
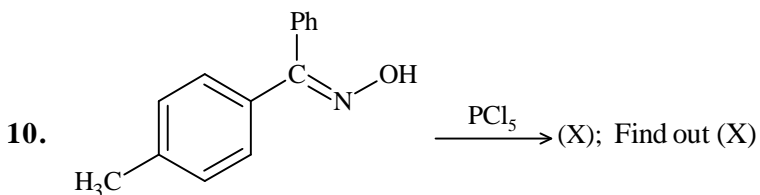
9. Find out the slowest step of the reaction

(a) I

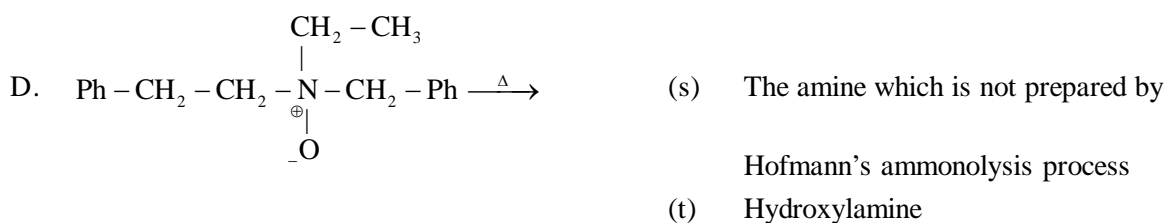
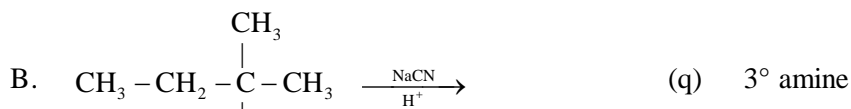
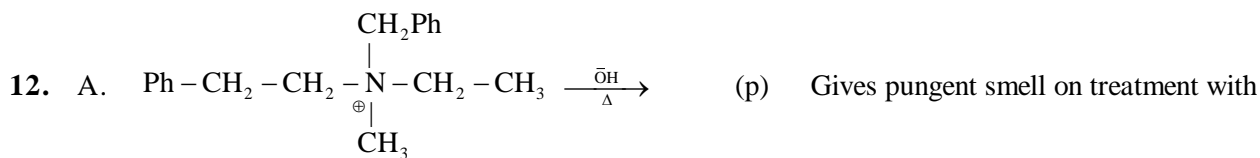
(b) II

(c) III

(d) IV

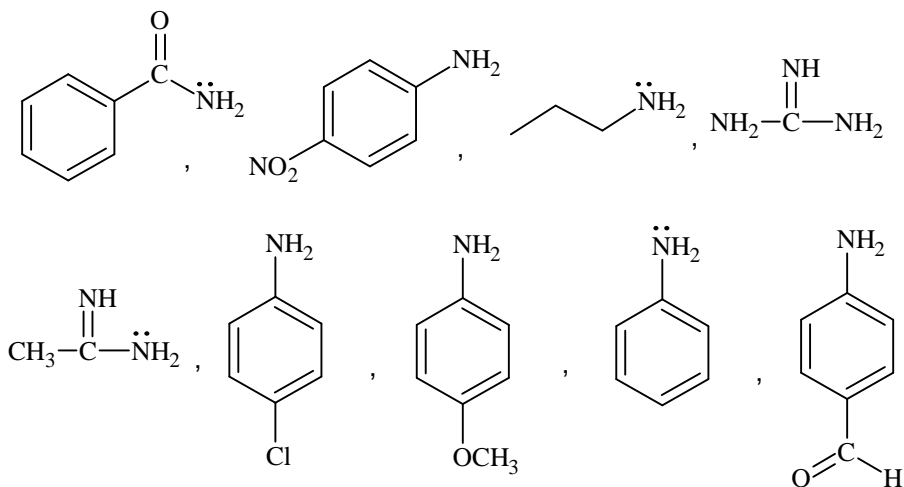


Match the following:



