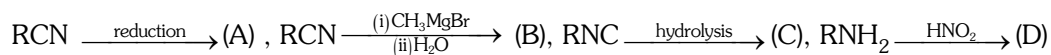


## SELECT THE CORRECT ALTERNATIVE (ONLY ONE CORRECT ANSWER)

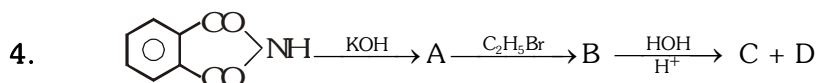
1. Tertiary butyl amine is a  
 (A) 1° Amine (B) 2° Amine  
 (C) 3° Amine (D) Quaternary salt

2. The correct set of the products obtained in the following reactions



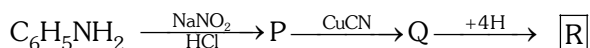
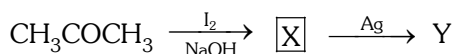
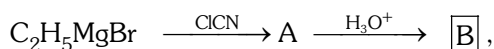
The answer is :

- |     | A        | B             | C        | D        |
|-----|----------|---------------|----------|----------|
| (A) | 2° Amine | Methyl ketone | 1° Amine | Alcohol  |
| (B) | 1° Amine | Methyl ketone | 1° Amine | Alcohol  |
| (C) | 2° Amine | Methyl ketone | 2° Amine | Acid     |
| (D) | 2° Amine | Methyl ketone | 2° Amine | Aldehyde |
3. Which one of the following tests can be used to identify primary amino group in a given organic compound  
 (A) Iodoform test (B) Victor Meyer's test  
 (C) Carbylamine reaction (D) Libermann's reaction

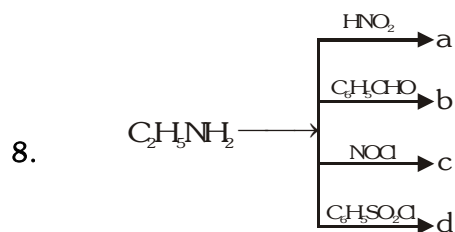


C and D in the above sequence are

- (A) Benzoic acid + aniline (B) Phthalic acid + ethylamine  
 (C) Phthalic acid + aniline (D) Benzoic acid + ethylamine
5. Lowest boiling point will be of the compound  
 (A) 2-propanamine (B) Ethylmethanamine  
 (C) 1-propanamine (D) N, N-dimethylmethanamine
6. How many primary amines can be formulated by  $\text{C}_3\text{H}_9\text{N}$  and how many 1° hydrogen are associated with carbon atoms of each compound  
 (A) Two primary amines [3, 6] (B) One primary amine [3]  
 (C) Three primary amines [3, 6, 6] (D) Two primary amines [5, 6]
7. Identify B, X and R respectively in the following sequence of reactions



- (A)  $\text{C}_2\text{H}_5\text{COOH}$ ,  $\text{CHI}_3$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$   
 (B)  $\text{C}_2\text{H}_5\text{COOH}$ ,  $\text{CH}_3\text{I}$ ,  $\text{C}_6\text{H}_5\text{COOH}$   
 (C)  $\text{C}_2\text{H}_5\text{CH}_2\text{NH}_2$ ,  $\text{CH}_3\text{I}$ ,  $\text{C}_6\text{H}_5\text{COOH}$   
 (D)  $\text{C}_2\text{H}_5\text{COOH}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{C}_6\text{H}_5\text{CONH}_2$



Which product is a Schiff's base :-

- (A) a (B) b (C) c (D) d

9. A + CS<sub>2</sub> + HgCl<sub>2</sub> gives C<sub>2</sub>H<sub>5</sub>—N=C=S. Thus compound A is :-

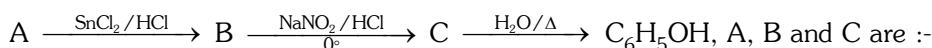
- (A) C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> (B) C<sub>2</sub>H<sub>5</sub>NHC<sub>2</sub>H<sub>5</sub> (C) CH<sub>3</sub>—CH=NOH (D) CH<sub>3</sub>CH<sub>2</sub>NO<sub>2</sub>

10. The end-product in the reaction sequence would be :



- (A) Ethyl cyanide (B) Ethyl amine (C) Methyl amine (D) Acetamide

11. In the reaction sequence :-



- (A) Benzene, nitrobenzene, aniline (B) Nitrobenzene, aniline and azo-compound  
(C) Nitrobenzene, benzene, aniline (D) Benzene, amino compound, aniline

12. Methylamine on treatment with chloroform and ethanolic caustic alkali gives foul smelling compound, the compound is

- (A) CH<sub>3</sub>NCO (B) CH<sub>3</sub>CNO (C) CH<sub>3</sub>CN (D) CH<sub>3</sub>NC

13. Which of the following is used as a solvent in the Friedel-Crafts reaction :-

- (A) Toluene (B) Nitrobenzene (C) Benzene (D) Aniline

14. CH<sub>3</sub>CH<sub>2</sub>CONH<sub>2</sub>  $\xrightarrow[\text{Br}_2]{\text{NaOH}}$  A,

Aqueous solution of A

- (A) Turns blue litmus to red (B) Turns red litmus to blue  
(C) Does not affect the litmus (D) Decolourise the litmus

15. Hinsberg reagent is used to distinguish between

- (A) —CHO, >C=O (B) —CH<sub>2</sub>OH, >CHOH, >C—OH  
(C) —O—, —OH (D) —NH<sub>2</sub>, —NH—, >N

16. Reactants of reaction – I are : CH<sub>3</sub>CONH<sub>2</sub>, KOH, Br<sub>2</sub>

Reactants of reaction-II are : CH<sub>3</sub>NH<sub>2</sub>, CHCl<sub>3</sub>, KOH

The intermediate species of reaction-I and reaction-II are respectively

- (A) Carbonium ion, carbene (B) Alkyl isocyanate, carbene  
(C) Carbene, nitrene (D) Carbocation, carbanion

17. Which of the following amine does not respond to carbylamine reaction :-

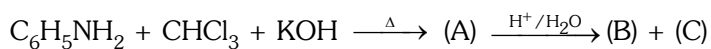
- (A) Ethylamine (B) (CH<sub>3</sub>)<sub>2</sub>NH (C) CH<sub>3</sub>NH<sub>2</sub> (D) Phenylamine



**SELECT THE CORRECT ALTERNATIVES (ONE OR MORE THEN ONE CORRECT ANSWERS)**

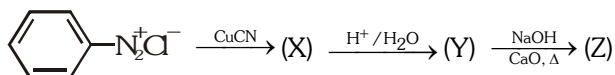
1. Carbylamine test is performed in alcoholic KOH by heating a mixture of :-  
(A) Chloroform and silver powder  
(B) Trihalogenated methane and a primary amine  
(C) An alkyl halide and a primary amine  
(D) An alkyl cyanide and a primary amine
2. Acetamide is treated separately with following reagents. Which one of these would give methylamine ?  
(A)  $\text{PCl}_5$  (B) Sodalime  
(C)  $\text{NaOH} + \text{Br}_2$  (D) Hot concentrated  $\text{H}_2\text{SO}_4$
3. Maximum basic in gas phase is ?  
(A)  $\text{NH}_3$  (B)  $\text{CH}_3\text{CH}_2\text{NH}_2$  (C)  $(\text{CH}_3\text{CH}_2)\text{NH}$  (D)  $(\text{CH}_3\text{CH}_2)_3\text{N}$
4. Benzenediazonium chloride on reaction with aniline in weakly basic medium gives  
(A) diphenyl ether (B) p-aminoazobenzene (C) Chlorobenzene (D) benzene
5. Which of the following statements is correct ?  
(A) Replacement of halogen by  $\text{NH}_2$  in alkyl halide is a nucleophilic substitution reaction  
(B) Aryl halides show more reactivity as compared to alkyl halides in the replacements of halogen by the  $\text{NH}_2$  group  
(C) During the replacement of halogen by  $-\text{NH}_2$  group, ammonia is taken in large excess so as to avoid the formation of 2° and 3° amines  
(D) Tertiary alkyl halide generally produces alkene instead of the replacement of halogen by  $\text{NH}_2$  group
6. Which of the following statements is correct ?  
(A) Primary amines show intermolecular hydrogen bonding  
(B) Secondary amines show intermolecular hydrogen bonding  
(C) Tertiary amines show intermolecular hydrogen bonding  
(D) Amines have lower boiling points as compared to those of alcohols and carboxylic acid of comparable molar masses.
7. Which of the following statements is correct ?  
(A) Aliphatic amines are stronger bases than ammonia  
(B) Aromatic amines are stronger bases than ammonia  
(C) The alkyl group in alkyl ammonium ion more stabilizes the ion relative to the amine  
(D) The aryl group in aryl ammonium ion less stabilizes the ion relative to the amine
8. Which of the following orders regarding the basic strength of substituted aniline is correct ?  
(A) p-methylaniline > p-chloroaniline > p-aminoacetophenone  
(B) p-methylaniline > p-aminoacetophenone > p-chloroaniline  
(C) p-aminoacetophenone > p-methylaniline > p-chloroaniline  
(D) p-aminoacetophenone > p-chloroaniline > p-methylaniline

