Chapter - Amines

Topic-1: Cyanides, Isocyanides, Nitrites & Nitro Compounds

1 MCQs with One Correct Answer

1. The correct stability order of the following resonance structures is [2009]

$H_2C=\overset{+}{N}=\overset{-}{N}$ (I)

$H_2\overset{+}{C}-N=\overset{-}{N}$ (II)

$H_2\overset{-}{C}-\overset{+}{N}\equiv N$ (III)

$H_2\overset{-}{C}-N=\overset{+}{N}$ (IV)

(a) (I) > (II) > (IV) > (III)
(b) (I) > (III) > (II) > (IV)
(c) (II) > (I) > (III) > (IV)
(d) (III) > (I) > (IV) > (II)

2. In the following reaction, [2006]

$$CH_3NH_2 + CHCl_3 + KOH \longrightarrow \text{Nitrogen containing compound} + KCl + H_2O.$$

The nitrogen containing compound is

(a) $CH_3-NH-CH_3$
(b) $CH_3-C\equiv N$
(c) $CH_3-\overset{+}{N}\equiv\overset{-}{C}$
(d) $CH_3-\overset{-}{N}\equiv\overset{+}{C}$

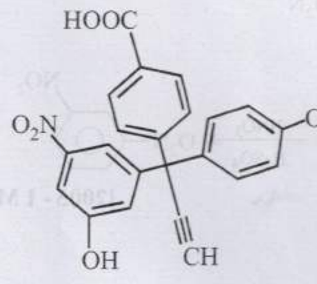
3. When benzenesulfonic acid and *p*-nitrophenol are treated with $NaHCO_3$, the gases released respectively are [2006]

(a) SO_2, NO
(b) SO_2, NO_2
(c) CO_2, CO_2
(d) SO_2, CO_2

4. Benzamide on reaction with $POCl_3$ gives [2004S]

(a) aniline
(b) chlorobenzene
(c) benzylamine
(d) benzonitrile

5.

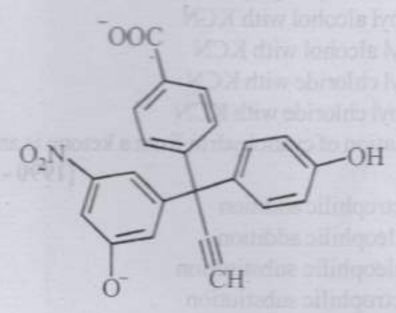


$\xrightarrow{\text{2 moles NaNH}_2} A$

[2003S]

The product A will be

(a)



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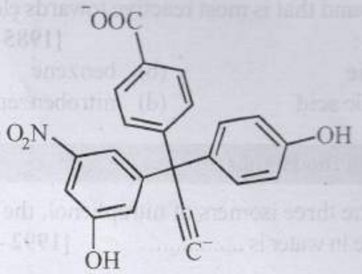

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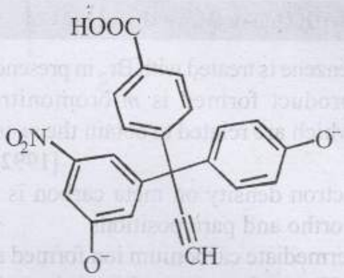

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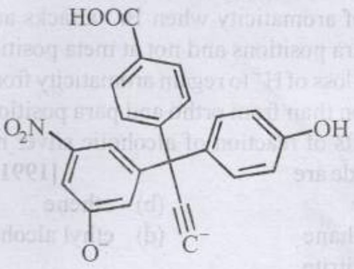
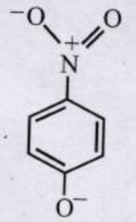


6. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is **[1999 - 2 Marks]**

(a)



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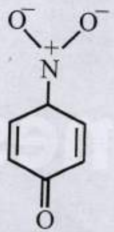

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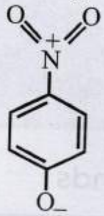

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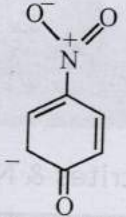


7. Butanenitrile may be prepared by heating : **[1992 - 1 Mark]**
   (a) Propyl alcohol with KCN
   (b) Butyl alcohol with KCN
   (c) Butyl chloride with KCN
   (d) Propyl chloride with KCN
8. The formation of cyanohydrin from a ketone is an example of : **[1990 - 1 Mark]**
   (a) Electrophilic addition
   (b) Nucleophilic addition
   (c) Nucleophilic substitution
   (d) Electrophilic substitution
9. The compound that is most reactive towards electrophilic nitration is : **[1985 - 1 Mark]**
   (a) toluene (b) benzene
   (c) benzoic acid (d) nitrobenzene

4 Fill in the Blanks

10. Amongst the three isomers of nitrophenol, the one that is least soluble in water is .... **[1992 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

11. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$, the major product formed is *m*-bromonitrobenzene. Statements which are related to obtain the *m*-isomer are **[1992 - 1 Mark]**
    (a) The electron density on meta carbon is more than that on ortho and para positions
    (b) The intermediate carbonium ion formed after initial attack of Br^+ at the meta position is least destabilised
    (c) Loss of aromaticity when Br^+ attacks at the ortho and para positions and not at meta position
    (d) Easier loss of H^+ to regain aromaticity from the meta position than from ortho and para positions.
12. The products of reaction of alcoholic silver nitrite with ethyl bromide are **[1991 - 1 Mark]**
    (a) ethane (b) ethene
    (c) nitroethane (d) ethyl alcohol
    (e) ethyl nitrite