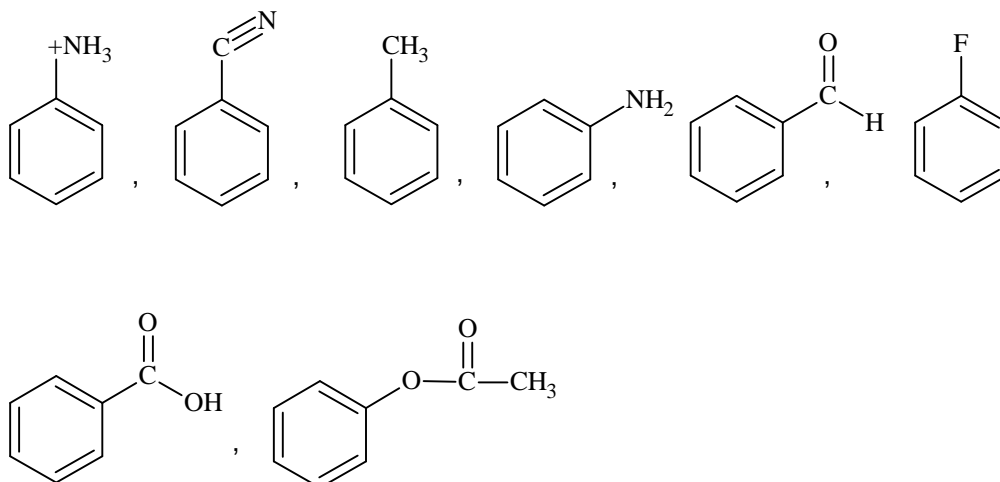
### INTEGER TYPE QUESTIONS

14. Of the following compounds, identify how many compounds are more basic than aniline

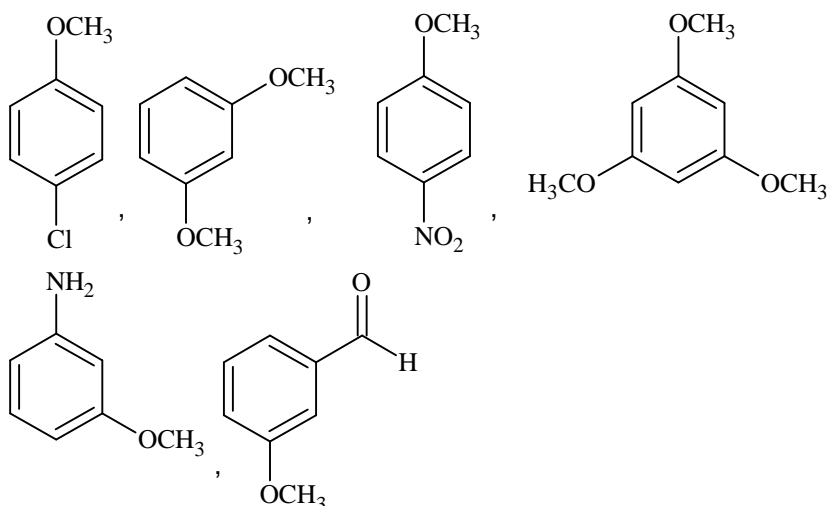




19. Find out how many of the following compounds cannot give Friedal craft's reaction.



20. Identify that how many compound will show coupling reaction with diazonium salts faster than anisole (Ph -  $\ddot{O}$  - CH<sub>3</sub>).



21. Which of the following reactions involve isocyanate as intermediate product:

- |                             |                            |
|-----------------------------|----------------------------|
| (a) Curtius rearrangement   | (b) Lossen rearrangement   |
| (c) Schmidt rearrangement   | (d) Hoffmann rearrangement |
| (e) Beckman's rearrangement | (f) Fries rearrangement    |

22. Which of the following give Schiff's base with aldehyde?

- |  |   |
|--|---|
| (a) CH <sub>3</sub> - CH <sub>2</sub> - NH <sub>2</sub>  | (b) C <sub>6</sub> H <sub>5</sub> - CH <sub>2</sub> - NH <sub>2</sub> |
| (c) C <sub>6</sub> H <sub>5</sub> - NH <sub>2</sub>      | (d) C <sub>6</sub> H <sub>5</sub> - NO <sub>2</sub>                   |
| (e) CH <sub>3</sub> - CH <sub>2</sub> - CN               |   |
| (f) C <sub>6</sub> H <sub>5</sub> - CH <sub>2</sub> - CN |   |

23. Which of the following reagents give aniline by reduction of Nitrobenzene?

- |                                       |   |            |            |
|---------------------------------------|---|------------|------------|
| (a) H <sub>2</sub> /Pd - C            | (b) Sn/HCl                              | (c) Cu/HCl | (d) Zn/HCl |
| (e) (NH <sub>4</sub> ) <sub>2</sub> S | (f) Na/C <sub>2</sub> H <sub>5</sub> OH |            |            |



# PREVIOUS YEAR QUESTIONS

## IIT-JEE/ JEE-ADVANCE QUESTIONS

1. Beckmann transformation of  $\begin{matrix} \text{C}_6\text{H}_5 \\ \diagdown \\ \text{C} = \text{N} \diagup \\ \diagup \\ \text{C}_6\text{H}_5\text{CH}_2 \\ \diagdown \\ \text{OH} \end{matrix}$  followed by hydrolysis will yield

- (a) Benzoic acid + benzylamine  
(b) Phenylacetic acid + benzylamine  
(c) Aniline + phenylacetic acid  
(d) Benzoic acid + aniline.

