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

$RCN \xrightarrow{\text{reduction}} (A)$, $RCN \xrightarrow[(ii)H_2O]{(i)CH_3MgBr} (B)$, $RNC \xrightarrow{\text{hydrolysis}} (C)$, $RNH_2 \xrightarrow{HNO_2} (D)$

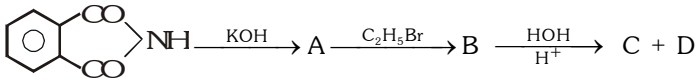
The answer is :

	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

4. 

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) Ethylmethylamine

(C) 1–propanamine (D) N, N–dimethylmethanamine

6. How many primary amines can be formulated by C_3H_9N 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

$C_2H_5MgBr \xrightarrow{ClCN} A \xrightarrow{H_3O^+} \boxed{B}$,

$CH_3COCH_3 \xrightarrow[NaOH]{I_2} \boxed{X} \xrightarrow{Ag} Y$

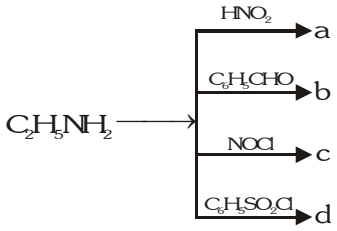
$C_6H_5NH_2 \xrightarrow[HCl]{NaNO_2} P \xrightarrow{CuCN} Q \xrightarrow{+4H} \boxed{R}$

(A) C_2H_5COOH, CHI_3, $C_6H_5CH_2NH_2$

(B) C_2H_5COOH, CH_3I, C_6H_5COOH

(C) $C_2H_5CH_2NH_2$, CH_3I, C_6H_5COOH

(D) C_2H_5COOH, C_2H_5I, $C_6H_5CONH_2$

8. 

Which product is a Schiff's base :-

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

9. A + CS_2 + $HgCl_2$ gives $C_2H_5-N=C=S$. Thus compound A is :-

(A) $C_2H_5NH_2$ (B) $C_2H_5NHC_2H_5$ (C) $CH_3-CH=NOH$ (D) $CH_3CH_2NO_2$

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

Ethyl amine $\xrightarrow{HNO_2}$ A $\xrightarrow{PCl_5}$ B $\xrightarrow{NH_3}$ C

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

11. In the reaction sequence :-

A $\xrightarrow{SnCl_2/HCl}$ B $\xrightarrow[0^\circ]{NaNO_2/HCl}$ C $\xrightarrow{H_2O/\Delta}$ C_6H_5OH, A, B and C are :-

(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_3NCO (B) CH_3CNO (C) CH_3CN (D) CH_3NC

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

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

14. $CH_3CH_2CONH_2 \xrightarrow[Br_2]{NaOH}$ 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) $-CH_2OH$, $>CHOH$, $\rightarrow C-OH$

(C) $-O-$, $-OH$ (D) $-NH_2$, $-NH-$, $\rightarrow N$

16. Reactants of reaction - I are : CH_3CONH_2, KOH, Br_2

Reactants of reaction-II are : CH_3NH_2, $CHCl_3$, 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) $(CH_3)_2NH$ (C) CH_3NH_2 (D) Phenylamine

18. (a) $CH_3CONH_2 + KOH + Br_2 \longrightarrow$

(b) CH_3COOH + soda lime $\longrightarrow$

(c) $CH_3COOAg + Br_2 \longrightarrow$

All the three reactions show similarity in -

(A) Descending of carbon atoms (B) Ascending of carbon atoms

(C) Both the above (D) None of the above

19. Which of the following reagents can convert benzenediazonium chloride into benzene ?

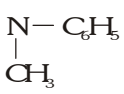
(A) Water (B) Acid (C) Hypophosphorous acid (D) HCl

20. Hofmann's method to separate amines in a mixture uses the reagent :-

(A) Benzenesulphonyl chloride (B) Diethyl oxalate

(C) Benzeneisocyanide (D) p–toluenesulphonic acid

21. Which of the following compounds will dissolve in an alkali solution after it has undergone reaction with Hinsberg reagent ?

(A) $(C_2H_5)_2NH$ (B)  (C) CH_3NH_2 (D) $C_6H_5NHC_6H_5$

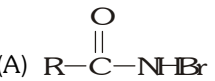
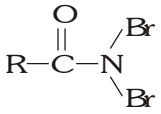
22. The number of resonating structures of aniline is :-

(A) 2 (B) 3 (C) 4 (D) 5

23. How many isomeric amines with formula C_7H_9N contain a benzene ring ?

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

24. Reaction of $RCONH_2$ with a mixture of Br_2 and KOH gives RNH_2 as the main product. The intermediate involved in the reaction is :-

(A)  (B) R – NHBr (C)  (D) R – C = N = O

25. The bromination of aniline in water produces :-

(A) 2-bromoaniline (B) 4-bromoaniline

(C) 2, 4, 6-tribromoaniline (D) 2, 6-dibromoaniline

CHECK YOUR GRASP				ANSWER KEY								EXERCISE -1								
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	A	B	C	B	D	D	A	B	A	B	B	D	B	B	D	B	B	A	C	B
Que.	21	22	23	24	25															
Ans.	C	D	D	A	C															

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 halie 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) PCl_5 (B) Sodalime
   (C) $NaOH + Br_2$ (D) Hot concentrated H_2SO_4

3. Maximum basic in gas phase is ?
   (A) NH_3 (B) $CH_3CH_2NH_2$ (C) $(CH_3CH_2)NH$ (D) $(CH_3CH_2)_3N$

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 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 NH_2 group
   (C) During the replacement of halogen by $-NH_2$ 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 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,

$C_6H_5NH_2 + CHCl_3 + KOH \xrightarrow{\Delta} (A) \xrightarrow{H^+/H_2O} (B) + (C)$

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

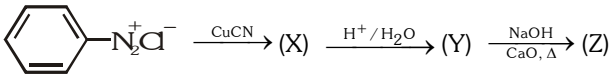
(A) C_6H_5COOH and NH_3 respectively (B) $C_6H_5NH_2$ and HCOOH respectively

(C) $C_6H_5NH_2$ and H_2O respectively (D) None of these

10. $CH_3CH_2NH_2$ is soluble in :-

(A) Dilute HCl (B) $CuSO_4$ solution (C) $AgNO_3$ (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 RCN, RCH = NR and RNH_2 is :-

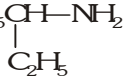
(A) RCN < RCH = NR < RH_2N (B) RNH_2 < RCN < RCH = NR