9. Consider the following reaction,



The compounds (B) and (C) are :-

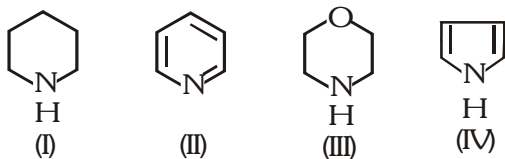
- (A)  $\text{C}_6\text{H}_5\text{COOH}$  and  $\text{NH}_3$  respectively (B)  $\text{C}_6\text{H}_5\text{NH}_2$  and  $\text{HCOOH}$  respectively  
 (C)  $\text{C}_6\text{H}_5\text{NH}_2$  and  $\text{H}_2\text{O}$  respectively (D) None of these
10.  $\text{CH}_3\text{CH}_2\text{NH}_2$  is soluble in :-  
 (A) Dilute  $\text{HCl}$  (B)  $\text{CuSO}_4$  solution (C)  $\text{AgNO}_3$  (D) None of these
11. The end product (Z) of the following reaction is :-



- (A) A cyanide (B) A carboxylic acid (C) An amine (D) An arene
12. 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)  $\text{RCH}=\text{NR} < \text{RNH}_2 < \text{RCN}$  (D)  $\text{RH}_2\text{N} < \text{RCH}=\text{NR} < \text{RCN}$
13. Amongst the following, the most basic compound is :-  
 (A) Benzylamine (B) Aniline (C) Acetanilide (D) p-nitroaniline
14. isocyanide test can be given by :  
 (A)  $\text{C}_2\text{H}_5\text{NH}_2$  (B)  $\text{C}_6\text{H}_5\text{NH}_2$  (C)  $\text{C}_6\text{H}_5\text{NHC}_2\text{H}_5$  (D)  $\text{C}_6\text{H}_5\text{CH}(\text{NH}_2)\text{C}_2\text{H}_5$

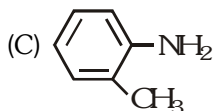
(D) II is an acceptable canonical structure

15. In the following compounds



the order of basicity is

- (A)  $\text{IV} > \text{I} > \text{III} > \text{II}$  (B)  $\text{III} > \text{I} > \text{IV} > \text{II}$   
 (C)  $\text{II} > \text{I} > \text{III} > \text{IV}$  (D)  $\text{I} > \text{III} > \text{II} > \text{IV}$
16. A positive carbylamine test is not given by :  
 (A) N, N-dimethylaniline (B) 2, 4-hydroxyazobenzene  
 (C) N-methyl-o-methylaniline (D) p-methylbenzylamine
17. Among the following, the strongest base is  
 (A)  $\text{C}_6\text{H}_5\text{NH}_2$  (B)  $\text{p-NO}_2\text{C}_6\text{H}_4\text{NH}_2$   
 (C)  $\text{m-NO}_2\text{C}_6\text{H}_4\text{NH}_2$  (D)  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
18. Phenyl cyanide on reduction with  $\text{Na}/\text{C}_2\text{H}_5\text{OH}$  yields  
 (A)  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  (B)  $\text{C}_6\text{H}_5\text{NHCH}_3$



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



## EXERCISE-03

## MISCELLANEOUS TYPE QUESTIONS

TRUE OR FALSE :

1. Secondary amines show carbylamine reaction.
2. The aqueous solution of ethylamine precipitates iron as ferric hydroxide when added to ferric chloride solution.
3. Nitrogen is evolved when ethylamine is treated with nitrous acid.
4. Primary, secondary and tertiary amines can be separated from their mixture by using ethyl oxalate.
5. Tertiary amines react with Grignard reagents to form hydrocarbon.
6. Primary amines are less soluble than tertiary amines.
7.  $\alpha$ -Amino acids on heating with  $\text{Ba(OH)}_2$  shows decarboxylation to produce primary amines.

FILL IN THE BLANKS :

1.  $(\text{CH}_3)_2\text{CHNH}_2$  is a ..... amine.
2. Methyl cyanide on reaction with sodium and  $\text{C}_2\text{H}_5\text{OH}$  forms .....
3. Acetamide on treatment with ..... forms ethyl amine.
4. Tertiary amines do not react with acetyl chloride since they do not have ..... on nitrogen.
5. The reaction  $\text{RCN} \xrightarrow{\text{SnCl}_2/\text{HCl}} (\text{A}) \xrightarrow{\text{H}_2\text{O}} \text{RCHO} + \text{NH}_4\text{Cl}$ , is known as .....
6. nitroalkanes when reduced with zinc dust and ammonium chloride form .....
7. Primary amines on heating with ..... and ..... form alkyl isocyanides.

MATCH THE COLUMN

1. Match the column I with column II.

Column-I		Column-II	
(A)	$\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$	(p)	Secondary amine
(B)	Conversion of amide to amine	(q)	Hofmann's bromamide reaction
(C)	Conversion of primary amine to isocyanide	(r)	Hinsberg's reagent
(D)	Dimethylamine	(s)	Carbylamine reaction

2. Match the column I with column II.

Column-I		Column-II	
(A)	Tetraethyl ammonium iodide	(p)	Quaternary salt
(B)	$\text{>C-NH}_2$	(q)	Tertiary amine
(C)	$\text{RCOOH} + \text{N}_3\text{H} + \text{Conc. H}_2\text{SO}_4$	(r)	Schmidt reaction
(D)	$\text{R}_3\text{N}$	(s)	Primary amine

3. Match list I with II and choose the correct answer from the codes given below :-

Column-I		Column-II	
(A)	Aniline	(p)	Used in making azodyes
(B)	Nitrobenzene	(q)	Sulpha drug
(C)	Sulphanilamide	(r)	Solvent in the Friedel Crafts reaction
(D)	Trinitrotoluene	(s)	Used as explosive

#### ASSERTION & REASON QUESTION :

These questions contains, Statement-I (assertion) and Statement-II (reason).

- (A) Statement-I is True, Statement-II is True ; Statement-II is a 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.

- Statement-I** : Alkyl isocyanide can be prepared by carbyl amine reaction.  
**Because**  
**Statement-II** : Ethyl amine when heated with chloroform in presence of alcoholic KOH, alkanamide is formed.
- Statement-I** :  $\text{CN}^-$  ion is an ambident nucleophile.  
**Because**  
**Statement-II** : Nucleophiles are electron rich species.
- Statement-I** : Conversion of alkyl halides into alkyl cyanide or isocyanides is a nucleophilic substitution reaction.  
**Because**  
**Statement-II** : When an alkyl halide is treated with alcoholic solution of AgCN, alkyl cyanides are formed as major product.
- Statement-I** : Nitrobenzene undergoes electrophilic substitution at m-position, while nucleophilic substitution occurs at o-and p-position.  
**Because**  
**Statement-II** : Nitro group in benzene ring significantly lowers the electron density at o- and p-positions, while at m-position, the electron density is only slightly lowered.
- Statement-I** : Nitrobenzene is used as a solvent in Friedel-Craft's reaction.  
**Because**  
**Statement-II** : Fusion of p-chloronitrobenzene with KOH gives a low yield of a mixture of p-nitro phenoles.
- Statement-I** : In Hoffmann bromide reaction, the amine formed has one carbon atom less than the parent  $1^\circ$  amide.  
**Because**  
**Statement-II** : N-methyl acetamide undergoes Hoffmann bromamide reaction.
- Statement-I** : Nitrobenzene does not undergo Friedel-Craft's alkylation.  
**Because**  
**Statement-II** : Nitrobenzene is used as solvent in laboratory and industry.
- Statement-I** : A reaction between a diazo salt and an aromatic amine or a phenol, giving an amino-azo or hydroxy-azo compound is called coupling reaction.  
**Because**  
**Statement-II** : Condensation of diazonium with phenol is carried out in weakly acidic medium.



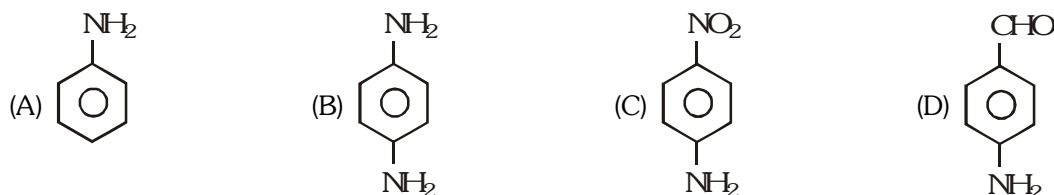
9. **Statement-I** : Aniline can be prepared by the reaction of chlorobenzene with  $\text{NaNH}_2/\text{Liq. NH}_3$ .  
**Because**  
**Statement-II** :  $\text{NH}_2^-$  ion is a stronger nucleophile.
10. **Statement-I** : Carbylamine reaction involves the reaction between  $1^\circ$  amine and chloroform in basic medium.  
**Because**  
**Statement-II** : In carbylamine reaction,  $-\text{NH}_2$  group is converted into  $-\text{NC}$  group via reaction with carbene intermediate.