2.  $\text{C}_6\text{H}_5\text{NMe}_2 + \text{HCONMe}_2 \xrightarrow{\text{POCl}_3} \text{Me}_2\text{N}-\text{C}_6\text{H}_4-\text{CHO}$

The above reaction is called

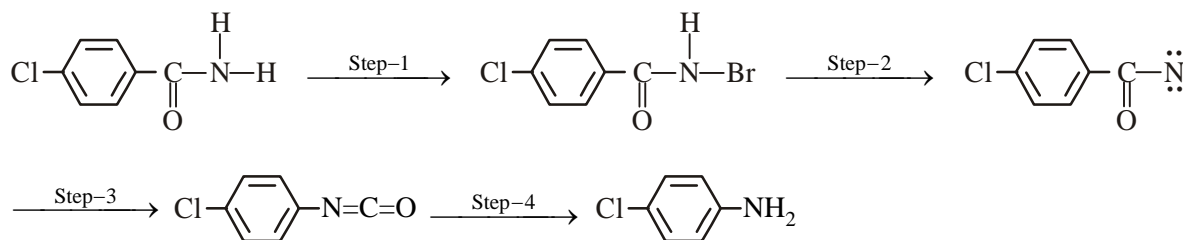
- (a) Hofmann mustard oil reaction  
(b) Vilsmeier-Haack reaction  
(c) Darzen's reaction  
(d) Arndt-Eistert reaction.

3. The product 'P' containing nitrogen is in the following reaction



- (a)  $\text{CH}_3 - \overset{\ominus}{\text{N}} \equiv \overset{\oplus}{\text{C}}$  (b)  $\text{CH}_3 - \overset{\cdot\cdot}{\text{N}}\text{HCl}$  (c)  $\text{CH}_3 - \overset{\oplus}{\text{N}} \equiv \overset{\ominus}{\text{C}}$  (d)  $\text{CH}_3 - \text{C} \equiv \text{N}:$

### Comprehension



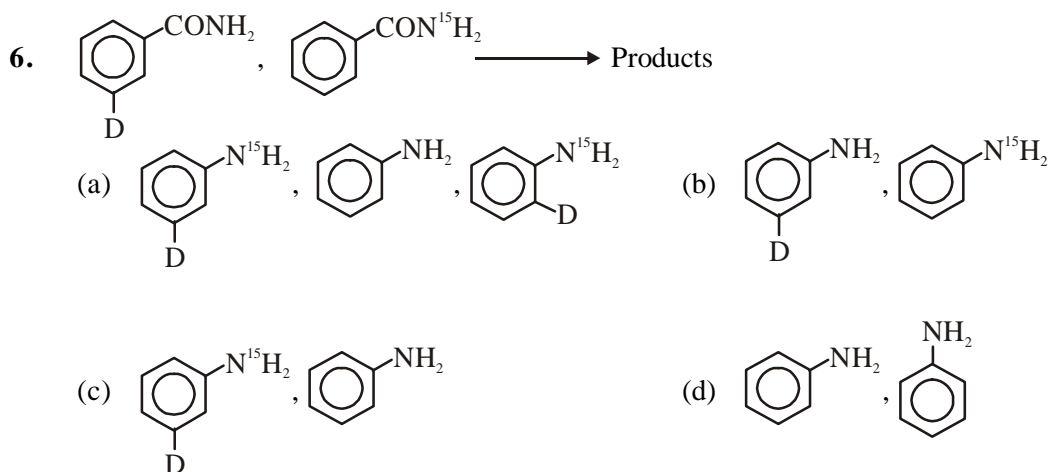
Due to formation of  $\text{RCONHBr}$  this reaction is named as Hoffmann Bromamide reaction

4. Reagents used in Step-1 are

- (a)  $\text{KBr} + \text{NaOH}$  (b)  $\text{KBr} + \text{NaOCH}_3$  (c)  $\text{Br}_2 + \text{NaOH}$  (d)  $\text{KBrO}_3 + \text{KOH}$

5. Rate determining step of the reaction

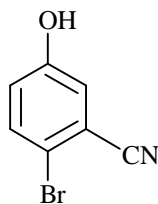
- (a) Step-2 (b) Step-1  
(c) formation of isocyanate (step-3) (d) formation of amine (step-4)



7. **STATEMENT-1:** 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.

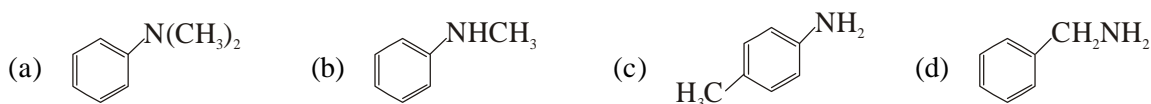
**STATEMENT-2:** The colour of the compound formed in the reaction of aniline with  $\text{NaNO}_2/\text{HCl}$  at  $0^\circ\text{C}$  followed by coupling with  $\beta$ -naphthol is due to the extended conjugation.

- (a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1  
 (b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1  
 (c) Statement-1 is True, Statement-2 is False  
 (d) Statement-1 is False, Statement-2 is True [IIT 2009]



- (a) 4-Bromo-3-cyanophenol  
 (b) 2-Bromo-5-hydroxybenzonitrile  
 (c) 2-Cyano-4-hydroxybromobenzene  
 (d) 6-Bromo-3-hydroxybenzonitrile

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



10. The total number of lone-pairs of electrons in melamine is

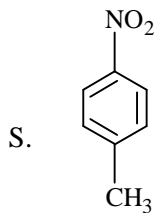
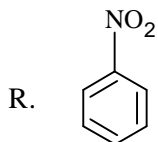
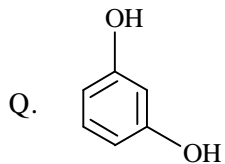
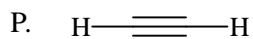
11. For the identification of  $\beta$ -naphthol using dye test, it is necessary to use

- (a) dichloromethane solution of  $\beta$ -naphthol  
 (b) acidic solution of  $\beta$ -naphthol  
 (c) neutral solution of  $\beta$ -naphthol  
 (d) alkaline solution of  $\beta$ -naphthol

12. 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.