7 Match the Following

13. Match each of the compounds in **Column-I** with its characteristic reaction(s) in **Column-II**. **[2009]**

Column-I	**Column-II**
(A) $CH_3CH_2CH_2CN$	(p) Reduction with Pd–C/H_2
(B) $CH_3CH_2OCOCH_3$	(q) Reduction with $SnCl_2$/HCl
(C) CH_3–CH=CH–CH_2OH	(r) Development of foul smell on treatment with chloroform and alcoholic KOH
(D) $CH_3CH_2CH_2CH_2NH_2$	(s) Reduction with diisobutylaluminium hydride(DIBAL-H)
	(t) Alkaline hydrolysis

9 Assertion and Reason/Statement Type Questions

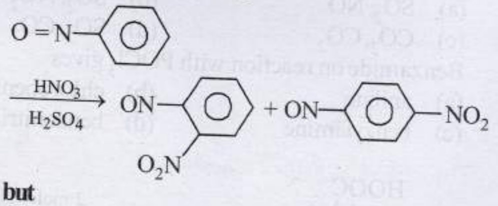
Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
(b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
(c) If Statement -1 is correct but Statement -2 is incorrect.
(d) If Statement -1 is incorrect but Statement -2 is correct.

14. **Statement - 1:** Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.
    Statement - 2 : Cyanide (CN^-) is a strong nucleophile. **[1998 - 2 Marks]**
15. **Statement - 1:** *p*-Nitrophenol is a stronger acid than *o*-nitrophenol.
    Statement - 2 : Intramolecular hydrogen bonding makes the *o*-isomer weaker than the *p*-isomer. **[1989 - 2 Marks]**

10 Subjective Problems

16. Give reasons for the following :
    (i)



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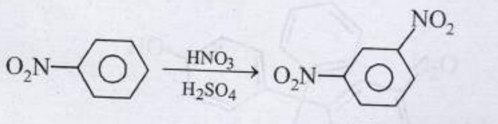
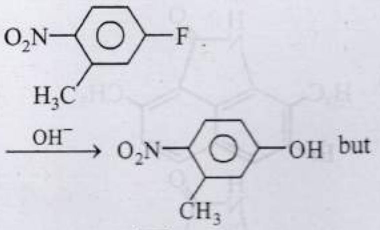


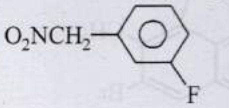
[2005 - 1 Mark]

(ii) (a)



but

(b)

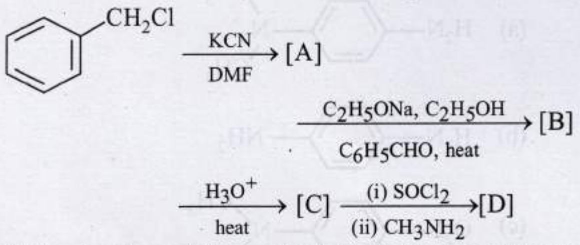


$\xrightarrow{OH^-}$ No release of F^- **[2005 - 1 Mark]**

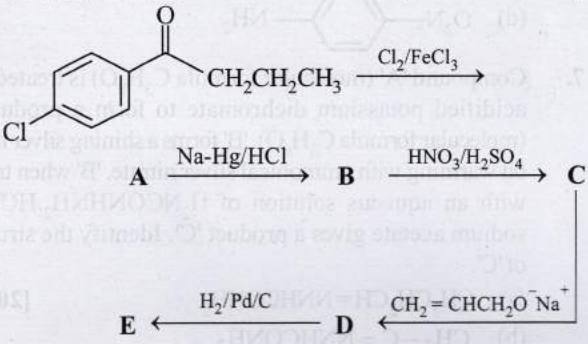
(iii) Nitrobenzene does not undergo Friedel-Craft's alkylation **[1998 - 2 Marks]**

(iv) *o*-Nitrophenol is steam volatile whereas *p*-nitrophenol is not; **[1985 - 1 Mark]**

17. Identify (A) to (D) in the following series of reactions. **[2004 - 4 Marks]**

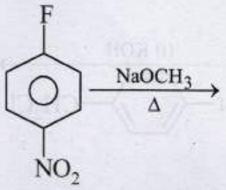


18. Write structures of the products **A, B, C, D** and **E** in the following scheme. **[2002 - 5 Marks]**



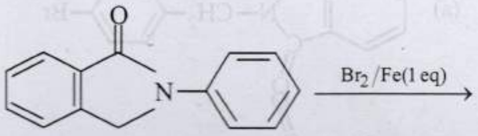
19. Identify the major product in the following reactions :

(i)



[2000 - 1 Mark]

(ii)



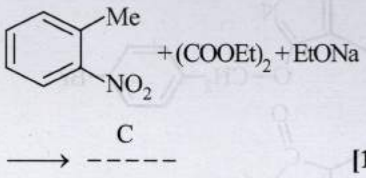
[2000 - 1 Mark]

(iii)

[1993 - 1 Mark]

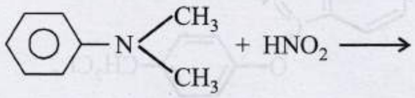
20. Complete the following with appropriate structures :

(i)



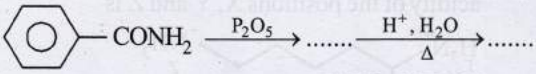
[1997 - 1 Mark]

(ii)



[1992 - 1 Mark]

(iii)



[1992 - 1 Mark]

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

(i) 4-nitrobenzaldehyde from benzene. **[1994 - 2 Marks]**

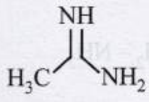
(ii) *p*-bromonitrobenzene from benzene in two steps. **[1993 - 2 Marks]**

(iii) toluene to *m*-nitrobenzoic acid? **[1987 - 1 Mark]**

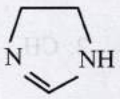
Topic-2: Aliphatic and Aromatic Amines

1 MCQs with One Correct Answer

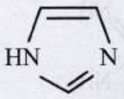
1. The order of basicity among the following compounds is **[Adv. 2017]**