## COMPREHENSION BASED QUESTIONS :

### Comprehension # 1

The origin of acidity and basicity in organic compound is great interest and provides an extensive comparison. Among hydrocarbons % s character is taken in account while to decide the acidity, in simple aliphatic acids, more the number of alkyl groups, (+I effect) less is the acidity & more the (-I effect) alkyl groups larger the acidity and vice-versa in the case of simple aliphatic bases. Benzoic acid is more stronger than carboxylic acid as benzoate ion is stabilised more by resonance. Aromatic amines are less basic than aliphatic amine as the electron pair is less available in case of aromatic amines. The presence of solvent also plays a very important role and at times governs the order too.

1. Amongst the following the most basic compound is -



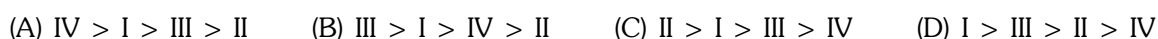
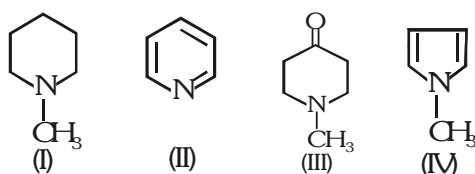
2. Among the following compounds the strongest acid is



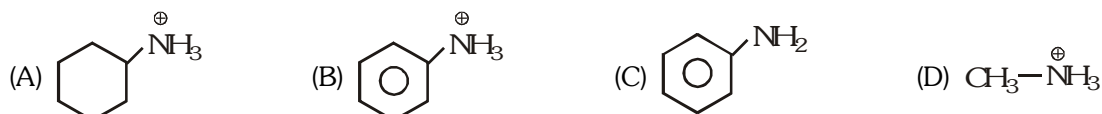
3. Which of the following orders regarding acid strength is correct ?



4. In the following compounds, the order of basicity

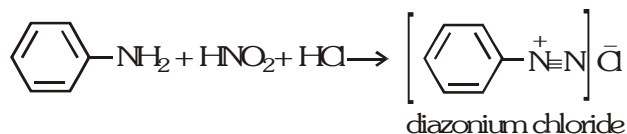


5. Which of the following is most acidic

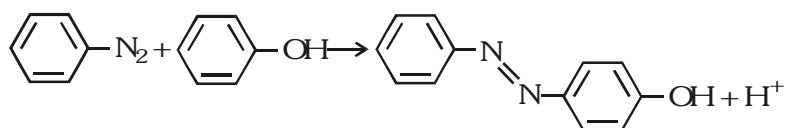


## Comprehension # 2

**Diazonium salt formation and coupling reactions :** When a reaction mixture of phenyl amine and nitrous acid is kept below  $10^{\circ}\text{C}$ , a diazonium salt is formed. This reaction is called diazotization reaction.

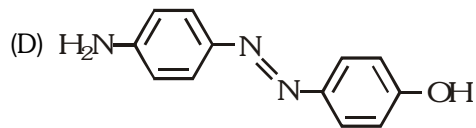
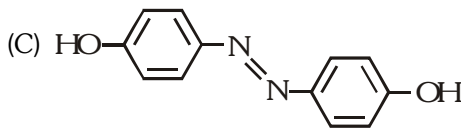
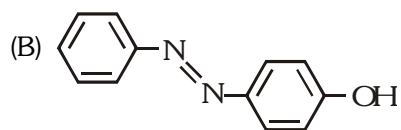
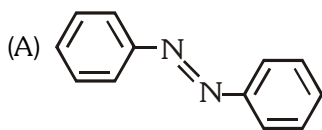


The diazonium ion,  $-\text{N}_2^+$ , is rather unstable and decomposes readily to nitrogen. However, delocalization of the diazonium from  $\pi$ -bond electron over a benzene ring stabilizes phenyl diazonium sufficiently for it to form at low temperatures. The phenyl diazonium ion behaves as an electrophile, and will attack another arene molecule such as phenol. Electrophilic substitution takes place at the 4 position, producing 4-hydroxy phenyl azobenzene. The reaction is known as coupling reaction.



The compound formed is an energetically stable, yellow azo dye (the azo group is  $-\text{N}=\text{N}-$ ). The stability is due to extensive delocalisation of electrons via the nitrogen- nitrogen double bonds.

1. The azo dye obtained on reacting 4-aminophenol with nitrous acid (in dilute hydrochloric acid) below  $10^{\circ}\text{C}$  and coupling the resulting diazonium salt with phenol is :



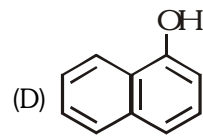
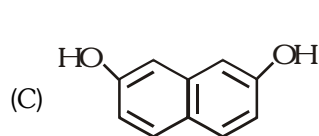
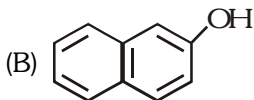
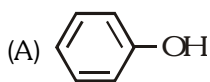
2. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives :

- (A) diphenyl ether  
(C) chlorobenzene

- (B) p-hydroxy azobenzene  
(D) benzene

3. The product which is a red azodye obtained on reacting benzene diazonium

chloride with one of the following compounds :



## Comprehension # 3

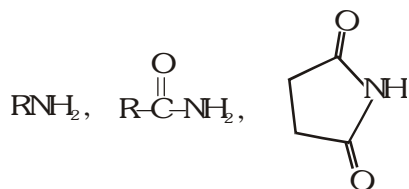
Amines are derivatives of ammonia and are classified as  $1^{\circ}$ ,  $2^{\circ}$ , and  $3^{\circ}$ . Primary and secondary (but not tertiary amines) form intermolecular hydrogen bonds and thus they boil at higher temperatures than expected. Like ammonia, all amines are basic, although they differ in their basic nature.

As amines are considered as derivatives of ammonia, quaternary ammonium salts are considered as derivatives of ammonium salts. Only the quaternary ammonium salts can show optical activity.

- Which of the following statement is correct ?  
 (A) All classes of amines form hydrogen bonds with each other  
 (B) Only primary and secondary amines form hydrogen bonds with water  
 (C) All classes of amines can form hydrogen bonds with water  
 (D) All amines are completely soluble in water
- When nitrogen is bonded to three different groups  
 (A) The molecule is optically inactive  
 (B) The molecule is tetrahedral  
 (C) The molecule is not superimposable on its mirror image  
 (D) The amine boils at nearly similar b.p as the 1°, and 2° amine of comparable molecular weight.
- Which of the following shows configurational isomerism ?  
 (A) Diethyldimethylammonium iodide (B) Dimethylpropylamine  
 (C) Methylallylphenylbenzyl ammonium bromide (D) None of these
- Methylethylpropyl amine is optically inactive because  
 (i) It is not tetrahedral  
 (ii) Its molecule is superimposable on its mirror image  
 (iii) The enantiomers are rapidly interconverted  
 (iv) The nitrogen is  $sp^2$  hybridized  
 Which of the above statement(s) is (are) true ?  
 (A) Only (i) (B) Only (iii) (C) (i) and (iii) (D) All the four

MISCELLANEOUS TYPE QUESTION	ANSWER KEY	EXERCISE -3
<ul style="list-style-type: none"> <li><b>True / False</b>            1. F      2. T      3. T      4. T      5. F            6. F      7. T         </li> <li><b>Fill in the Blanks</b>            1. Primary      2. ethyl amine      3. <math>LiAlH_4</math>            4. replaceable hydrogen      5. Stephen's reaction      6. hydroxyl amine            7. <math>CHCl_3</math>, KOH or NaOH         </li> <li><b>Match the Column</b>            1. (A) → r ; (B) → q ; (C) → s ; (D) → p      2. (A) → p ; B → s ; (C) → r ; (D) → q            3. (A) → p ; (B) → r ; (C) → q ; (D) → s         </li> <li><b>Assertion - Reason Questions</b>            1. C      2. B      3. C      4. B      5. B            6. C      7. B      8. C      9. D      10. A         </li> <li><b>Comprehension Based Questions</b>            Comprehension #1 : 1. (B)      2. (A)      3. (B)      4. (D)      5. (B)            Comprehension #2 : 1. (C)      2. (B)      3. (B)            Comprehension #3 : 1. (C)      2. (C)      3. (C)      4. (B)         </li> </ul>		