**List I**



**List II**

1. **Scheme I**

(i)  $\text{KMnO}_4$ ,  $\text{HO}^+$ , heat (ii)  $\text{H}^+$ ,  $\text{H}_2\text{O}$  (iii)  $\text{SOCl}_2$  (iv)  $\text{NH}_3$   
 $?\longrightarrow\text{C}_7\text{H}_6\text{N}_2\text{O}_3$

2. **Scheme II**

(i)  $\text{Sn./HCl}$  (ii)  $\text{CH}_3\text{COCl}$  (iii) conc.  $\text{H}_2\text{SO}_4$   
 (iv)  $\text{HNO}_3$  (v) dil.  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4$  (vi)  $\text{HO}^-$   
 $?\longrightarrow\text{C}_6\text{H}_5\text{NO}_2$

3. **Scheme III**

(i) red hot iron, 873 K (ii) fuming  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , heat  
 (iii)  $\text{H}_2\text{S.NH}_3$  (iv)  $\text{NaNO}_2$ ,  $\text{H}_2\text{SO}_4$  (v) hydrolysis  
 $?\longrightarrow\text{C}_6\text{H}_5\text{NO}_3$

4. **Scheme IV**

(i) conc.  $\text{H}_2\text{SO}_4$ ,  $60^\circ\text{C}$   
 (ii) conc.  $\text{HNO}_3$ , conc.  $\text{H}_2\text{SO}_4$  (iii) dil.  $\text{H}_2\text{SO}_4$ , heat  
 $?\longrightarrow\text{C}_6\text{H}_5\text{NO}_4$

**Codes:**

	P	Q	R	S
(a)	1	4	2	3
(b)	3	1	4	2
(c)	3	4	2	1
(d)	4	1	3	2

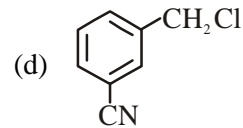
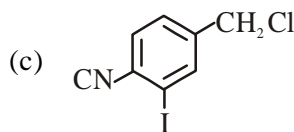
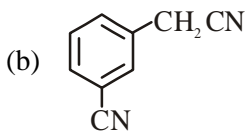
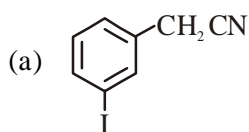
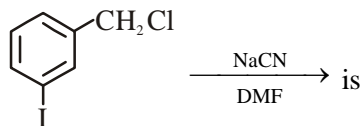
**DCE QUESTIONS**

- 
- Which one is basic dye  
 (a) Orange-I (b) Phenolphthalein (c) Anthraquinone (d) Aniline yellow
  - Which amine among the following will give positively the carbylamine test (*i.e.*, heating with  $\text{CHCl}_3$  and  $\text{KOH}$ )?  
 (a)  $\text{C}_6\text{H}_5 - \text{NH} - \text{CH}_3$  (b)  $\text{Me} - \text{C}_6\text{H}_4 - \text{NH}_2$  (c)  $\text{C}_6\text{H}_5 - \text{NH} - \text{C}_4\text{H}_9$  (d)  $\text{C}_6\text{H}_5 - \text{N}(\text{C}_2\text{H}_5)_2$
  - Which of the following statement is *not correct*?  
 (a) Methylamine is more basic than  $\text{NH}_3$   
 (b) Amines form hydrogen bonds  
 (c) Ethylamine has higher boiling point than propane  
 (d) Dimethylamine is less basic than methylamine.
  - Benzenediazonium chloride on reaction with phenol in weakly basic medium gives  
 (a) Diphenyl ether (b) *p*-Hydroxyazobenzene  
 (c) Chlorobenzene (d) Benzene
  - Consider the following reaction  

$$\text{C}_6\text{H}_5\text{NO}_2 \xrightarrow{\text{Sn/HCl}} \text{X} \xrightarrow{\text{C}_6\text{H}_5\text{COCl}} \text{Y} + \text{HCl}$$
 What is Y?  
 (a) Acetanilide (b) Benzanilide (c) Azobenzene (d) Hydrazobenzene
  - An organic compound with M.F.  $\text{C}_3\text{H}_5\text{N}$  on hydrolysis forms an acid which reduces Fehling's solution. The compound can be  
 (a) Ethanenitrile (b) Ethyl carbylamine (c) Ethoxyethane (d) Propanenitrile
  - $\text{CH}_3\text{CH}_2\text{CONH}_2 \xrightarrow{\text{X}} \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ , X is  
 (a)  $\text{Pt}/\text{H}_2$  (b)  $\text{Ni}/\text{H}_2$  (c)  $\text{LiAlH}_4$  (d)  $\text{Zn}$
  - Increasing order of basic nature in aqueous solutions  
 (a)  $\text{C}_6\text{H}_5\text{NH}_2 > \text{NH}_3 > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH}$   
 (b)  $\text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2 > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH}$   
 (c)  $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2$   
 (d)  $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > \text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2$
  - Which one of the following is the most basic?  
 (a)  $\text{FCH}_2\text{NH}_2$  (b)  $\text{FCH}_2\text{CH}_2\text{NH}_2$  (c)  $\text{C}_6\text{H}_5\text{NH}_2$  (d)  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