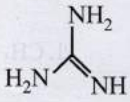
I



II



III



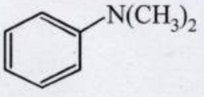
IV

(a) II > I > IV > III (b) IV > II > III > I

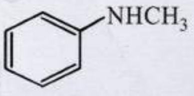
(c) IV > I > II > III (d) I > IV > III > II

2. Amongst the compounds given, the one that would form a brilliant colored dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β-naphthol is **[2011 - II]**

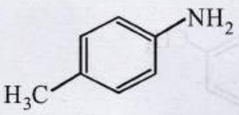
(a)



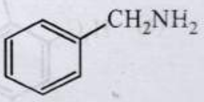
(b)



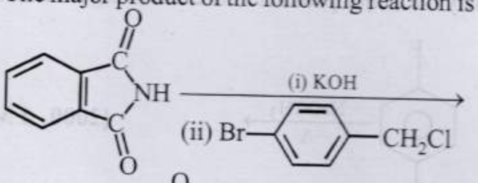
(c)



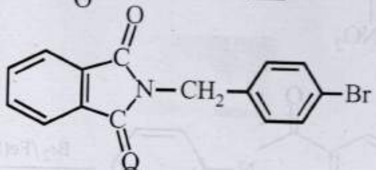
(d)



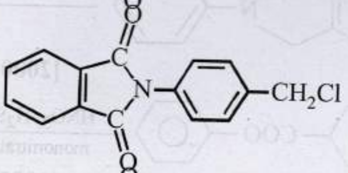
3. The major product of the following reaction is **[2011 - I]**



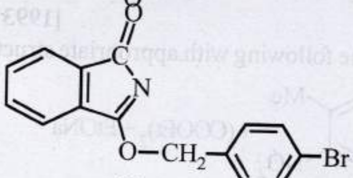
(a)



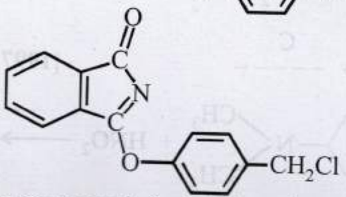
(b)



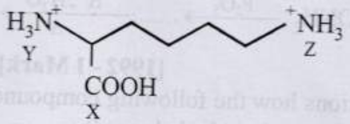
(c)



(d)

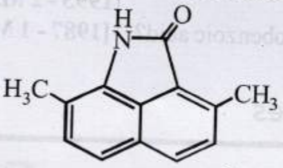


4. In the compound given below, the correct order of the acidity of the positions X, Y and Z is **[2004S]**

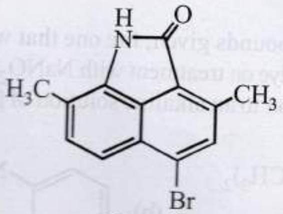


(a) Z > X > Y
(b) X > Y > Z
(c) X > Z > Y
(d) Y > X > Z

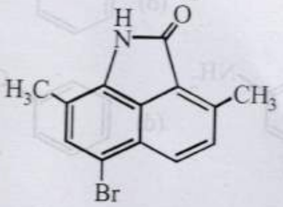
5. The major product obtained when Br_2/Fe is treated with **[2004S]**



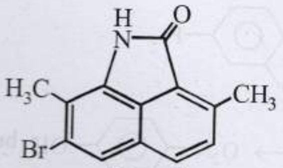
(a)



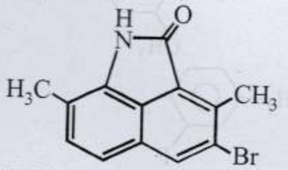
(b)



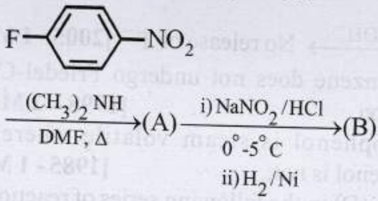
(c)



(d)

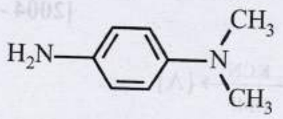


6. **[2003S]**



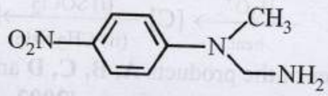
(B). (B) is:

(a)



(b)

(c)

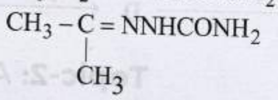


(d)

7. Compound 'A' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product 'B' (molecular formula C_3H_6O). 'B' forms a shining silver mirror on warming with ammonical silver nitrate. 'B' when treated with an aqueous solution of $H_2NCONHNH_2.HCl$ and sodium acetate gives a product 'C'. Identify the structure of 'C'. **[2002S]**

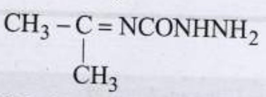
(a) $CH_3CH_2CH=NNHCONH_2$

(b)



$CH_3-\underset{CH_3}{\underset{|}{C}}=NNHCONH_2$

(c)

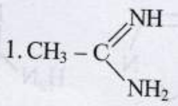


$CH_3-\underset{CH_3}{\underset{|}{C}}=NCONHNH_2$

(d) $CH_3CH_2CH=NCONHNH_2$

8. The correct order of basicities of the following compounds is **[2001S]**

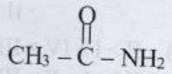
1.



2. $CH_3-CH_2-NH_2$

3. $(CH_3)_2NH$

4.



$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$

(a) 2 > 1 > 3 > 4
(b) 1 > 3 > 2 > 4
(c) 3 > 1 > 2 > 4
(d) 1 > 2 > 3 > 4

9. Among the following, the strongest base is **[2000S]**
(a) $C_6H_5NH_2$ (b) $p\text{-}NO_2.C_6H_4NH_2$
(c) $m\text{-}NO_2.C_6H_4.NH_2$ (d) $C_6H_5CH_2NH_2$

10. In the reaction p-chlorotoluene with KNH_2 in liq. NH_3, the major product is: **[1997 - 1 Mark]**
(a) o-toluidine (b) m-toluidine
(c) p-toluidine (d) p-chloroaniline.