1. Arrange the following in decreasing basic order with proper reasoning.



2. Sulphanilic acid is not soluble in organic solvents. Explain ?

3. What is the order of basicity of the following compounds ?

(I)  $\text{CH}_3\text{NH}_2, (\text{CH}_3)_2\text{NH}, (\text{CH}_3)_3\text{N}$  (in aprotic solvent)

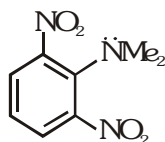
(II)  $\text{C}_2\text{H}_5\text{NH}_2, (\text{C}_2\text{H}_5)_2\text{NH}, (\text{C}_2\text{H}_5)_3\text{N}$  (in aprotic solvent)

4. What is the order of basicity of the following compounds ?

(I)  $\text{CH}_3\text{NH}_2, (\text{CH}_3)_2\text{NH}, (\text{CH}_3)_3\text{N}$  (in protic solvent)

(II)  $\text{C}_2\text{H}_5\text{NH}_2, (\text{C}_2\text{H}_5)_2\text{NH}, (\text{C}_2\text{H}_5)_3\text{N}$  (in protic solvent)

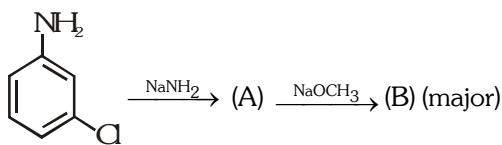
5. Unlike other aromatic amines, why is the following amine strongly basic ?



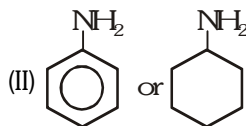
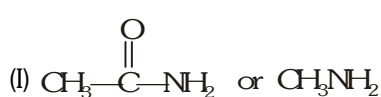
6. In this compound  $\text{OH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$  which site acts as an acid and which as a base ?

7. Alkyl cyanides ( $\text{CH}_3\text{CN}$ ) when treated with hydrogen in presence of Pt or with  $\text{LiAlH}_4$  produces same carbon number compound. What is the formula of that compound ?

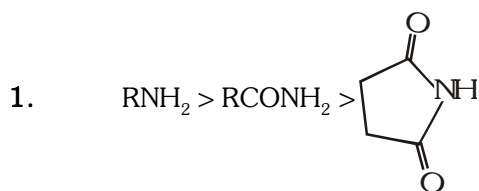
8. Write the compound (A) and (B) formed in this



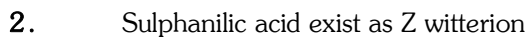
9. Identify the stronger base in each of the following pairs :



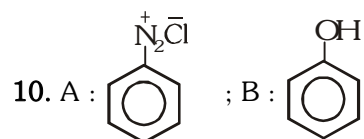
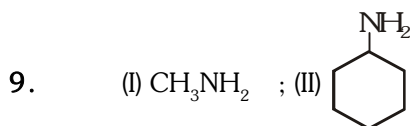
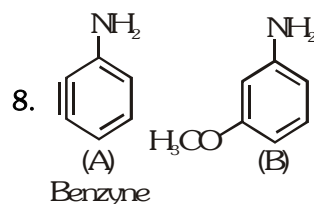
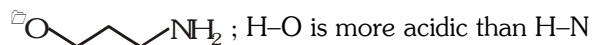
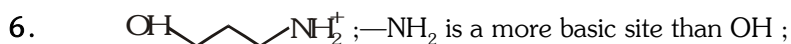
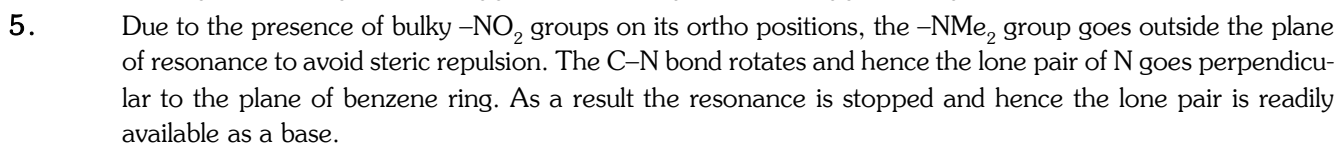
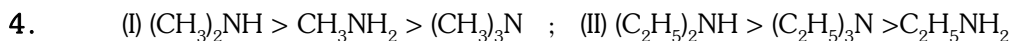
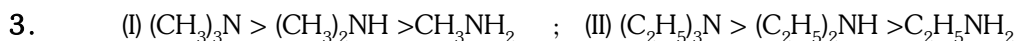
10.  $\xrightarrow[0-5^\circ\text{C}]{\text{NaNO}_2/\text{HCl}}$  A  $\xrightarrow[\text{H}_2\text{O}]{\text{warm}}$  B ; what are A & B ?



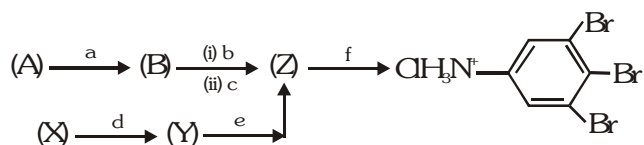
the lone pair of electrons on N is accommodated by  $\text{sp}^3$  hybrid atomic orbital in  $\text{RNH}_2$  and does not involve in resonance, whereas in  $\text{RCONH}_2$  and succinamide the lone pair of  $-\text{NH}_2$  is delocalised.



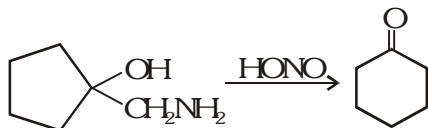
Due to its ionic character it is insoluble in organic solvents.



- An organic compound (A) composed of C, H and O gives characteristic colour with ceric ammonium nitrate. On treatment with  $\text{Na}_2\text{S}_2\text{O}_5$  gives (B), which reacts with KCN to form (C). The reduction of (C) with warm  $\text{Na}/\text{C}_2\text{H}_5\text{OH}$  produces (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.
- Compound (A) having M.F.  $\text{C}_8\text{H}_8\text{O}$  on treatment with  $\text{NH}_2\text{OH} \cdot \text{HCl}$  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  $\text{C}_8\text{H}_9\text{NO}$ . When (D) is boiled with alcoholic KOH, an oil (F)  $\text{C}_6\text{H}_7\text{N}$  separated out. (F) reacts rapidly with  $\text{CH}_3\text{COCl}$  to give back (D). On the other hand, (E) on boiling with alkali followed by acidification gives a white solid (G),  $\text{C}_7\text{H}_6\text{O}_2$ . Identify the compounds (A) to (G).
- Two isomeric compounds (A) and (B) have  $\text{C}_4\text{H}_{11}\text{N}$  as molecular formula. Both on separately treating with  $\text{HNO}_2$  lose their  $\text{N}_2$  producing two isomeric alcohols (C) and (D) respectively of molecular formula  $\text{C}_4\text{H}_{10}\text{O}$ . (C) reacts with Lucas reagent immediately and undergoes oxidation. (D) does not react with Lucas reagent in cold but can be easily oxidized. Complete methylation of either (A) or (B) is made which on decomposition does not produce 1-butene. Identify A to D.
- A 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 ( $\text{C}_7\text{H}_5\text{N}$ ) associated with an unpleasant odour. The alkaline aqueous layer on the other hand, when heated with chloroform and then acidified gave a mixture of two isomeric compounds D and E of molecular formula  $\text{C}_7\text{H}_6\text{O}_2$ . Identify the compound A, B, C, D and E write their structures.
- Give structures of (A), (B), (X), (Y) in the given scheme of reactions, if reagents a, b, c, d, e and f are  $\text{Br}_2/\text{CH}_3\text{COOH}$ ,  $\text{NaNO}_2/\text{H}_2\text{SO}_4$ ,  $\text{CuBr}$ ,  $\text{HNO}_3/\text{H}_2\text{SO}_4$ ,  $\text{Br}_2/\text{Fe}$  and  $\text{Sn}/\text{HCl}$  respectively.



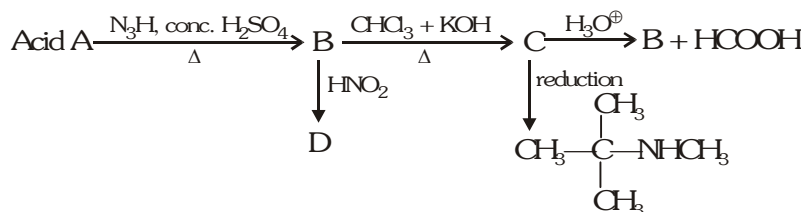
- Explain the mechanism of the following change :



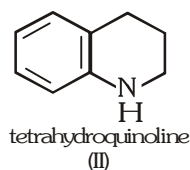
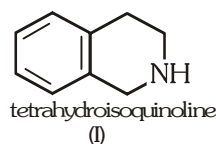
- $$\text{CH}_3\text{CH}_2\text{N}^+\text{CH}_3 \text{---} \text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\Delta} \text{A} + \text{B} + \text{C}$$
 Identify A, B (both alkene) and C.