(C) RCH = NR < RNH_2 < RCN (D) RH_2N < RCH = NR < RCN

13. Amongst the following, the most basic compound is :-

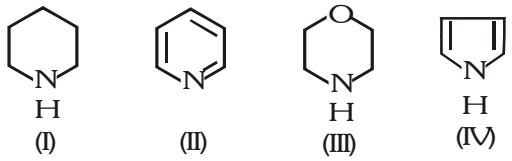
(A) Benzylamine (B) Aniline (C) Acetanilide (D) p–nitroaniline

14. isocyanide test can be given by :

(A) $C_2H_5NH_2$ (B) $C_6H_5NH_2$ (C) $C_6H_5NHC_2H_5$ (D) 

(D) II is an acceptable canonical structure

15. In the following compounds



(I) (II) (III) (IV)

the order of basicity is

(A) IV > I > III > II (B) III > I > IV > II

(C) II > I > III > IV (D) I > III > II > IV

16. A positive carbylamine test is not given by :

(A) N, N-dimethylaniline (B) 2, 4-hyroxyazobenzene

(C) N-methyl-o-methylaniline (D) p-methylbenzylamine

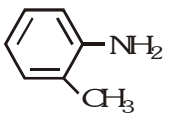
17. Among the following, the strongest base is

(A) $C_6H_5NH_2$ (B) p-$NO_2C_6H_4NH_2$

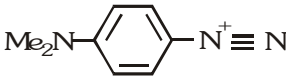
(C) m-$NO_2C_6H_4NH_2$ (D) $C_6H_5CH_2NH_2$

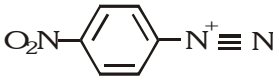
18. Phenyl cyanide on reduction with Na/C_2H_5OH yields

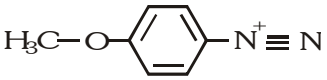
(A) $C_6H_5CH_2NH_2$ (B) $C_6H_5NHCH_3$

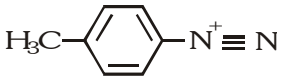
(C)  (D) $C_6H_5NH_2$

19. Conisider the following ions

(I) 

(II) 

(III) 

(IV) 

The reactiveities of these ions in azo-coupling reaction (under similar conditions) will be such that

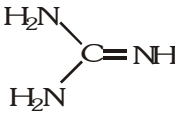
(A) (I) < (IV) < (II) < (III)

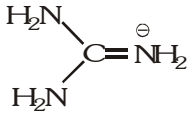
(B) (I) < (III) < (IV) < (II)

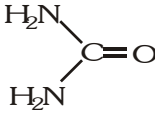
(C) (III) < (I) < (II) < (IV) < (II)

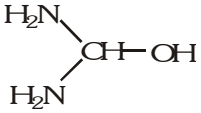
(D) (III) < (I) < (IV) < (II)

20. The strongest base among the following is

(A) 

(B) 

(C) 

(D) 

BRAIN TEASERS						ANSWER KEY									EXERCISE -2
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	B	C	D	B	A,C,D	A,B,D	A,C,D	A	B	A,B,C	D	A	A	A,B,D	D
Que.	16	17	18	19	20										
Ans.	A,B,C	D	A	B	A										

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 soluiton.
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. α-Amino acids on heating with $Ba(OH)_2$ shows decarboxylation to produce primary amines.

FILL IN THE BLANKS :

1. $(CH_3)_2CHNH_2$ is a ..... amine.
2. Methyl cyanide on reaction with sodium and C_2H_5OH forms .....
3. Acetamide on treatment with ..... forms ethyl amine.
4. Tertiary amines do not react with acetyl chloride since they to not have ..... on nitrogen.
5. The reaction RCN $\xrightarrow{SnCl_2/HCl}$ (A) $\xrightarrow{H_2O}$ RCHO + NH_4Cl, is known as .....
6. nitroalkanes when reduced with zinc dust and ammonium chloride form .....
7. Primary amines on heating with ..... and ..... form alkul isocyanides.

MATCH THE COLUMN

1. Match the column I with column II.

	Column-I		Column-II
(A)	$C_6H_5SO_2Cl$	(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)		(q)	Tertiary amine
(C)	RCOOH + N_3H + Conc. H_2SO_4	(r)	Schmidt reaction
(D)	R_3N	(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.

1. **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.

2. **Statement-I :** CN^- ion is an ambident nucleophile.

Because

Statement-II : Nucleophiles are electron rich species.

3. **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.

4. **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.

5. **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.

6. **Statement-I :** In Hoffmann bromide reaction, the amine formed has one carbon atom less than the parent 1 amide.

Because

Statement-II : N-methyl acetamide undergoes Hoffmann bromamide reaction.

7. **Statement-I :** Nitrobenzene does not undergo Friedel-Craft's alkylation.

Because

Statement-II : Nitrobenzene is used as solvent in laboratory and industry.

8. **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 $NaNH_2$/Liq. NH_3.

Because

Statement-II : $\overline{N}H_2$ ion is a stronger nucleophile.

10. **Statement-I :** Carbylamine reaction involves the reaction between 1 amine and chloroform in basic medium.

Because

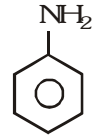
Statement-II : In carbylamine reaction, $-NH_2$ group is converted into –NC group via reaction with carbene intermediate.

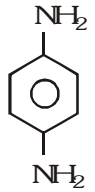
COMPREHENSION BASED QUESTIONS :

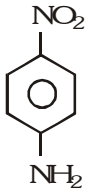
Comprehension # 1

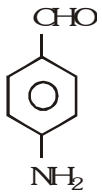
The origin of acidity and basicity in organic compound is great interest and provides an extensive comparison. Among hydrocarbons % s character is taken in acconut while to decide the acidity, in simple aliphatic acids, more the number of alkyl groups, (+I effect) less is the acidity & more the (– I effect) alkyl groups larger the acidity and vice-versa in the case of simple aliphatic bases. Benzoic acid is more stronge 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 -

(A) 

(B) 

(C) 

(D) 

2. Among the following compounds the strongest acid is

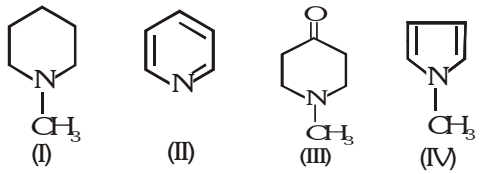
(A) HC ≡ CH (B) NH_3 (C) $C_2H_5NH_2$ (D) CH_3NH_2