11. Amongst the following, the most basic compound is : **[1990 - 1 Mark]**
(a) Benzylamine (b) Aniline
(c) Acetanilide (d) p-Nitroaniline

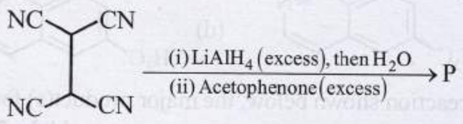
12. Carbylamine test is performed in alcoholic KOH by heating a mixture of: **[1984 - 1 Mark]**
(a) chloroform and silver powder
(b) trihalogenatedmethane and a primary amine
(c) an alkyl halide and a primary amine
(d) an alkyl cyanide and a primary amine

13. Acetamide is treated separately with the following reagents. Which one of these would give methylamine? **[1983 - 1 Mark]**
(a) PCl_5 (b) $NaOH + Br_2$
(c) soda lime (d) hot conc. H_2SO_4

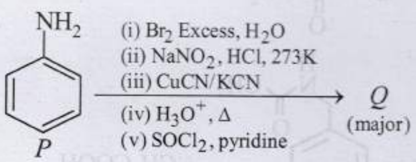
14. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosoamine is **[1981 - 1 Mark]**
(a) methylamine (b) ethylamine
(c) diethylamine (d) triethylamine

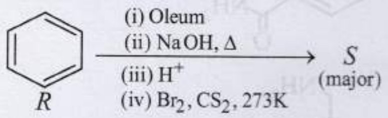
2 Integer Value Answer

15. The total number of sp^2 hybridised carbon atoms in the major product P (a non–heterocyclic compound) of the following reaction is ______. **[Adv. 2023]**



16. Schemes 1 and 2 describes the conversion of P to Q and R to S, respectively, scheme 3 describes the synthesis of T from Q and S. The total number of Br atoms in a molecule of T is ______ **[Adv. 2019]**

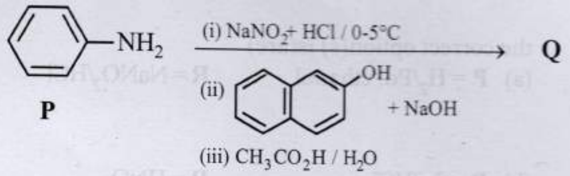
Scheme 1 :


Scheme 2 :


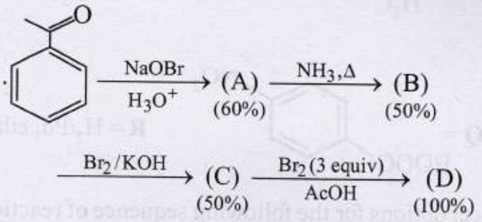
Scheme 3 : $S \xrightarrow[\text{(ii) Q}]{\text{(i) NaOH}} \underset{\text{(major)}}{T}$

3 Numeric / New Stem Based Questions

17. Consider the reaction sequence from **P** to **Q** shown below. The overall yield of the major product **Q** from **P** is 75%. What is the amount in grams of **Q** obtained from 9.3 mL of **P**? (Use density of **P** = 1.00 g mL^{-1}; Molar mass of C = 12.0, H = 1.0, O = 16.0 and N = 14.0 g mol^{-1}) **[Adv. 2020]**



18. In the following reaction sequence, the amount of **D** (in g) formed from 10 moles of acetophenone is ______. (Atomic weights in g mol^{-1}: H = 1, C = 12, N = 14, O = 16, Br = 80. The yield (%) corresponding to the product in each step is given in the parenthesis) **[Adv. 2018]**



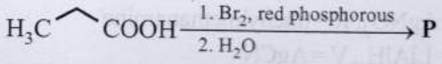
4 Fill in the Blanks

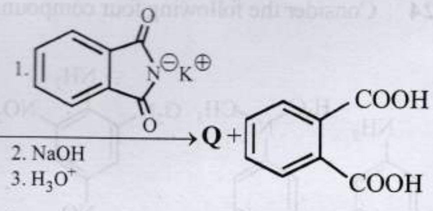
19. The high melting point and insolubility in organic solvents of sulphanilic acid are due to its........structure. **[1994 - 1 Mark]**

20. In an acidic medium, ... behaves as the strongest base. (nitrobenzene, aniline, phenol) **[1981 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

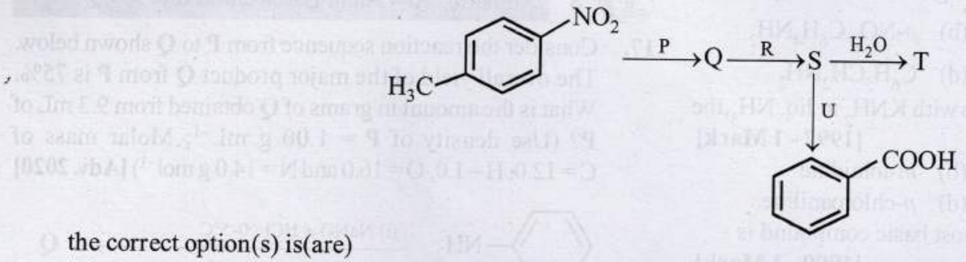
21. Considering the reaction sequence given below, the correct statement(s) is(are) **[Adv. 2022]**





(a) **P** can be reduced to a primary alcohol using $NaBH_4$.
(b) Treating **P** with conc. NH_4OH solution followed by acidification gives **Q**.
(c) Treating **Q** with a solution of $NaNO_2$ in aq. HCl liberates N_2.
(d) **P** is more acidic than CH_3CH_2COOH.