- Write isomeric amines of the formula  $\text{C}_3\text{H}_9\text{N}$ .

- Identify A, B, C and D.



10. The two amines shown differ by a factor of about 40,000 in their ionisation constants. Which is stronger base? Explain:

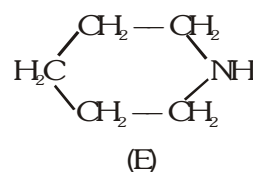
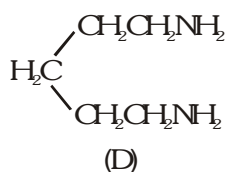
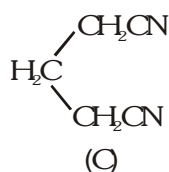
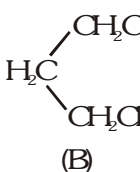
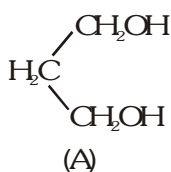


BRAIN STORMING SUBJECTIVE EXERCISE

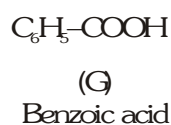
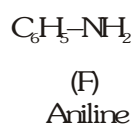
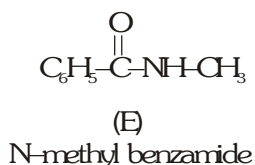
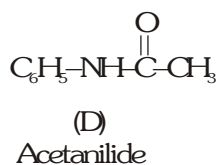
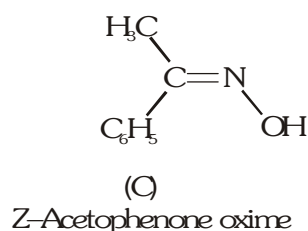
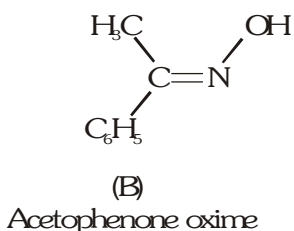
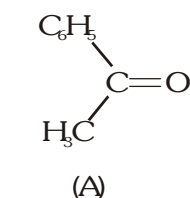
ANSWER KEY

EXERCISE -4(B)

1.



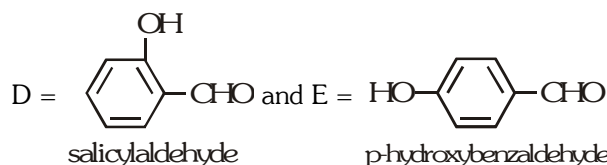
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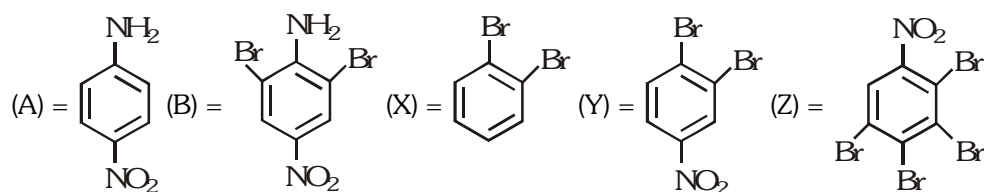
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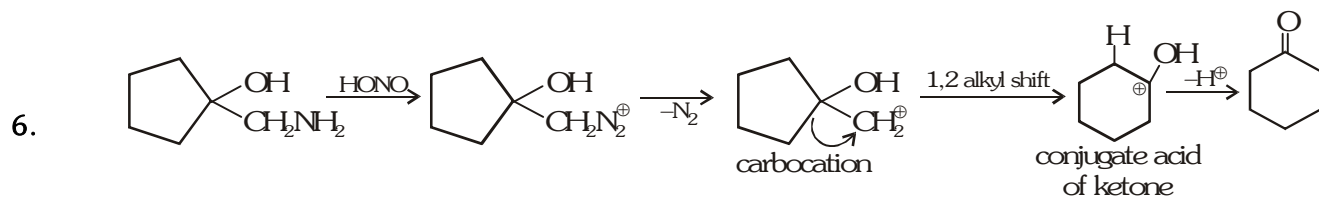


4.

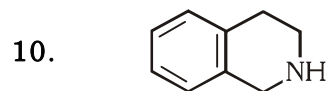
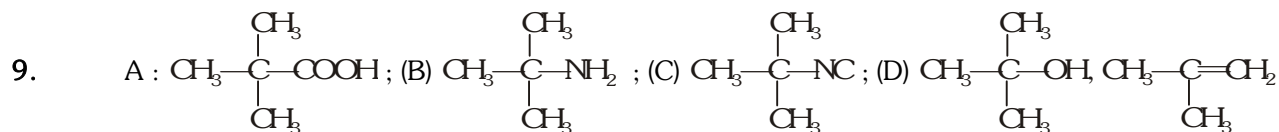
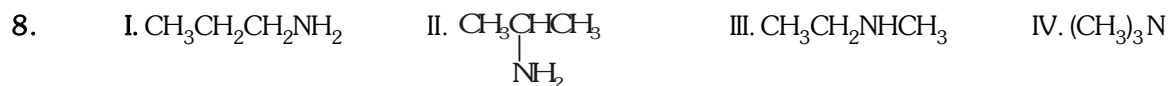
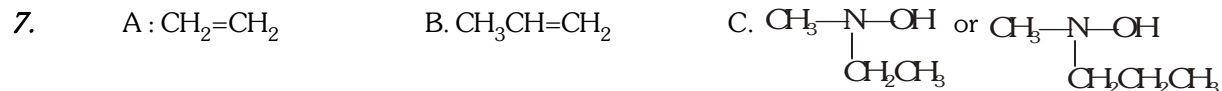


5.





Thus, it involves pinacol-type ring expansion via the carbocation.

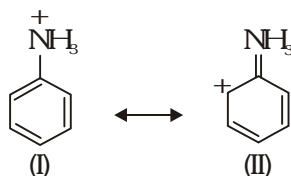


tetrahydroisoquinoline

is a stronger base. In tetrahydroquinoline (II), lone-pair on nitrogen is used in delocalisation of  $\pi$ -electrons of benzene ring hence, basicity of II is decreased. I resembles aliphatic amine II resembles aniline.



- Among the following compounds, which will react with acetone to give a product containing  $>C=N-$ ?  
 (A)  $C_6H_5NH_2$  (B)  $(CH_3)_3N$  [IIT-90]  
 (C)  $C_6H_5NHC_6H_5$  (D)  $C_6H_5NHNH_2$
- The compound that will react most readily with NaOH to form methanol is [IIT-90]  
 (A)  $(CH_3)_4N^+I^-$  (B)  $CH_3OCH_3$  (C)  $(CH_3)_3S^+I^-$  (D)  $(CH_3)_3CCl$
- Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below : [IIT-93]



- II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions
  - II is not an acceptable canonical structure because it is non-aromatic
  - II is not an acceptable canonical structure because the nitrogen has ten valence electrons
  - Both (A) & (C)
- Allyl isocyanide contains  $\sigma$  and  $\pi$  bonds are - [IIT-95]  
 (A)  $9\sigma$  and  $3\pi$  (B)  $9\sigma$  and  $9\pi$  (C)  $3\sigma$  and  $4\pi$  (D)  $5\sigma$  and  $7\pi$
- Nitrobenzene can be prepared from benzene by using a mixture of conc.  $HNO_3$  and conc.  $H_2SO_4$ . In the nitrating mixture, nitric acid acts as - [IIT-97]  
 (A) base (B) acid (C) reducing agent (D) catalyst
- Among following statements on the nitration of aromatic compounds, the false one is - [IIT-97]  
 (A) the rate of nitration of benzene is almost the same as that of hexadeuterobenzene  
 (B) the rate of nitration of toluene is greater than that of benzene  
 (C) the rate of nitration of benzene is greater than that of hexadeuterobenzene  
 (D) nitration is an electrophilic substitution reaction.
- p-Chloroaniline and anilinium hydrochloride can not be distinguished by [IIT-98]  
 (A) Sandmeyer reaction (B)  $NaHCO_3$  (C)  $AgNO_3$  (D) Carbylamine test
- Read the following statement and explanation and answer as per the option given below : [IIT-98]  
**Statement I :** Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide  
**Because**  
**Statement II :** Cyanide ( $CN^-$ ) is a strong nucleophile  
  - If both assertion and reason are correct, and reason is the correct explanation of the assertion
  - If both assertion and reason are correct, but reason is not correct explanation of the assertion
  - If assertion is correct but reason is incorrect
  - If assertion is incorrect but reason is correct
- Benzenediazonium chloride on reaction with phenol in weakly basic medium gives [IIT-98]  
 (A) Diphenyl ether (B) p-Hydroxyazobenzene  
 (C) Chlorobenzene (D) Benzene