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

((A) HCOOH < CH_3COOH < PhCOOH (B) HCOOH > PhCOOH > CH_3COOH

(C) HCOOH > CH_3COOH > PhCOOH (D) CH_3COOH > HCOOH > PhCOOH

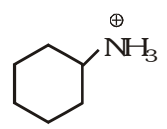
4. In the following compounds, the order of basicity

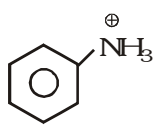


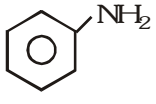
(I) (II) (III) (IV)

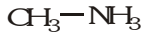
(A) IV > I > III > II (B) III > I > IV > II (C) II > I > III > IV (D) I > III > II > IV

5. Which of the following is most acidic

(A) 

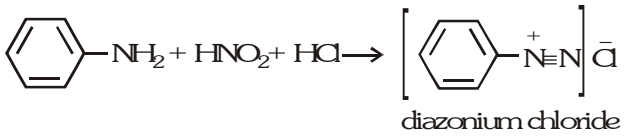
(B) 

(C) 

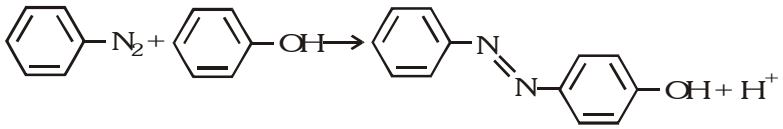
(D) 

Comprehension # 2

Diazonium salt formation and coupling reactions : When a reaction mixture of phenyl amine and nitrous acid is kept below 10°C, a diazonium salt is formed. This reaction is called diazotization reaction.

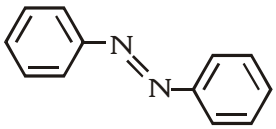


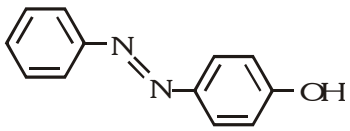
The diazonium ion, $-N_2^+$, is rather unstable and decomposes readily to nitrogen. However, delocalization of the diazonium from π-bond electron over a benzene ring stabilizes phenyl diazonium sufficiently for it to form at low temperatures. The phenyl diazonium ion behaves as an electrophile, and will 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.

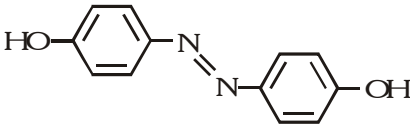


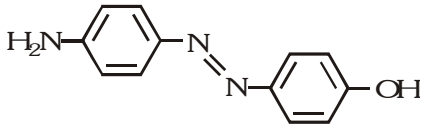
The compound formed is an energetically stable, yellow azo dye (the azo group is –N = N–). The stability is due to extensive delocalisation of electrons via the nitrogen- nitrogen double bonds.

1. The azo dye obtained on reacting 4-aminophenol with nitrous acid (in dilute hydrochloric acid) below 10°C and coupling the resulting diazonium salt with phenol is :

(A) 

(B) 

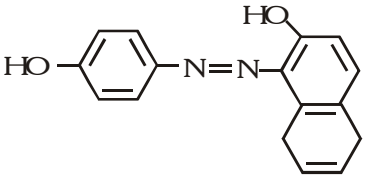
(C) 

(D) 

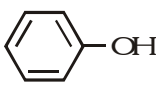
2. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives :

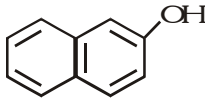
(A) diphenyl ether (B) p-hydroxy azobenzene

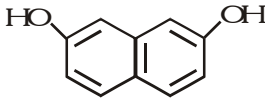
(C) chlorobenzene (D) benzene

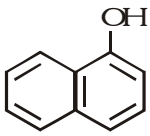
3. The product 

which is a red azodye obtained on reacting benzene diazonium chloride with one of the following compounds :

(A) 

(B) 

(C) 

(D) 

Comprehension # 3

Amines are derivatives of ammonia and are classified as 1°, 2°, and 3°. Primary and secondary (but not tertiary amines) form intermolecular hydrogen bonds and thus they boil at highter 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 shown optical activity.

1. Which of the follwoing 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

2. When nitrogen is bounded 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.

3. Which of the following shows configurational isomerism ?

(A) Diethyldimethylammonium iodide (B) Dimethylpropylamine

(C) Methylallylphenylbenzyl ammonium bromide (D) None of these

4. 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

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MISCELLANEOUS TYPE QUESTION **ANSWER KEY** EXERCISE -3

- ***True / False***

1. F **2.** T **3.** T **4.** T **5.** F

6. F **7.** T

- ***Fill in the Blanks***

1. Primary **2.** ethyl amine **3.** $LiAlH_4$

4. replaceable hydrogen **5.** stephen's reaction **6.** hydroxyl amine

7. $CHCl_3$,KOH or NaOH

- ***Match the Column***

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

- ***Assertion - Reason Questions***

1. C **2.** B **3.** C **4.** B **5.** B

6. C **7.** B **8.** C **9.** D **10.** A

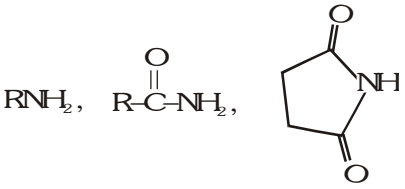
- ***Comprehension Based Questions***

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)

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) CH_3NH_2,$(CH_3)_2NH$,$(CH_3)_3$ N (in aprotic solvent)

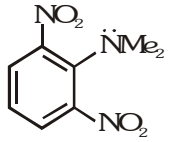
(II) $C_2H_5NH_2$,$(C_2H_5)_2NH$,$(C_2H_5)_3$ N (in aprotic solvent)

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

(I) CH_3NH_2,$(CH_3)_2$ NH,$(CH_3)_3$ N (in protic solvent)

(II) $C_2H_5NH_2$,$(C_2H_5)_2$ NH,$(C_2H_5)_3$ N (in protic solvent)

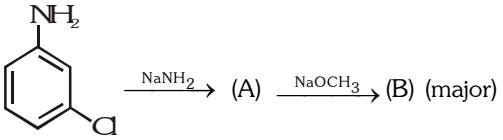
5. Unlike other aromatic amines, why is the following amine stongly basic ?



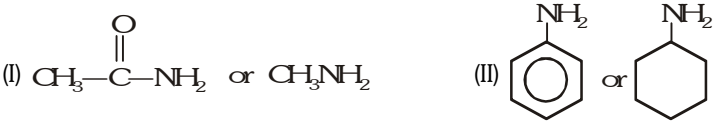
6. In this compound which site acts as an acid and which as a base ?