### **MAINS QUESTIONS**

- Acetyl bromide reacts with excess of  $\text{CH}_3\text{MgI}$  followed by treatment with a saturated solution of  $\text{NH}_4\text{Cl}$  gives:  
 (a) 2-Methyl-2-propanol (b) Acetamide (c) Acetone (d) Acetyl iodide
  - The structure of the major product formed in the following reaction
-



3. Towards electrophilic substitution, the most reactive will be
- (a) Nitrobenzene (b) Aniline  
(c) Aniline hydrochloride (d) N-Acetylaniline.
4. Match the compounds in List I with their nature from List II, as seen in aqueous medium from the combinations shown:

List I	List II	List I	List II
I. Acetamide	A. Acidic	II. Benzonitrile	B. Basic
III. Triethylamine	C. Neutral	IV. Phenol	
(a) I-C; II-C; III-B; IV-A		(b) I-B; II-C; III-C; IV-A	
(c) I-C; II-B; III-B; IV-C		(d) I-A; II-A; III-C; IV-B	

5. Which of the following gives primary amine on reduction?
- (a)  $\text{CH}_3\text{CH}_2\text{NO}_2$  (b)  $\text{CH}_3\text{CH}_2\text{-O-N}=\text{O}$  (c)  $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5$  (d)  $\text{CH}_3\text{CH}_2\text{NC}$
6. *m*-Bromotoluene is prepared by
- (a) Bromination of toluene  
(b) Friedel-Crafts reaction of bromobenzene with  $\text{CH}_3\text{Cl}$   
(c) Bromination of nitrobenzene and subsequent replacement of the nitro group with methyl group  
(d) Bromination of aceto-*p*-toluidide followed by hydrolysis and deamination
7. Regular use of which of the following fertilizers increases the acidity of soil?
- (a) Superphosphate of lime (b) Ammonium sulphate  
(c) Potassium nitrate (d) Urea
8. Which one of the following is the strongest base in aqueous solution?
- (a) Dimethylamine (b) Methylamine (c) Trimethylamine (d) Aniline
9. In the chemical reaction
- $$\text{CH}_3\text{CH}_2\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \longrightarrow (\text{A}) + (\text{B}) + 3\text{H}_2\text{O}$$
- the compounds (A) and (B) are respectively
- (a)  $\text{C}_2\text{H}_5\text{NC}$  and  $\text{K}_2\text{CO}_3$  (b)  $\text{C}_2\text{H}_5\text{NC}$  and  $3\text{KCl}$   
(c)  $\text{C}_2\text{H}_5\text{CN}$  and  $3\text{KCl}$  (d)  $\text{CH}_3\text{CH}_2\text{CONH}_2$  and  $3\text{KCl}$
10. Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product

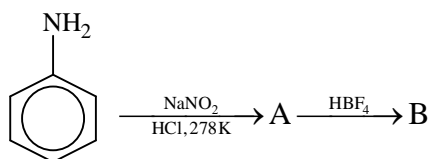
so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains

- (a) mixture of *o*- and *p*-dibromobenzenes      (b) mixture of *o*- and *p*-bromoanilines  
 (c) mixture of *o*- and *m*-bromotoluenes      (d) mixture of *o*- and *p*-bromotoluenes

11. The electrophile,  $E^{\oplus}$  attacks the benzene ring to generate the intermediate  $\sigma$ -complex. Of the following, which  $\sigma$ -complex is of lowest energy?



12. In the chemical reactions,



the compounds 'A' and 'B' respectively are

- (a) benzene diazonium chloride and fluorobenzene (b) nitrobenzene and chlorobenzene  
 (c) nitrobenzene and fluorobenzene (d) phenol and benzene
13. The correct order of increasing basicity of the given conjugate bases ( $R = CH_3$ ) is  
 (a)  $RCO\bar{O} < \bar{N}H_2 < HC \equiv \bar{C} < \bar{R}$  (b)  $RCO\bar{O} < HC \equiv \bar{C} < \bar{N}H_2 < \bar{R}$   
 (c)  $RCO\bar{O} < HC \equiv \bar{C} < \bar{R} < \bar{N}H_2$  (d)  $\bar{R} < HC \equiv \bar{C} < RCO\bar{O} < \bar{N}H_2$
14. Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is:  
 (a) Diethyl ether (b) 2-Butanone (c) Ethyl chloride (d) Ethyl ethanoate
15. A compound with molecular mass 180 is acylated with  $CH_3COCl$  to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is:  
 (a) 4 (b) 6 (c) 2 (d) 5
16. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is  
 (a) an alkyl cyanide (b) an alkyl isocyanide (c) an alkanol (d) an alkanediol
17. Considering the basic strength of amines in aqueous solution, which one has the smallest  $pK_b$  value? [JEE-Mains 2014]  
 (a)  $(CH_3)_3N$  (b)  $C_6H_5NH_2$  (c)  $(CH_3)_2NH$  (d)  $CH_3NH_2$