10. A positive carbylamine test is given by [IIT-99]  
 (A) N, N-Dimethylaniline (B) 2, 4-Dimethylaniline  
 (C) N-Methyl-o-methylaniline (D) o-methylbenzylamine

11. Among the following, the strongest base is : [IIT-2000]  
 (A)  $C_6H_5NH_2$  (B)  $p\text{-NO}_2\text{-C}_6\text{H}_4\text{NH}_2$  (C)  $m\text{-NO}_2\text{-C}_6\text{H}_4\text{NH}_2$  (D)  $C_6H_5CH_2NH_2$

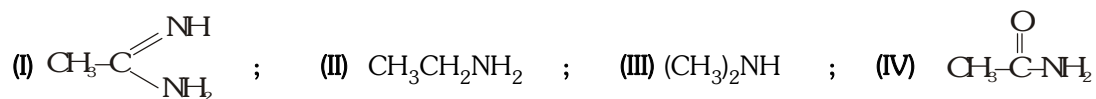
12. Read the following statement and explanation and answer as per the option given below : [IIT-01]

**Statement I** : In strongly acidic solutions, aniline becomes less reactive towards electrophilic reagents.

**Beacuse**

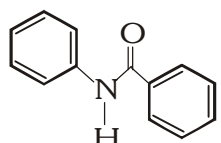
**Statement II** : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

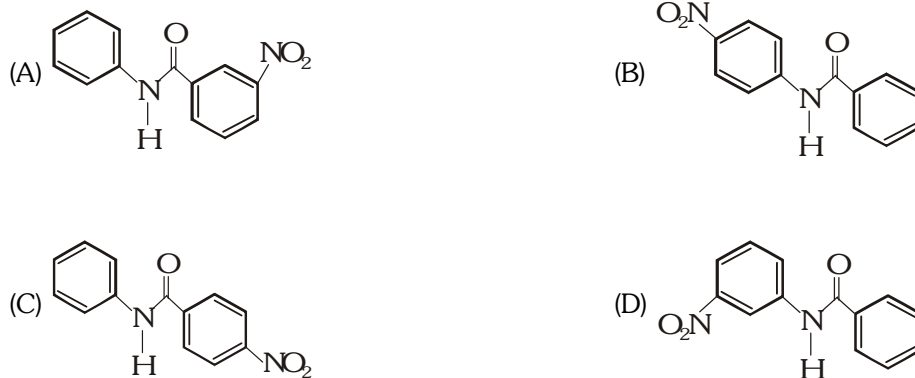
- (A) If both assertion and reason are correct, and reason is the correct explanation of the assertion  
 (B) If both assertion and reason are correct, but reason is not correct explanation of the assertion  
 (C) If assertion is correct but reason is incorrect  
 (D) If assertion is incorrect but reason is correct
13. The correct order of basicities of the following compounds is - [IIT-01]



- (A) II > I > III > IV (B) I > III > II > IV (C) III > I > II > IV (D) I > II > III > IV
14. When benzamide is treated with  $\text{POCl}_3$ , the product formed is : [IIT-04]  
 (A) Benzonitrile (B) Aniline (C) Chlorobenzene (D) Benzylamine

15.  $\text{CH}_3\text{NH}_2 + \text{CHCl}_3 \xrightarrow{\text{KOH}}$  Product, Product is- [IIT-06]  
 (A)  $\text{CH}_3\text{-N}^+\equiv\text{C}^-$  (B)  $\text{CH}_3\text{-N}^+\equiv\text{C}^+$  (C)  $\text{CH}_3\text{-NH-CH}_3$  (D)  $\text{CH}_3\text{-C}\equiv\text{N}$

16. In the following reaction,  X, the structure of the major product 'X' is -



[IIT-07]

17. An aromatic compound contains 69.4% carbon and 5.8% hydrogen. A sample of 0.303 g of this compound was analysed for nitrogen by Kjeldahl's method. The ammonia evolved was absorbed in 50ml of 0.05 M sulphuric acid. The excess of acid required 25 ml of 0.1 M sodium hydroxide for neutralization. Determine the molecular formula of the compound if its molecular weight is 121. Draw two possible structures for this compound. [IIT-82]

18. Compound 'X' containing chlorine, on treatment with  $\text{NH}_3$  gives a solid 'Y' which is free from chlorine. (Y) analysed as C = 49.31%, H = 9.59% and N = 19.18% and reacts with  $\text{Br}_2$  and caustic soda to give a basic compound (Z), (Z) reacts with  $\text{HNO}_2$  to give ethanol. Suggest structure for (X), (Y) and (Z).

[IIT-88]

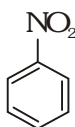
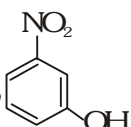
19. Show with equations how the following compounds are prepared (equations need not be balanced) :

(i) 4-nitroaniline to 1, 2,3-tribromobenzene.

[IIT-90]

(ii) Aniline  $\longrightarrow$  Benzylamine (in 3 steps)

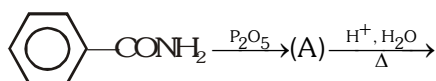
[IIT-2000]

(iii) Convert  to  in not more than four steps.

[IIT-04]

20. Complete the following with appropriate structures :

[IIT-92]

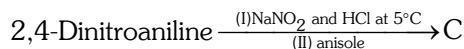


21. The aqueous solution of a nitrogen and chlorine containing compound (A) is acidic to litmus. (A) on treatment with aqueous NaOH gives a compound (B) containing nitrogen, but not chlorine. Compound (B) on treatment with  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$  in presence of NaOH gives an insoluble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

[IIT-93]

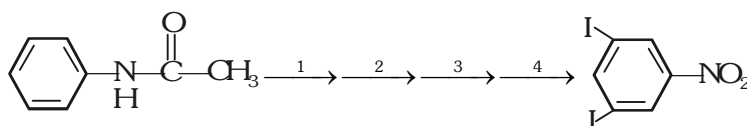
22. Complete the following with appropriate structures :

[IIT-95]



23. Complete the following reaction with appropriate reagents :

[IIT-99]

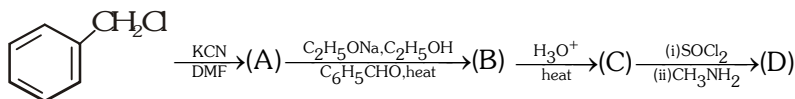


24. Compound (A),  $\text{C}_5\text{H}_{11}\text{NO}$  is not soluble in cold alkaline or acidic solutions. When (A) is refluxed in NaOH solution, a gas (B) is evolved and salt (C) is formed. Acetyl chloride reacts with (B) to give (D), ( $\text{C}_4\text{H}_9\text{NO}$ ). (B) reacts with  $\text{HNO}_2$  to give a yellow oil (E). Give structures of (A) to (E) with reason.

[IIT-99]

25. Identify (A) to (D) in the following series of reactions :

[IIT - 04]



26.  $\text{C}_5\text{H}_{13}\text{N}$  (optically active)  $\xrightarrow[\text{-N}_2]{\text{aq. NaNO}_2 / \text{HCl}}$  Y (Tertiary alcohol) + Some other products

[IIT-05]

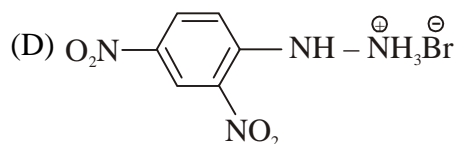
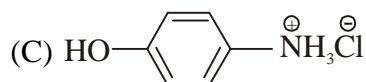
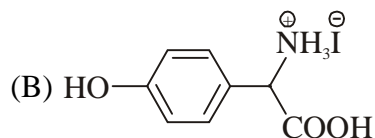
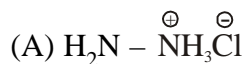
(i) Identify (X) and (Y)

(ii) Is (Y) optically active ?

(iii) Give structure (s) of intermediate (s), if any, in the formation of (Y) from (X).

27. 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 given in the ORS.