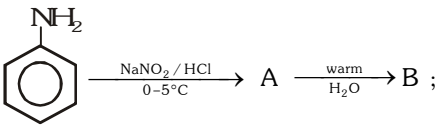
7. Alkyl cyanides (CH_3CN) when treated with hydrogen in presence of Pt or with $LiAlH_4$ produces same carbon number compound. What is the formula of that compound ?

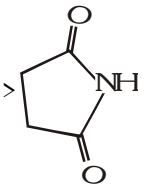
8. Write the compound (A) and (B) formed in this



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



10.  ; what are A & B ?

1. $RNH_2 > RCONH_2 >$ 

the lone pair of electrons on N is accommodated by sp^3 hybrid atomic orbital in RNH_2 and does not involve in resonance, whereas in $RCONH_2$ and succinamide the lone pair of $-NH_2$ is delocalised.

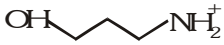
2. Sulphanilic acid exist as Z witterion

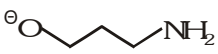
Due to its ionic character it is insoluble in organic solvents.

3. (I) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$; (II) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2$

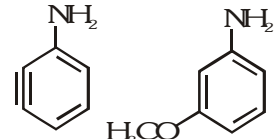
4. (I) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$; (II) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2$

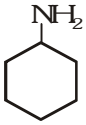
5. Due to the presence of bulky $-NO_2$ groups on its ortho positions, the $-NMe_2$ group goes outside the plane of resonance to avoid steric repulsion. The C–N bond rotates and hence the lone pair of N goes perpendicular to the plane of benzene ring. As a result the resonance is stopped and hence the lone pair is readily available as a base.

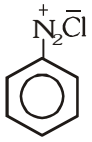
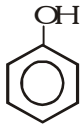
6.  ; $-NH_2$ is a more basic site than OH ;

 ; H–O is more acidic than H–N

7. $CH_3CH_2\ NH_2$

8. 
(A) (B)
Benzyne

9. (I) CH_3NH_2 ; (II) 

10. A :  ; B : 

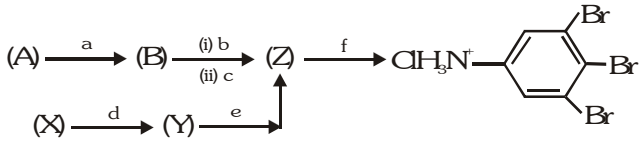
1. An organic compound (A) composed of C, H and O gives characteristic colour with ceric ammonium nitrate. Treatement of (A) with PCl_5 gives (B), which reacts with KCN to form (C). The reduction of (C) with warm Na/C_2H_5OH produces (D).which on heating gives (E) with evolution of ammonia. Pyridine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

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

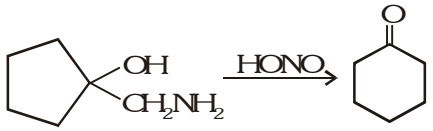
3. Two isomeric compounds (A) and (B) have $C_4H_{11}N$ as molecular formula. Both on separately treating with HNO_2 lose their N_2 producing two isomeric alcohols (C) and (D) respectively of molecular formula $C_4H_{10}O$. (C) reacts with Lucas reagent immediately and units oxidation. (D) does not reacts 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.

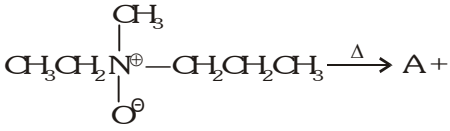
4. A mixture of two aromatic compounds A and B was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound A, when heated with alcoholic solution of KOH produced a compound C (C_7H_5N) associated with an unplesant odour. The alkaline 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 $C_7H_6O_2$. Identify the compound A, B,C,D and E write their structures.

5. Give structures of (A), (B), (X), (Y) in the given scheme of reactions, if reagents a, b, c, d, e and f are Br_2/CH_3COOH, $NaNO_2/H_2SO_4$, CuBr, HNO_3/H_2SO_4, Br_2/Fe and Sn/HCl respectively.



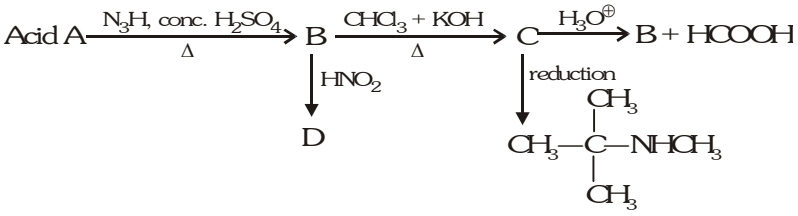
6. Explain the mechanism of the following change :



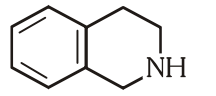
7.  Identify A, B (both alkene) and C.

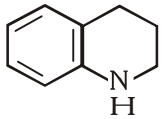
8. Write isomeric amines of the formula C_3H_9N.

9. Identify A, B, C and D.

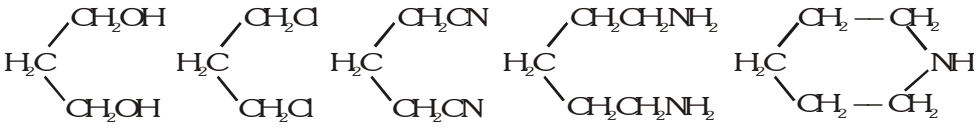


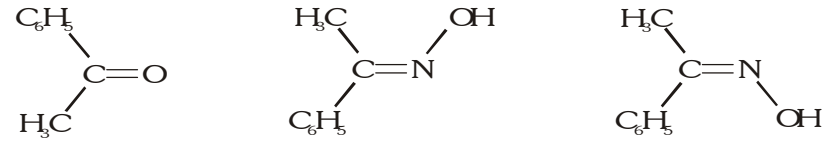
10. The two amines shown differ by a factor of about 40, 000 in their ionisation constants. Which is stronger base ? Explain :


tetrahydroisoquinoline
(I)


tetrahydroquinoline
(II)

BRAIN STORMING SUBJECTIVE EXERCISE — ANSWER KEY — EXERCISE -4(B)

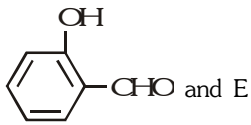
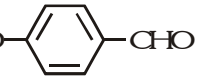
1. 
(A) (B) (C) (D) (E)