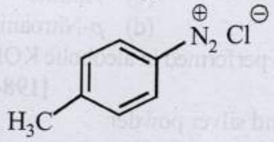
22. Considering the following reaction sequence, **[Adv. 2022]**



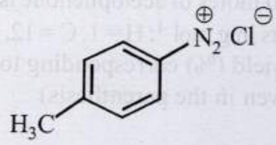
the correct option(s) is(are)

(a) **P** = H_2/Pd, ethanol **R** = $NaNO_2$/HCl **U** = 1. H_3PO_2 2. $KMnO_4$ - KOH, heat

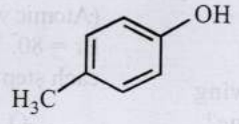
(b) **P** = Sn/HCl **R** = HNO_2 **S** =



(c) **S** =

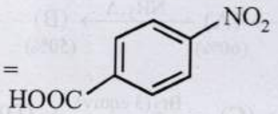


T =

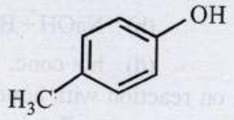


U = 1. CH_3CH_2OH 2. $KMnO_4$ - KOH, heat

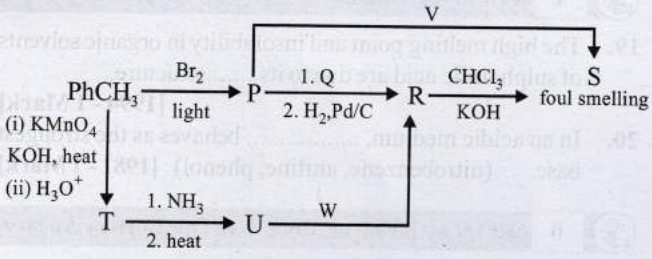
(d) **Q** =



R = H_2/Pd, ethanol **T** =



23. Correct options for the following sequence of reactions is (are)



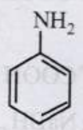
(a) Q = KNO_2, W = $LiAlH_4$ **[Adv. 2021]**

(b) R = benzenamine, V = KCN

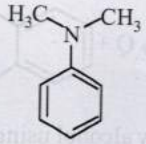
(c) Q = $AgNO_2$, R = phenylmethanamine

(d) W = $LiAlH_4$, V = AgCN

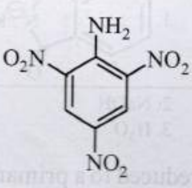
24 Consider the following four compounds **I**, **II**, **III**, and **IV**.



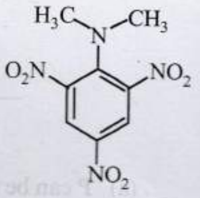
I



II



III



IV

Choose the correct statement(s). **[Adv. 2020**

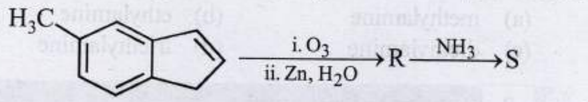
(a) The order of basicity is **II** > **I** > **III** > **IV**.

(b) The magnitude of pK_b difference between **I** and **II** is more than that between **III** and **IV**.

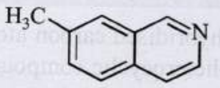
(c) Resonance effect is more in **III** than in **IV**.

(d) Steric effect makes compound **IV** more basic than **III**.

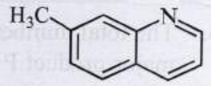
25. In the following reactions, the product S is **[Adv. 2015]**



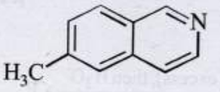
(a)



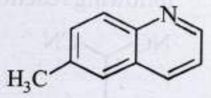
(b)



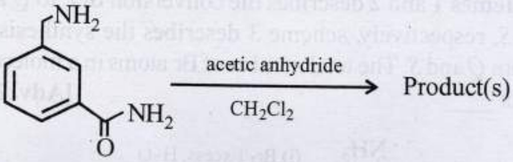
(c)



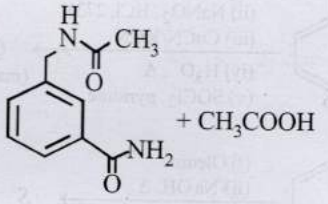
(d)



26. In the reaction shown below, the major product(s) formed is/are **[Adv. 2014]**

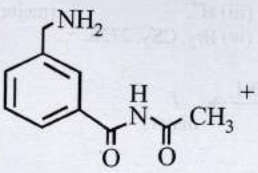


(a)

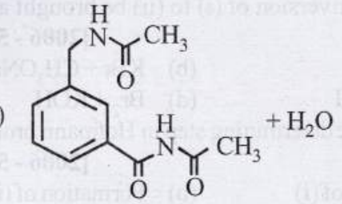


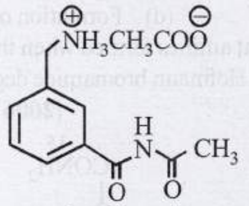
+ CH_3COOH

(b)



+ CH_3COOH

(c) 

(d) 

27. Hydrogen bonding plays a central role in the following phenomena **[Adv. 2014]**
(a) Ice floats in water
(b) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions
(c) Formic acid is more acidic than acetic acid
(d) Dimerisation of acetic acid in benzene

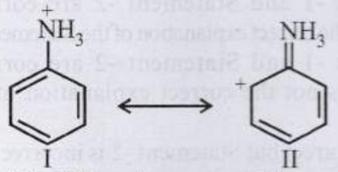
28. In the reaction $2X + B_2H_6 \rightarrow [BH_2(X)_2]^+[BH_4]^-$ the amine(s) X is (are) **[2009]**
(a) NH_3 (b) CH_3NH_2
(c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

29. A positive carbylamine test is given by **[1999 - 2 Marks]**
(a) N, N—dimethylaniline
(b) 2, 4–dimethylaniline
(c) N–methyl-*o*-methylaniline
(d) *p*-methylbenzylamine

30. Among the following compounds, which will react with acetone to give a product containing $>C=N$–bond ? **[1998 - 2 Marks]**
(a) $C_6H_5NH_2$ (b) $(CH_3)_3N$
(c) $C_6H_5NHC_6H_5$ (d) $C_6H_5NHNH_2$.