# SUBJECTIVE PROBLEMS

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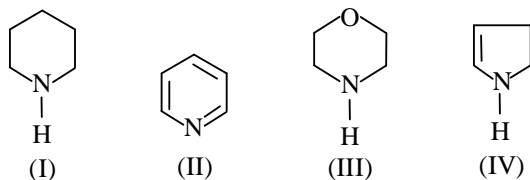
1. Aspartame, an artificial sweetener, is a peptide and has the following structures :



- (a) Identify the four functional groups.
  - (b) Write the zwitterionic structure
  - (c) Write the structures of the amino acids obtained from the hydrolysis of aspartame.
  - (d) Which of the two amino acids is more hydrophobic ?
2. Compound A (molecular formula  $\text{C}_9\text{H}_{11}\text{NO}$ ) gives a positive Tollen's test and is soluble in dilute HCl. It gives no reaction with benzene sulphonyl chloride or with  $\text{NaNO}_2$  and HCl at  $0^\circ\text{C}$ . (A) upon oxidation with  $\text{KMnO}_4$  gives an acid (B). When (B) is heated with soda-lime, compound (C) is formed which reacts with  $\text{NaNO}_2$  and HCl at  $0 - 5^\circ\text{C}$ . What is (A) ?
3. An organic compound A, when treated with nitrous acid yields an alcohol B,  $\text{C}_4\text{H}_{10}\text{O}$  with the evolution of  $\text{N}_2$ . B on careful oxidation yields a substance C of vapour density 36 which forms oxime; B can react with  $\text{NaHSO}_3$  but does not reduce Fehling solution. Identify compound A and write the structural formulae of the isomeric compounds that behave with  $\text{HNO}_2$  in the same manner.
4. An organic compound (A),  $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$ , is insoluble in both dilute acid and base and its dipole moment is zero. Deduce the structure of (A).
5. Explain the following observations :
- (1) Aniline dissolves in aqueous HCl.
  - (2) The amino group in ethylamine is basic whereas that in acetamide it is not basic.
  - (3) Dimethylamine is a stronger base than trimethylamine.
  - (4) Sulphanilic acid although has acidic as well as basic group, it is soluble in alkali but insoluble in mineral acids.
  - (5) Glycine exists as  $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$  while anthranilic acid,  $p\text{-NH}_2\text{C}_6\text{H}_4\text{COOH}$  does not exist as dipolar ion.
  - (6) Benzenesulphonic acid is a stronger acid than benzoic acid.
  - (7) A weakly basic solution favours coupling with phenol.
  - (8) It is difficult to prepare pure amines by ammonolysis of alkyl halides.
  - (9) Although trimethylamine and n-propylamine have same molecular weight, the former boils at a lower temperature ( $3^\circ\text{C}$ ) than the latter ( $49^\circ\text{C}$ ).
  - (10) Dimethylamine is a stronger base than methylamine but trimethylamine is a weaker base than both dimethylamine and methylamine.
  - (11) Although boron trifluoride adds on trimethylamine, it does not add on triphenylamine. Comment.
  - (12) Silver chloride dissolves in aqueous solution of methylamine. Explain.
  - (13) An aqueous solution of ethylamine gives a red precipitate with ferric chloride. Explain.
  - (14) Tertiary amines do not undergo acetylation. Comment
-

(15) 2, 6-Dimethyl -N N-dimethylaniline, although has a free p-position, does not undergo coupling with benzenediazonium chloride. Comment.

(16) In the following compounds :



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

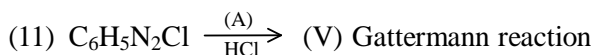
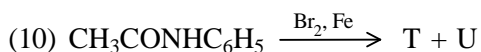
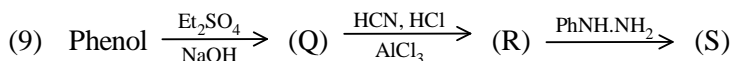
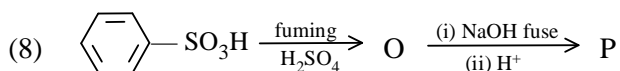
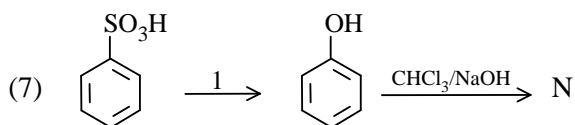
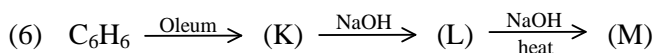
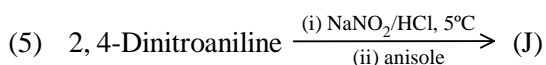
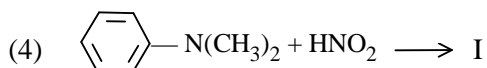
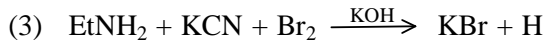
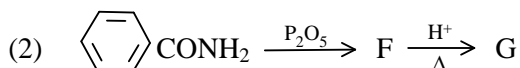
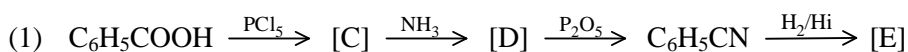
(17) tert-Butylamine cannot be prepared by the action of  $\text{NH}_3$  on tert-Butyl bromide. Explain, why ?