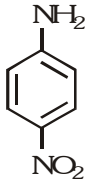
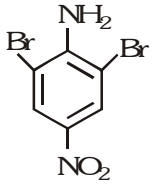
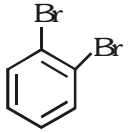
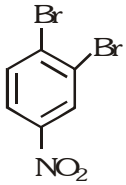
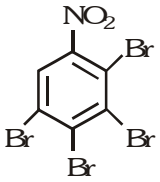
2. 
(A) Acetophenone (B) Acetophenone oxime (C) Z–Acetophenone oxime

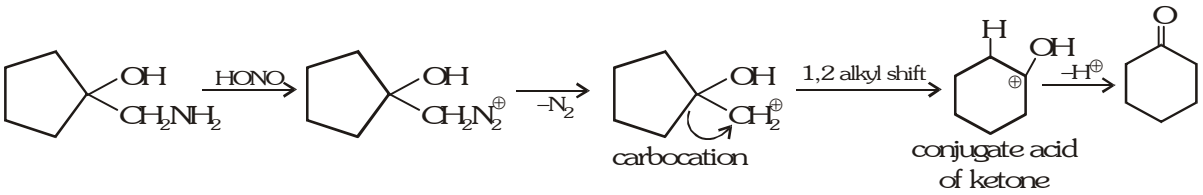

(D) Acetanilide (E) N–methyl benzamide (F) Aniline (G) Benzoic acid

3. $A = (CH_3)_3C - NH_2$, $B = (CH_3)_2CH-CH_2-NH_2$
$C = (CH_3)_3C-OH$, $D = (CH_3)_2CHCH_2OH$

4. $A = C_6H_5NH_2$ (aniline), $B = C_6H_5OH$(phenol), $C = C_6H_5NC$ = (phenyl isocyanide).

D =  and E = 
salicylaldehyde p-hydroxybenzaldehyde

5. (A) =  (B) =  (X) =  (Y) =  (Z) = 

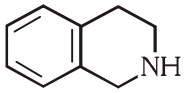
6. 

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

7. A : $CH_2=CH_2$ B. $CH_3CH=CH_2$ C. $CH_3-N(OH)-CH_2CH_3$ or $CH_3-N(OH)-CH_2CH_2CH_3$

8. I. $CH_3CH_2CH_2NH_2$ II. $CH_3CH(NH_2)CH_3$ III. $CH_3CH_2NHCH_3$ IV. $(CH_3)_3N$

9. A : $CH_3-C(CH_3)_2-COOH$; (B) $CH_3-C(CH_3)_2-NH_2$; (C) $CH_3-C(CH_3)_2-NC$; (D) $CH_3-C(CH_3)_2-OH$, $CH_3-C(CH_3)=CH_2$

10. 

tetrahydroisoquinoline

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

1. Among the following compounds , which will react with acetone to give a product containing >C=N– ? [IIT-90]

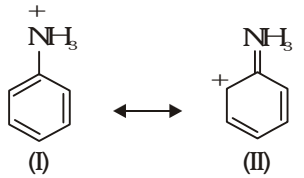
(A) $C_6H_5NH_2$ (B) $(CH_3)_3N$

(C) $C_6H_5NHC_6H_5$ (D) $C_6H_5NHNH_2$

2. The compound that willl 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) $(CH_3)_3CCl$

3. Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below : [IIT-93]



(I) (II)

(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 ten valence electrons

(D) Both (A) & (C)

4. Allyl isocyanide contains σ and π bonds are - [IIT-95]

(A) 9σ and 3π (B) 9σ and 9π (C) 3σ and 4π (D) 5σ and 7π

5. 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

6. 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.

7. p-Chloroaniline and anilinium hydrochloride can not be distinguished by [IIT-98]

(A) Sandmeyer reaction (B) $NaHCO_3$ (C) $AgNO_3$ (D) Carbylamine test

8. 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

(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

9. 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) $p\text{-}NO_2\text{-}C_6H_4NH_2$ (C) $m\text{-}NO_2\text{-}C_6H_4NH_2$ (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.

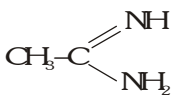
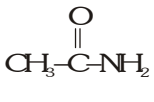
(A) If both assertion and reason are correct, and reason is the correct explanation of the assertion

(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]**

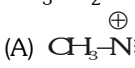
(I)  ; (II) $CH_3CH_2NH_2$; (III) $(CH_3)_2NH$; (IV) 

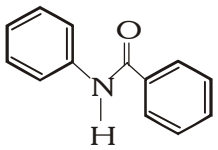
(A) II > I > III > IV (B) I > III > II > IV (C) III > I > II > IV (D) I > II > III > IV

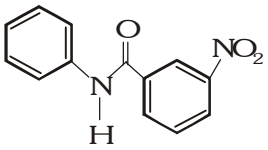
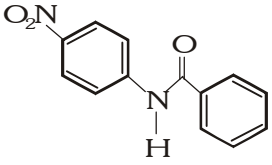
14. When benzamide is treated with $POCl_3$, the product formed is : **[IIT-04]**

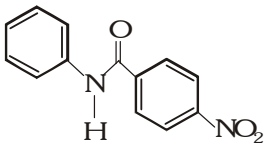
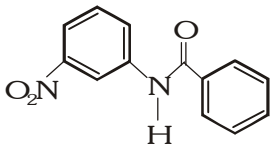
(A) Benzonitrile (B) Aniline (C) Chlorobenzene (D) Benzylamine

15. $CH_3NH_2 + CHCl_3 \xrightarrow{KOH}$ Product, Product is- **[IIT-06]**

(A)  (B) (C) $CH_3\text{-}NH\text{-}CH_3$ (D) $CH_3\text{-}C \equiv N$

16. In the following reaction,  $\xrightarrow[\text{conc. } H_2SO_4]{\text{conc. } HNO_3}$ X, the structure of the major product 'X' is - **[IIT-07]**

(A)  (B) 

(C)  (D) 

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]**

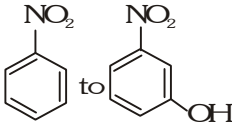
18. Compound 'X' containing chlorine, on treatment with NH_3 gives a solid 'Y' which is free from chlorine. (Y) analysed as C = 49.31%, H = 9.59% and N = 19.18% and reacts with Br_2 and caustic soda to give a basic compound (Z), (Z) reacts with HNO_2 to give ethanol. Suggest structure for (X), (Y) and (Z).