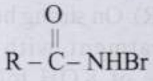
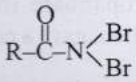
31. *p*-Chloroaniline and anilinium hydrochloride can be distinguished by **[1998 - 2 Marks]**
(a) Sandmeyer reaction (b) $NaHCO_3$
(c) $AgNO_3$ (d) Carbylamine test

32. Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below: **[1993 - 1 Mark]**



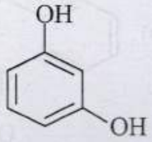
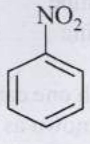
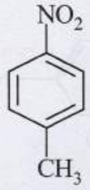
(a) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions.
(b) II is not an acceptable canonical structure because it is non-aromatic.
(c) II is not an acceptable canonical structure because its nitrogen has 10 valence electrons.
(d) II is an acceptable canonical structure.

33. Reaction of $R-\overset{O}{\overset{\|}{C}}-NH_2$ with a mixture of Br_2 and KOH gives $R-NH_2$ as the main product. The intermediates involved in this reaction are : **[1992 - 1 Mark]**

(a) 
$R-\overset{O}{\overset{\|}{C}}-NHBr$
(b) $R-NHBr$
(c) $R-N=C=O$
(d) 
$R-\overset{O}{\overset{\|}{C}}-N\begin{smallmatrix}Br\\Br\end{smallmatrix}$

7 Match the Following

34. **[Adv. 2014]**

	List - I		List - II
P.	$H-C\equiv C-H$	1.	**Scheme I** (i) $KMnO_4$, HO^-, heat (ii) H^+, H_2O (iii) $SOCl_2$ (iv) NH_3 $? \longrightarrow C_7H_6N_2O_3$
Q.		2.	**Scheme II** (i) Sn/HCl (ii) CH_3COCl (iii) conc. H_2SO_4 (iv) HNO_3 (v) dil. H_2SO_4, heat (vi) HO^- $? \longrightarrow C_6H_6N_2O_2$
R.		3.	**Scheme III** (i) red hot iron, 873 K (ii) fuming HNO_3, H_2SO_4, heat (iii) $H_2S.NH_3$ (iv) $NaNO_2$, H_2SO_4 (v) hydrolysis $? \longrightarrow C_6H_5NO_2$
S.		4.	**Scheme IV** (i) conc. H_2SO_4, 60°C, (ii) conc. HNO_3, conc. H_2SO_4, (iii) dil. H_2SO_4, heat $? \longrightarrow C_6H_5NO_4$

Code:

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

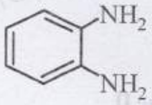
8 Comprehension Passage Based Questions

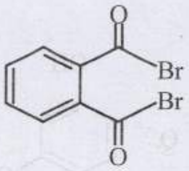
Passage - I

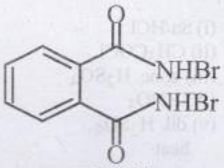
Treatment of compound (O) with $KMnO_4/H^+$ gave (P), which on heating with ammonia gave (Q). The compound (Q) on treatment with Br_2/NaOH produced (R). On strong heating, (Q) gave (S), which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound (T). **[Adv. 2016]**

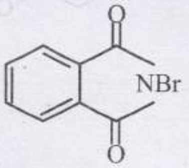
(O)

35. The compound (R) is

(a)


(b)


(c)


(d)


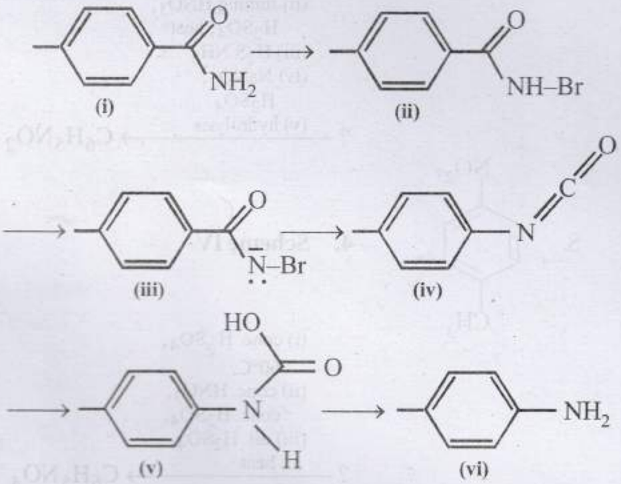
36. The compound (T) is

(a) glycine (b) alanine

(c) valine (d) serine

Passage - II

The conversion of an amide to an amine with one carbon atom less by the action of alkaline hypohalite is known as Hofmann bromamide degradation.



In this reaction, RCONHBr is formed from which the reaction has derived its name. Hofmann reaction is accelerated if the migrating group is more electron-releasing. Hofmann degradation reaction is an intramolecular reaction.