(18) Isocyanides are hydrolysed by dilute acids but not by alkalies to form amine and formic acid. Explain.

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

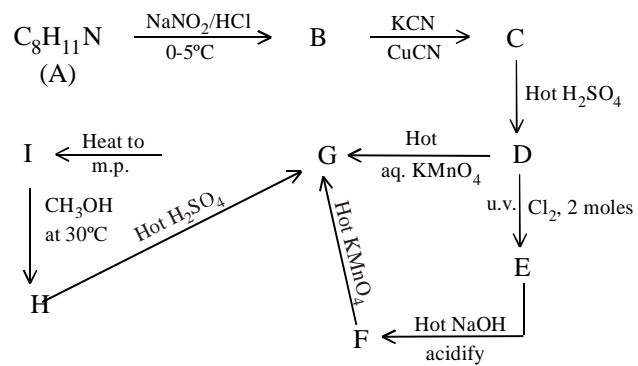
(20) Aniline does not undergo Friedal Craft's reaction. Explain ?

6. Complete the following reactions: (Identify A to V):





7. Give structures for the compounds (A) to (I) :



8. 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 ?

# ANSWERS

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## Objective Questions

- |               |             |             |             |             |
|---------------|-------------|-------------|-------------|-------------|
| 1. (a)        | 2. (a, b)   | 3. (c)      | 4. (d)      | 5. (b)      |
| 6. (d)        | 7. (b)      | 8. (c)      | 9. (d)      | 10. (a)     |
| 11. (c)       | 12. (b)     | 13. (b)     | 14. (c)     | 15. (c)     |
| 16. (b)       | 17. (d)     | 18. (b)     | 19. (d)     | 20. (d)     |
| 21. (c)       | 22. (b)     | 23. (a)     | 24. (d)     | 25. (b)     |
| 26. (a,b,c)   | 27. (a,b,c) | 28. (a,c,d) | 29. (b,c,d) | 30. (a,b,d) |
| 31. (a,b,c,d) | 32. (a,c,d) | 33. (a,b,c) | 34. (a,c,d) | 35. (a,c)   |

## Miscellaneous Assignment

- |  |   |         |         |         |
|--|---|---------|---------|---------|
| 1. (b)   | 2. (a)                                      | 3. (c)  | 4. (b)  | 5. (b)  |
| 6. (d)   | 7. (b)                                      | 8. (a)  | 9. (b)  | 10. (c) |
| 11. (d)  | 12. A-(q), B-(p),(r),(s), C-(r), (t), D-(t) |         |         |         |
| 13. A-(r), B-(s),(t), C-(p),(q),(s), D-(p),(q),(s) |   |         | 14. (5) | 15. (3) |
| 16. (5)  | 17. (4)                                     | 18. (5) | 19. (6) | 20. (3) |
| 21. (4)  | 22. (3)                                     | 23. (5) |         |         |

## Previous Year Questions

### IIT-JEE/JEE-ADVANCE QUESTIONS

- |         |         |        |        |        |
|---------|---------|--------|--------|--------|
| 1. (c)  | 2. (b)  | 3. (c) | 4. (c) | 5. (c) |
| 6. (b)  | 7. (d)  | 8. (b) | 9. (c) | 10. 6  |
| 11. (d) | 12. (c) |        |        |        |

### DCE QUESTIONS

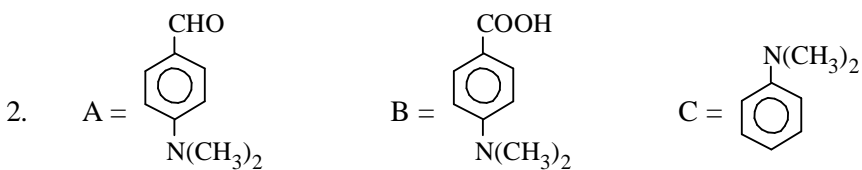
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|--------|--------|--------|--------|--------|
| 1. (d) | 2. (b) | 3. (d) | 4. (b) | 5. (b) |
| 6. (b) | 7. (c) | 8. (c) | 9. (d) |        |

### MAINS QUESTIONS

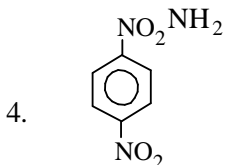
- |         |         |         |         |         |
|---------|---------|---------|---------|---------|
| 1. (a)  | 2. (a)  | 3. (b)  | 4. (a)  | 5. (a)  |
| 6. (d)  | 7. (b)  | 8. (a)  | 9. (b)  | 10. (d) |
| 11. (a) | 12. (a) | 13. (b) | 14. (d) | 15. (d) |
| 16. (b) | 17. (c) |         |         |         |
-