[IIT-88]

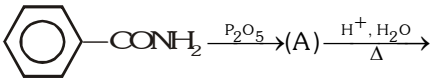
19. Show with equations how the following compounds are prepared (equations need not be balanced) :

(i) 4-nitroaniline to 1, 2,3-tribromobenzene. **[IIT-90]**

(ii) Aniline $\longrightarrow$ Benzylamine (in 3 steps) **[IIT-2000]**

(iii) Convert  in not more than four steps. **[IIT-04]**

20. Complete the following with appropriate structures : **[IIT-92]**

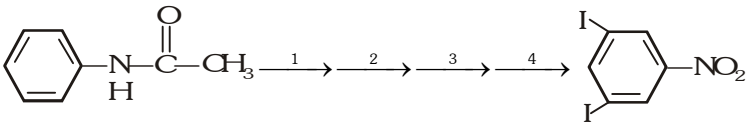


21. The aqueous solution of a nitrogen and chlorine containing compound (A) is acidic to litmus. (A) on treatement with aqueous NaOH gives a compound (B) containing nitrogen, but not chlorine. Compound (B) on treatment with $C_6H_5SO_2Cl$ in presence of NaOH gives an insoluble product (C), $C_{13}H_{13}NO_2S$. Give structure of (A) and (B). **[IIT-93]**

22. Complete the following with appropriate structures : **[IIT-95]**

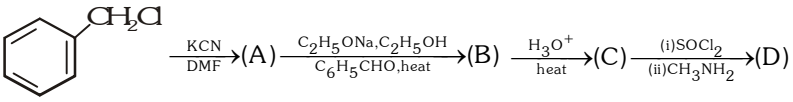
2,4-Dinitroaniline $\xrightarrow[\text{(II) anisole}]{\text{(I)}NaNO_2 \text{ and HCl at } 5°C}$ C

23. Complete the following reaction with appropriate reagents : **[IIT-99]**



24. Compound (A), $C_5H_{11}NO$ 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), (C_4H_9NO). (B) reacts with 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. $C_5H_{13}N$ (optically active) $\xrightarrow[-N_2]{aq.NaNO_2/HCl}$ Y (Tertiary alcohol) + Some other products **[IIT-05]**

(i) Identify (X) and (Y)

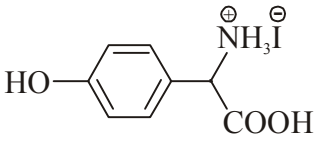
(ii) Is (Y) optically active ?

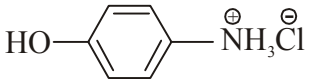
(iii) Give structure (s) of intermediate (s), if any, in the formation of (Y) from (X).

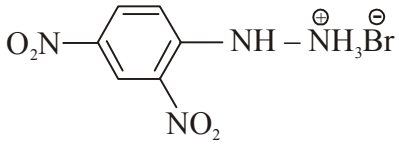
27. Match the compounds in **Column I** with their characteristic test(s)/reaction(s) given in **Column II**. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.

Column I **Column II** **[IIT 2008]**

(A) $H_2N - \overset{\oplus}{N}H_3\overset{\ominus}{Cl}$

(B) 

(C) 

(D) 

(P) sodium fusion extract of the compound gives Prussian blue colour with $FeSO_4$

(Q) gives positive $FeCl_3$ test

(R) gives white precipitate with $AgNO_3$

(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]**

(A) $CH_3CH_2CH_2CN$

(B) $CH_3CH_2OCOCH_3$

(C) $CH_3 - CH = CH - CH_2OH$

(D) $CH_3CH_2CH_2CH_2NH_2$

(P) Reduction with Pd–C / H_2

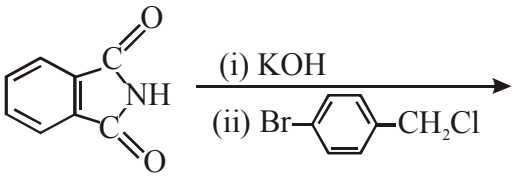
(Q) Reduction with $SnCl_2$ / HCl

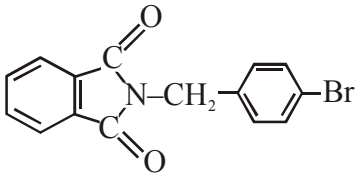
(R) Development of foul smell on treatment with chloroform and alcoholic KOH

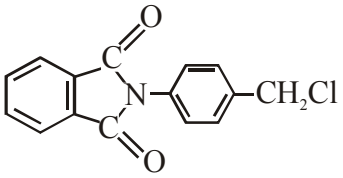
(S) Reduction with diisobutylaluminium hydride (DIBAL – H)

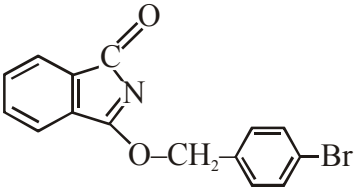
(T) Alkaline hydrolysis

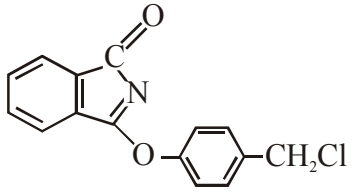
29. The major product of the following reaction is **[IIT 2011]**



(A) 

(B) 

(C) 

(D) 

EXERCISE–05[B] PREVIOUS YEARS QUESTIONS

1. Reaction - **[AIEEE-2002]**

Primary amine + $CHCl_3$ + 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) $Fe_4[Fe(CN)_6]_3$ (2) $Na_3[Fe(CN)_6]$ (3) $Fe(CN)_3$ (4) $Na_4[Fe(CN)_5)NOS]$

3. Which one of the following methods is neither meant for the synthesis nor for separation of amines- **[AIEEE-2005]**

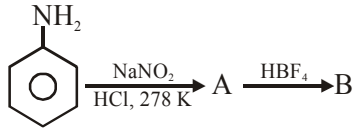
(1) Hofmann method (2) Hinsberg method (3) Curtius reaction (4) Wurtz reaction

4. In the chemical reaction, $CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow$ (A) + (B) + $3H_2O$, the compounds (A) and (B) are respectively - **[AIEEE-2007]**

(1) C_2H_5CN and 3KCl (2) CH_3CH_2 $CONH_2$ and 3KCl

(3) C_2H_5NC and K_2CO_3 (4) C_2H_5NC and 3KCl

5. In the chemical reactions, **[AIEEE-2010]**

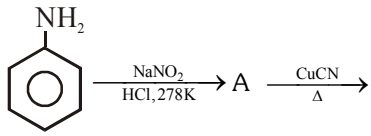


the compounds 'A' and 'B' respectively are :-

(1) Nitrobenzene and chlorobenzene (2) Nitrobenzene and fluorobenzene

(3) Phenol and benzene (4) Benzene diazonium chloride and fluorobenzene

6. In the chemical reactions

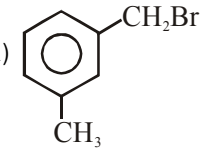


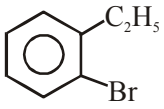
, the compounds A and B respectively are : **[AIEEE-2011]**