37. How can the conversion of (i) to (ii) be brought about? **[2006 - 5M, –2]**

(a) KBr (b) KBr + CH_3ONa

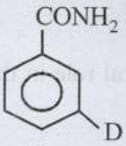
(c) KBr + KOH (d) Br_2 + KOH

38. Which is the rate determining step in Hofmann bromamide degradation? **[2006 - 5M, –2]**

(a) Formation of (i) (b) Formation of (ii)

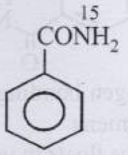
(c) Formation of (iii) (d) Formation of (iv)

39. What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation? **[2006 - 5M, –2]**

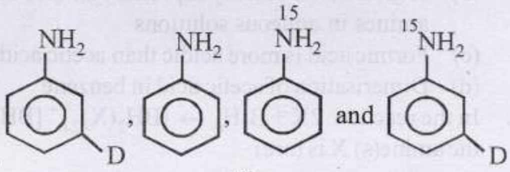


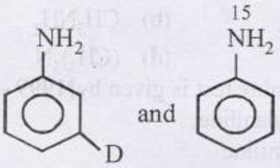
(i)

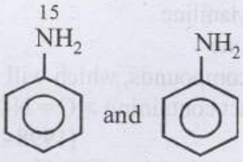
and

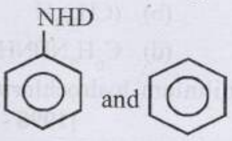


(ii)

(a)


(b)


(c)


(d)


9 Assertion and Reason Statement Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.

(b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.

(c) If Statement -1 is correct but Statement -2 is incorrect.

(d) If Statement -1 is incorrect but Statement -2 is correct.

40. **Statement-1 :** In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

Statement-2 : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance. **[2001S]**

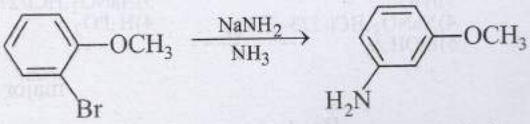
10 Subjective Problems

41. $$\underset{\substack{\text{(Optical active)}\\ \text{(X)}}}{C_5H_{13}N} \xrightarrow[-N_2]{\text{aq.}NaNO_2/HCl} \underset{\text{Tertiary alcohol}}{\text{(Y)}} + \text{Some other products}$$ **[2005 - 4 Marks]**

(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).

42. There is a solution of p–hydroxybenzoic acid and p-aminobenzoic acid. Discuss one method by which we can separate them and also write down the confirmatory tests of the functional groups present. **[2003 - 4 Marks]**

43. Explain briefly the formation of the products giving the structures of the intermediates. **[1999 - 2 Marks]**

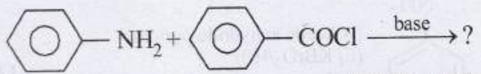


44. Compound A (C_8H_8O) on treatment with NH_2OH. HCl gives B and C. B and C rearrange to give D and E, respectively, on treatment with acid. B, C, D and E are all isomers of molecular formula (C_8H_9NO). When D is boiled with alcoholic KOH an oil F (C_6H_7N) separates out. F reacts rapidly with CH_3COCl 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 A-G. **[1999 - 7 Marks]**

45. Complete the following with appropriate structures :

(i) $CH_3CH_2NH_2 \xrightarrow{(CH_3CO)_2O,\text{heat}}$ 2 products **[1998 - 2 Marks]**

(ii) $CH_3CONHC_6H_5 \xrightarrow{Br_2,\ Fe}$ 2 products **[1998 - 2 Marks]**

(iii)


[1986 - 1 Mark]

46. Give reasons for the following :
(i) Dimethylamine is a stronger base than trimethylamine. **[1998 - 2 Marks]**
(ii) Cyclohexylamine is a stronger base than aniline. **[1982 - 1 Mark]**

47. Acetophenone on reaction with hydroxylamine hydrochloride can produce two isomeric oximes. Write structures of the oximes. **[1997 - 2 Marks]**

48. Write the structure of the foul-smelling compound obtained when aniline is treated with chloroform in the presence of KOH. **[1996 - 1 Mark]**

49. Identify, A (C_3H_9N) which reacts with benzensulphonyl chloride to give a solid, insoluble in alkali. **[1993 - 1 Mark]**

50. A basic, volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic potash. A 0.295 g sample of the substance. dissolved in aq. HCl and treated with $NaNO_2$ solution at 0°C, liberated a colorless, odourless gas whose volume corresponded to 112 mL at STP. After the evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance. Assume that it contains one N atom per molecule. **[1993 - 4 Marks]**

51. A mixture of two aromatic compounds A and B was separated by dissolving a chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound A, when heated with alcoholic solution of KOH produced a compound C(C_7H_5N) associated with an unpleasant odour. The alkaline aqueous 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 compounds A, B, C, D, E and write their structures. **[1990 - 4 Marks]**

52. Give a chemical test and the reagents used to distinguish between the following pair of compounds :
Ethylamine and diethylamine. **[1988 - 1 Mark]**

53. An organic compound A, containing C, H, N and O, on analysis gives 49.32% carbon, 9.59% hydrogen and 19.18% nitrogen. A on boiling with NaOH gives off NH_3 and a salt which on acidification gives a monobasic nitrogen free acid B. The silver salt of B contains 59.67% silver. Deduce the structures of A and B. **[1988 - 3 Marks]**

54. Arrange the following :
(i) methylamine, dimethylamine, aniline, N-methylaniline in incerasing order of base strength. **[1988 - 1 Mark]**
(ii) p-toluidine, N, N-dimethyl-p-toluidine, p-nitroaniline, aniline in increasing basicity. **[1986 - 1 Mark]**

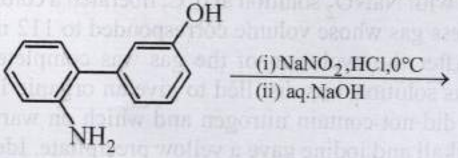
55. Write balanced equations for the following reaction :
Acetamide is reacted with bromine in the presence of potassium hydroxide. **[1987 - 1 Mark]**