**Column I**



**Column II**

[IIT 2008]

(P) sodium fusion extract of the compound gives Prussian blue colour with  $\text{FeSO}_4$

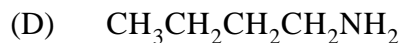
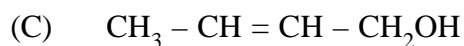
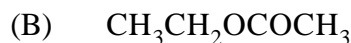
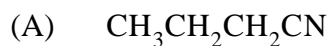
(Q) gives positive  $\text{FeCl}_3$  test

(R) gives white precipitate with  $\text{AgNO}_3$

(S) reacts with aldehydes to form the corresponding hydrazone derivative

28. Match each of the compound in Column I with its characteristic reaction(s) in Column II.

**Column I**



**Column II**

[IIT 2009]

(P) Reduction with  $\text{Pd-C} / \text{H}_2$

(Q) Reduction with  $\text{SnCl}_2 / \text{HCl}$

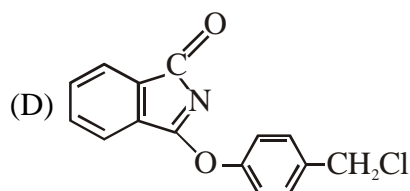
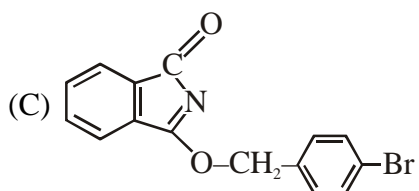
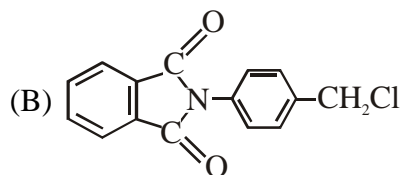
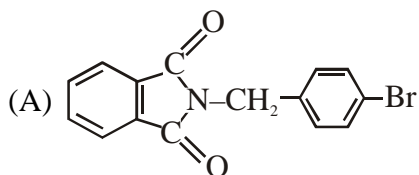
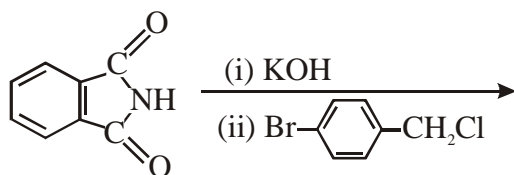
(R) Development of foul smell on treatment with chloroform and alcoholic  $\text{KOH}$

(S) Reduction with diisobutylaluminium hydride (DIBAL - H)

(T) Alkaline hydrolysis

29. The major product of the following reaction is

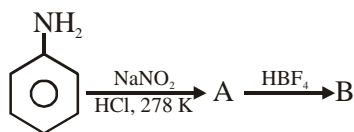
[IIT 2011]



## EXERCISE-05[B]

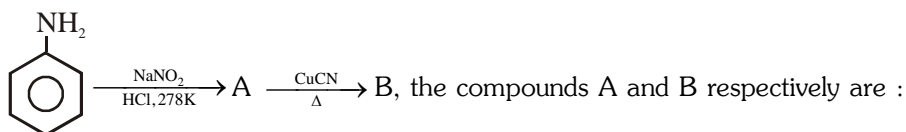
## PREVIOUS YEARS QUESTIONS

1. Reaction - [AIEEE-2002]  
 Primary amine +  $\text{CHCl}_3 + \text{KOH} \rightarrow$  product, here product will be -  
 (1) Cyanide (2) Isocyanide (3) Amine (4) Alcohol
2. The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is- [AIEEE-2004]  
 (1)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  (2)  $\text{Na}_3[\text{Fe}(\text{CN})_6]$  (3)  $\text{Fe}(\text{CN})_3$  (4)  $\text{Na}_4[\text{Fe}(\text{CN})_5]\text{NOS}$
3. Which one of the following methods is neither meant for the synthesis nor for separation of amines- [AIEEE-2005]  
 (1) Hofmann method (2) Hinsberg method (3) Curtius reaction (4) Wurtz reaction
4. In the chemical reaction,  $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow (\text{A}) + (\text{B}) + 3\text{H}_2\text{O}$ , the compounds (A) and (B) are respectively - [AIEEE-2007]  
 (1)  $\text{C}_2\text{H}_5\text{CN}$  and  $3\text{KCl}$  (2)  $\text{CH}_3\text{CH}_2\text{CONH}_2$  and  $3\text{KCl}$   
 (3)  $\text{C}_2\text{H}_5\text{NC}$  and  $\text{K}_2\text{CO}_3$  (4)  $\text{C}_2\text{H}_5\text{NC}$  and  $3\text{KCl}$
5. In the chemical reactions, [AIEEE-2010]



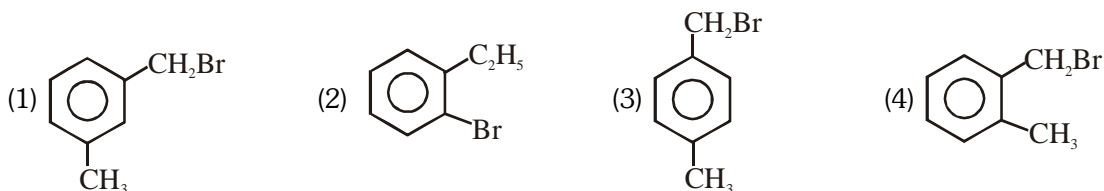
the compounds 'A' and 'B' respectively are :-

- (1) Nitrobenzene and chlorobenzene (2) Nitrobenzene and fluorobenzene  
 (3) Phenol and benzene (4) Benzene diazonium chloride and fluorobenzene
6. In the chemical reactions



[AIEEE-2011]

- (1) Fluorobenzene and phenol (2) Benzene diazonium chloride and benzonitrile  
 (3) Nitrobenzene and chlorobenzene (4) Phenol and bromobenzene
7. Compound (A),  $\text{C}_8\text{H}_9\text{Br}$ , gives a white precipitate when warmed with alcoholic  $\text{AgNO}_3$ . Oxidation of (A) gives an acid (B),  $\text{C}_8\text{H}_6\text{O}_4$ . (B) easily forms anhydride on heating. Identify the compound (A): [AIEEE-2013]

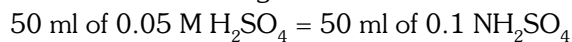


8. An organic compound A upon reacting with  $\text{NH}_3$  gives B. On heating, B gives C. C in presence of  $\text{KOH}$  reacts with  $\text{Br}_2$  to give  $\text{CH}_3\text{CH}_2\text{NH}_2$ . A is :- [AIEEE-2013]  
 (1)  $\text{CH}_3\text{COOH}$  (2)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$  (3)  $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{COOH}$  (4)  $\text{CH}_3\text{CH}_2\text{COOH}$

1. (D)    2. (C)    3. (C)    4.(A)    5. (A)    6. (C)    7.(C)    8. (D)    9. (B)

10. (B,D)    11. (D)    12. (A)    13. (B)    14. (A)    15. (A)    16. (B)

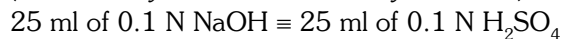
17. Calculation of % nitrogen



( $\therefore$  Normality of  $\text{H}_2\text{SO}_4$ ) = 2  $\times$  molarity)

Excess of acid requires 25 ml of 0.1 M or 0.1 N NaOH

( $\therefore$  Normality of NaOH = molarity of NaOH)

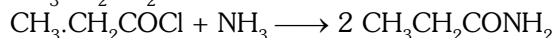


$\therefore$  vol. of 0.1  $\text{N H}_2\text{SO}_4$  used for the neutralisation of  $\text{NH}_3 = 50 - 25 = 25 \text{ ml}$

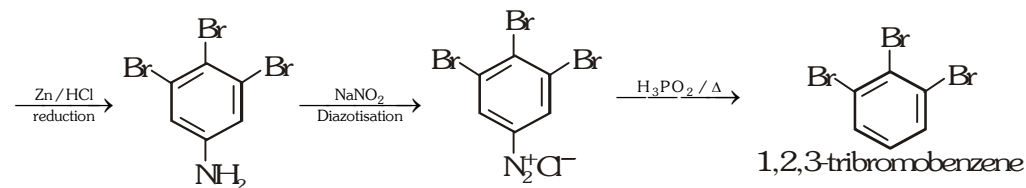
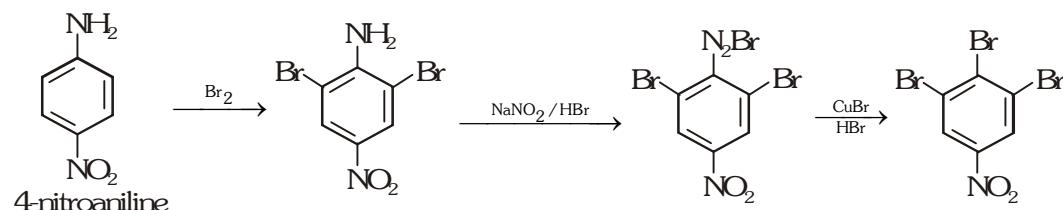
$$\text{Now we know that, \% of nitrogen} = \frac{1.4 \times \text{Normality of acid} \times \text{Vol. of acid}}{\text{Wt. of compound}}$$

$$= \frac{1.4 \times 0.1 \times 25}{0.303} = 11.55\% ; \text{Hence \% of oxygen} = 100 - (69.4 + 5.8 + 11.55) = 13.25$$