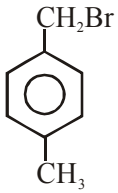
(1) Fluorobenzene and phenol (2) Benzene diazonium chloride and benzonitrile

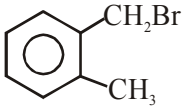
(3) Nitrobenzene and chlorobenzene (4) Phenol and bromobenzene

7. Compound (A), C_8H_9Br, gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A): **[AIEEE-2013]**

(1) 

(2) 

(3) 

(4) 

8. An organic compound A upon reacting with NH_3 gives B. On heating, B gives C. C in presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. A is :- **[AIEEE-2013]**

(1) CH_3COOH (2) $CH_3CH_2CH_2COOH$ (3) $CH_3–\underset{\displaystyle CH_3}{\underset{|}{CH}}–COOH$ (4) CH_3CH_2COOH

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

50 ml of 0.05 M H_2SO_4 = 50 ml of 0.1 NH_2SO_4

(∵ Normality of H_2SO_4) = 2 molarity)

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

(∵ Normality of NaOH = molarity of NaOH)

25 ml of 0.1 N NaOH ≡ 25 ml of 0.1 N H_2SO_4

∴ vol. of 0.1 NH_2SO_4 used for the neutralisation of NH_3 = 50 – 25 = 25 ml

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

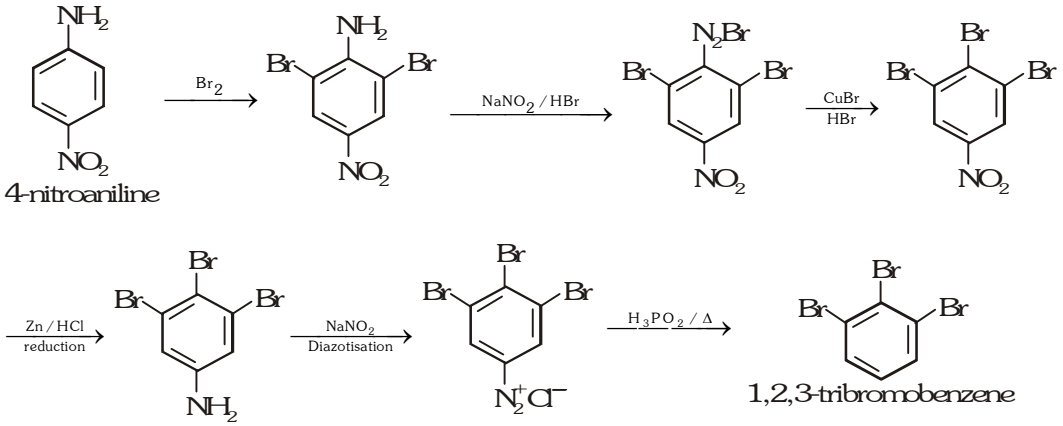
= $\frac{1.4 \times 0.1 \times 25}{0.303} = 11.55\%$; Hence % of oxygen = 100 –(69.4 + 5.8 + 11.55) = 13.25

18. Empirical formula of (Y) is C_3H_7NO

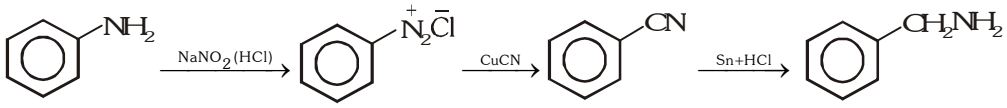
$CH_3CH_2NH_2$

$CH_3.CH_2COCl + NH_3 \longrightarrow 2\ CH_3CH_2CONH_2$

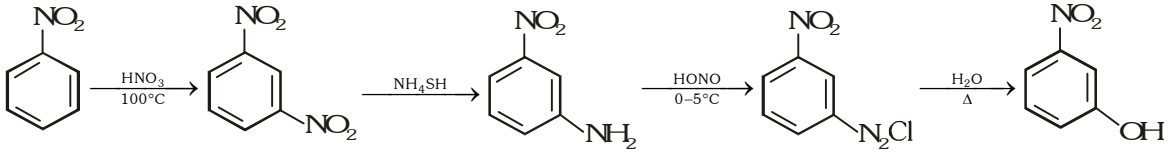
19. (i)



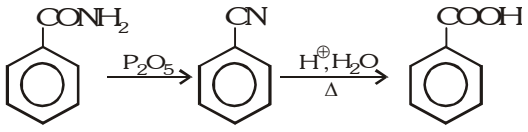
(ii)



(iii)



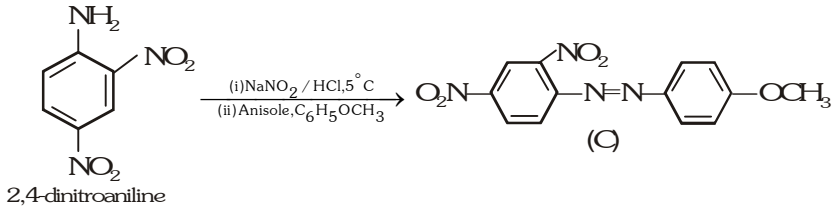
20.



21. Aminhydrochloride $\underset{(A)}{\rightleftharpoons}$ Amine . HCl $\xrightarrow{NaOH}$ $\underset{(B)}{\text{Amine}}$ $+H_2O$ $+NaCl$

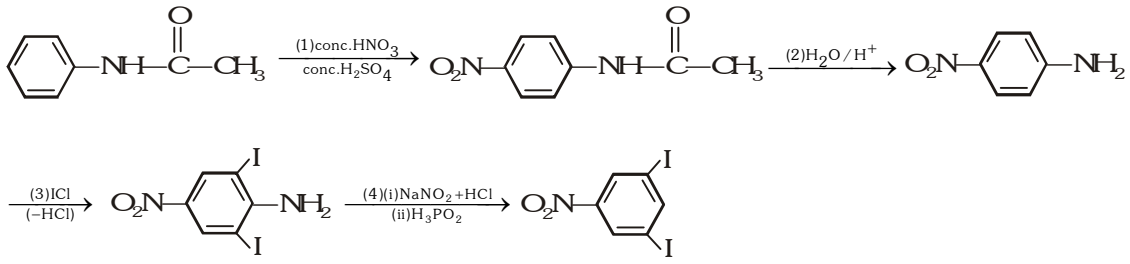
A = $[C_6H_5NH_2CH_3]\ Cl^-$ and B = $C_6H_5NHCH_3$

22.