## Subjective Problems

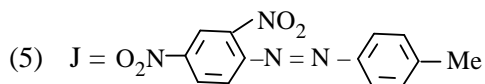
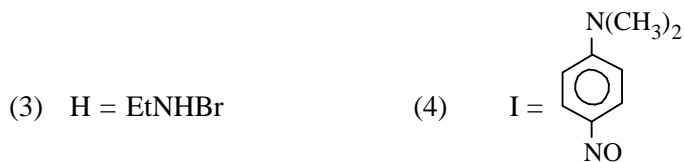
1. The hydrolysed products are aspartic acid and phenylalanine.



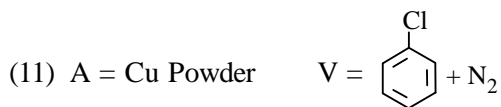
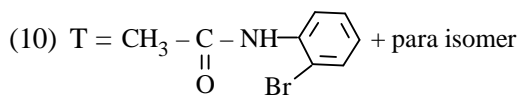
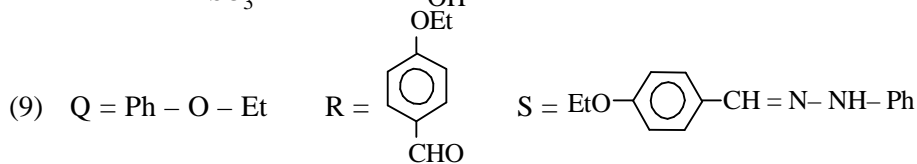
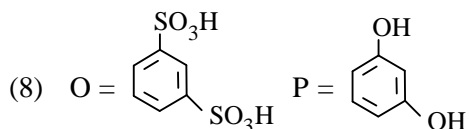
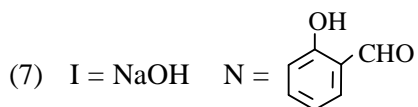
3.  $\text{CH}_3 - \underset{\text{NH}_2}{\text{CH}} - \text{C}_2\text{H}_5$ , The other isomers should be 1°-amines only

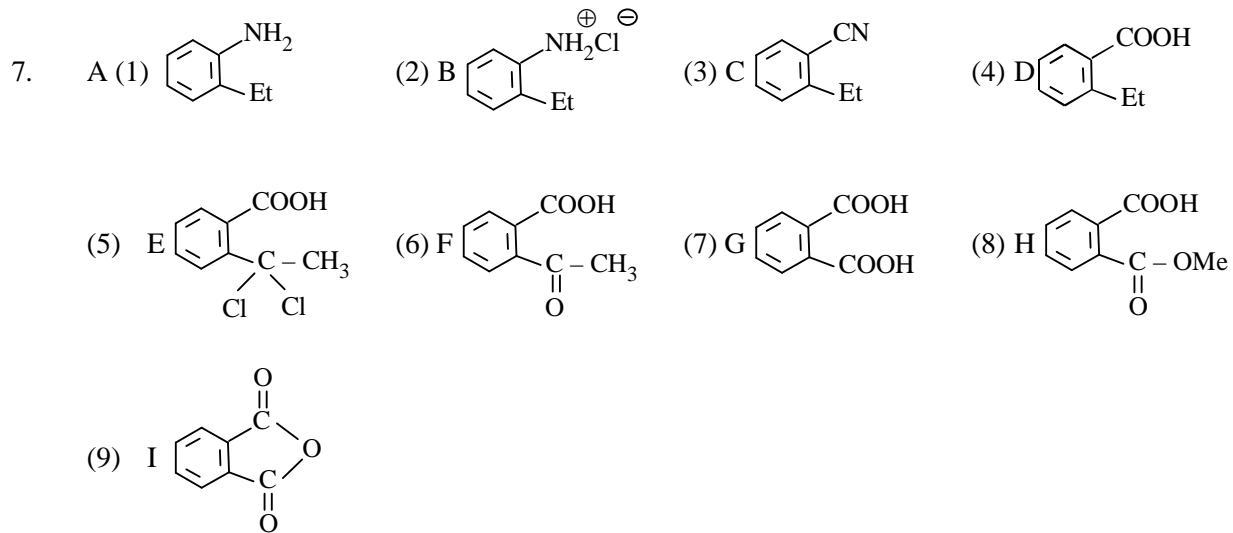


- 6 (1) C =  $\text{C}_6\text{H}_5\text{COCl}$  D =  $\text{C}_6\text{H}_5\text{CONH}_2$  E =  $\text{C}_6\text{H}_5\text{CHNH}_2$   
 (2) F =  $\text{C}_6\text{H}_5\text{CN}$  G =  $\text{C}_6\text{H}_5\text{COOH}$



- (6) 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 =  $\text{C}_6\text{H}_5\text{OH}$





8.  $C_2H_5NH_2$

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