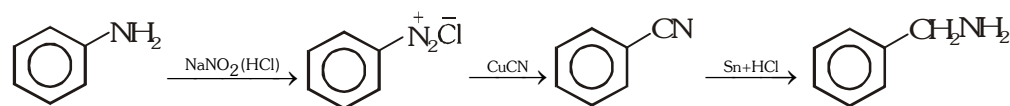
18. Empirical formula of (Y) is  $\text{C}_3\text{H}_7\text{NO}$



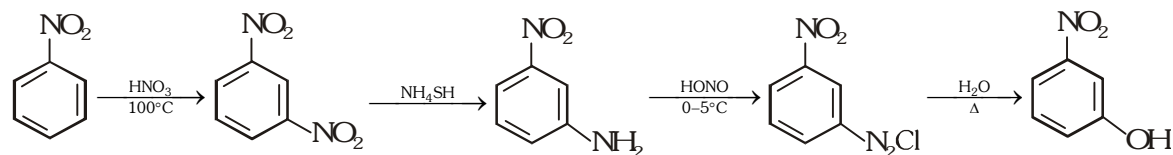
19. (i)



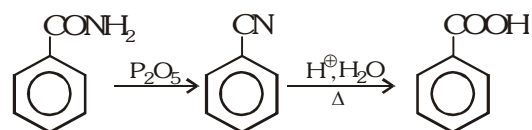
(ii)



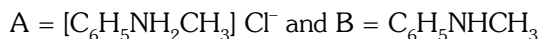
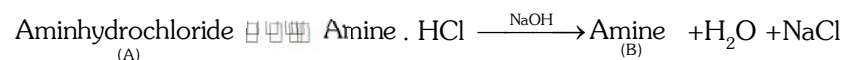
(iii)

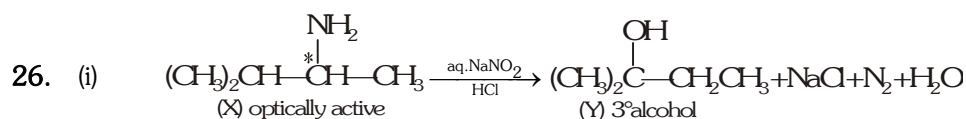
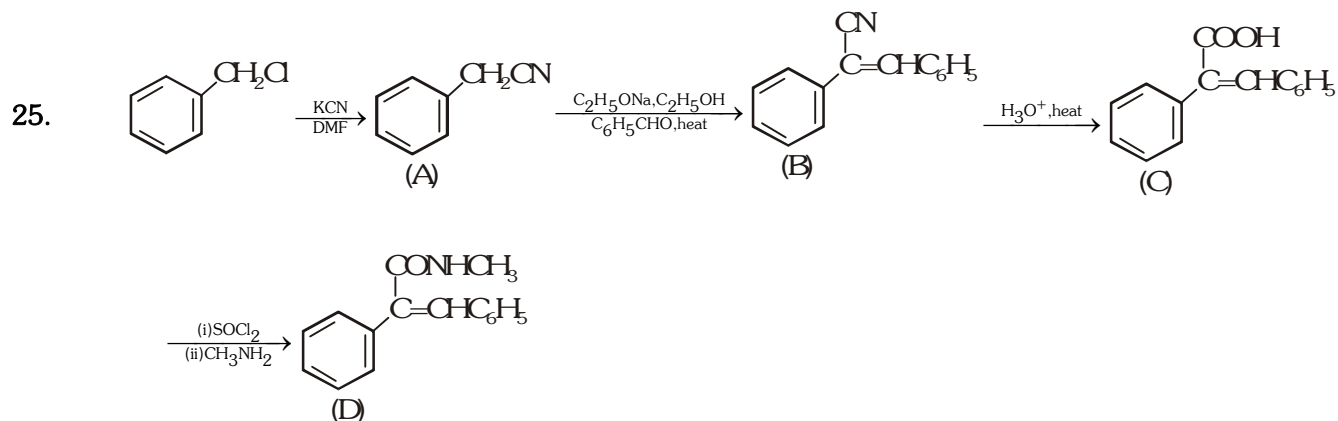
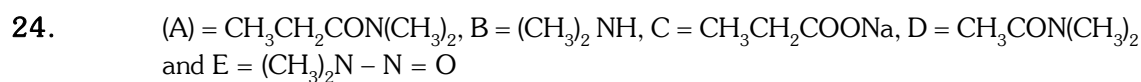
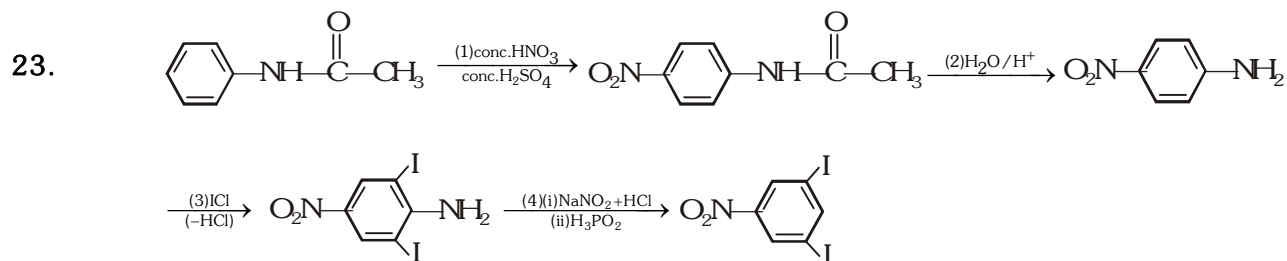
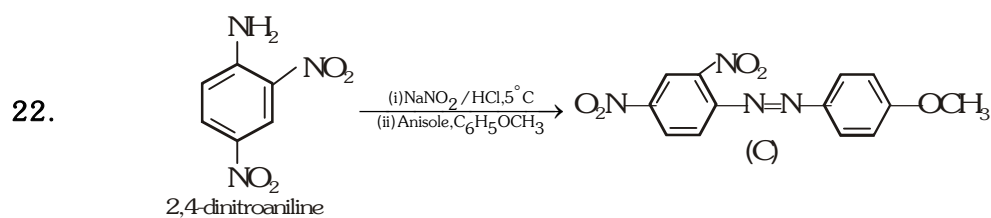


20.



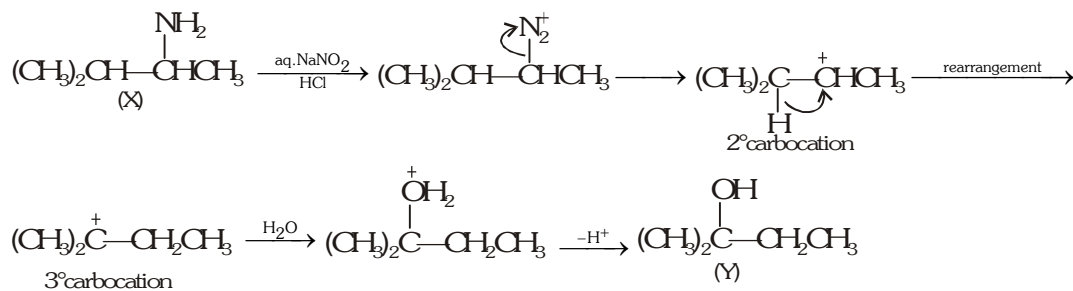
21.





(ii) [Y], a 3° alcohol is optically inactive

(iii) Formation of [Y] from [X]



27. (A) R, S; (B) P, Q; (C) P, Q, R; (D) P, S

28. (A) P, Q, S, T (B) P, S, T (C) P (D) R

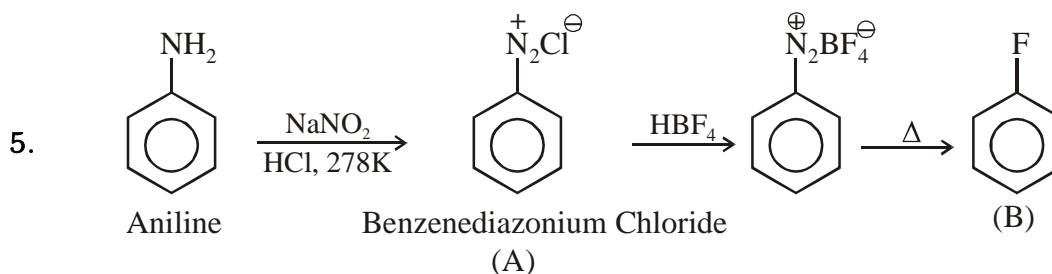
29. A

1. 2      2. 1      3. 4      4. 4      5. 4      6. 2  
 7. 4      8. 4

1. Carbylamine Test

3. Wurtz reaction  $R\text{Cl} \xrightarrow[\text{dry ether}]{Na} R-R + NaX$

4. Isocyanide test (carbylamine test). Pungent smelling isocyanide is formed as a major product.



Sandmeyer's Reaction