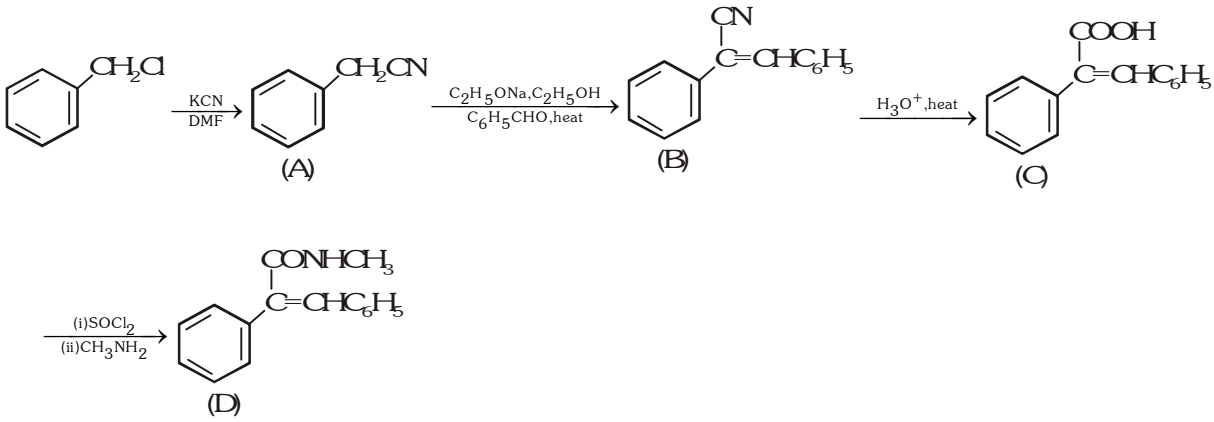
2,4-dinitroaniline

23.

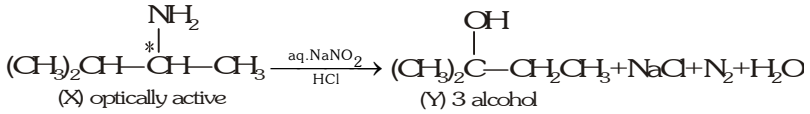


24. (A) = $CH_3CH_2CON(CH_3)_2$, B = $(CH_3)_2$ NH, C = CH_3CH_2COONa, D = $CH_3CON(CH_3)_2$ and E = $(CH_3)_2N - N = O$

25.



26. (i)

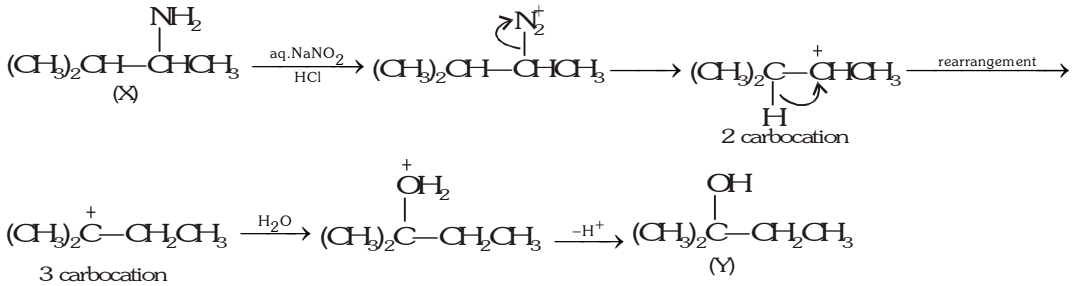


(X) optically active

(Y) 3 alcohol

(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

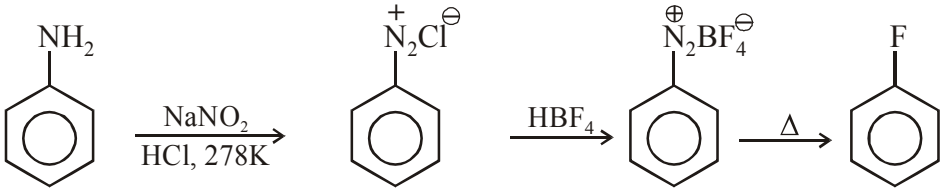
29. A

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

1. Carbylamine Test

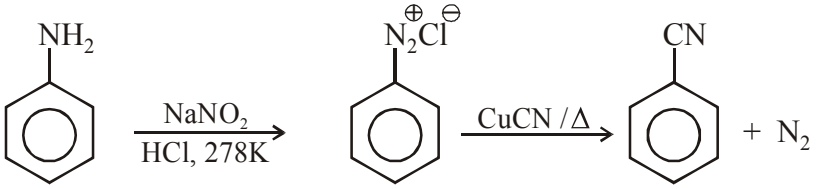
3. Wurtz reaction $R \xrightarrow[\text{dry ether}]{\text{Na}} R - R + NaX$

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

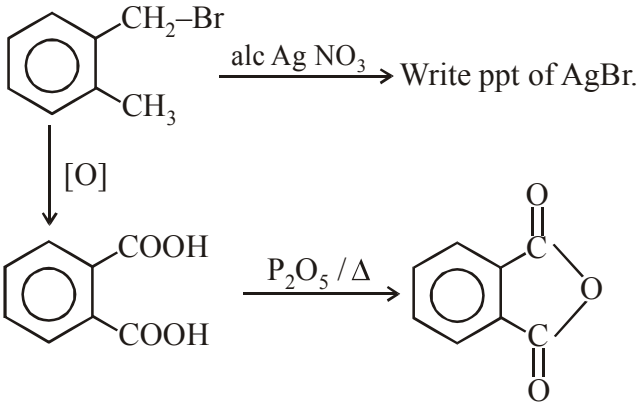
5. 

Aniline Benzenediazonium Chloride (A) (B)

Sandmeyer's Reaction

6. 

Aniline Benzenediazonium Chloride (A) (B)

7. 

8. $CH_3CH_2 - \overset{O}{\overset{\|}{C}} - OH \longrightarrow CH_3CH_2 - \overset{O}{\overset{\|}{C}} - ONH_4 \xrightarrow[-H_2O]{\Delta} CH_3CH_2 - \overset{O}{\overset{\|}{C}} - NH_2 \xrightarrow[Br_2]{KOH} CH_3 - CH_2 - NH_2$