56. Show with equations how the following compounds are prepared (equations need not be balanced) :
(i) aniline to chlorobenzene **[1985 - 1 Mark]**
(ii) Acetoxime from acetaldehyde using the reagents, $[K_2Cr_2O_7/H^+, Ca(OH)_2$ and $NH_2OH.HCl]$. **[1984 - 2 Marks]**
(iii) Aniline from benzene **[1983 - 1 Mark]**
(iv) chlorobenzene from aniline (in two steps). **[1982 - 1 Mark]**
(v) n-propyl amine from ethyl chloride (in two steps) **[1982 - 1 Mark]**

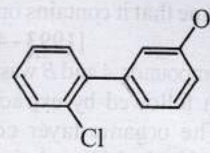
Topic-3: Diazonium Salts

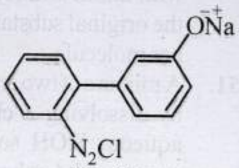
1 MCQs with One Correct Answer

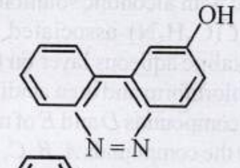
1. The major product of the following reaction is

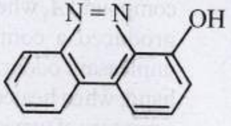


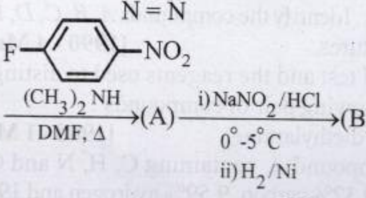
[Adv. 2017]

(a) 

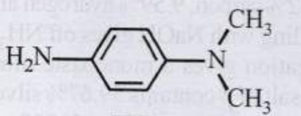
(b) 

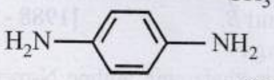
(c) 

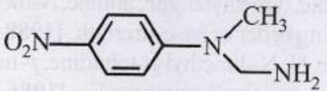
(d) 

2. 

(B) is: [2003S]

(a) 

(b) 

(c) 

(d) 

3 Numeric / New Stem Based Questions

Questions Stem

A trinitro compound, 1,3,5-tris-(4-nitrophenyl)benzene, on complete reaction with an excess of Sn/HCl gives a major product, which on treatment with an excess of NaNO$_2$/HCl at 0 °C provides P as the product. P, upon treatment with excess of H$_2$O at room temperature, gives the product Q. Bromination of Q in aqueous medium furnishes the product R. The compound P upon treatment with an excess of phenol under basic conditions gives the product S. The molar mass difference between compounds Q and R is 474 g mol^{-1} and between compounds P and S is 172.5 g mol^{-1}.

3. The number of heteroatoms present in one molecule of R is ______ . [Adv. 2023]

[Use: Molar mass (in g mol^{-1}): H = 1, C = 12, N = 14, O = 16, Br = 80, Cl = 35.5

Atoms other than C and H are considered as heteroatoms]

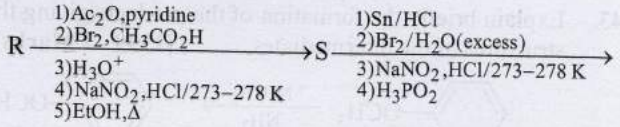
4. The total number of carbon atoms and heteroatoms present in one molecule of S is ______ . [Adv. 2023]

[Use: Molar mass (in g mol^{-1}): H = 1, C = 12, N = 14, O = 16, Br = 80, Cl = 35.5

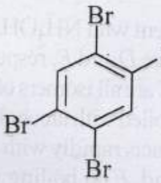
Atoms other than C and H are considered as heteroatoms]

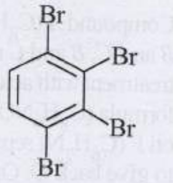
6 MCQs with One or More than One Correct Answer

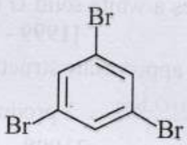
5. Aniline reacts with mixed acid (conc. HNO$_3$ and conc. H$_2$SO$_4$) at 288 K to give **P** (51 %), **Q** (47%) and **R** (2%). The major product(s) of the following reaction sequence is (are) [Adv. 2018]

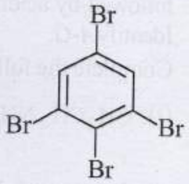


major product(s)

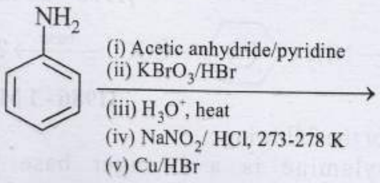
(a) 

(b) 

(c) 

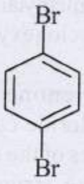
(d) 

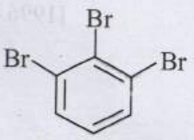
6. The product(s) of the following reaction sequence is (are)

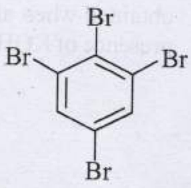


[Adv. 2016]

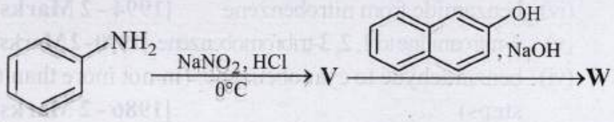
(a) 

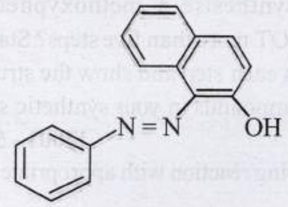
(b) 

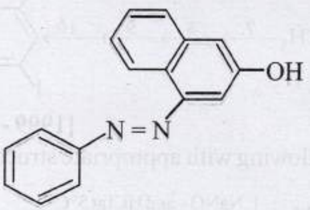
(c) 

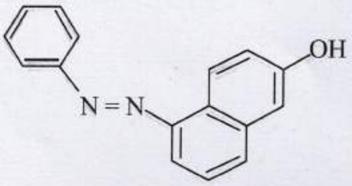
(d) 

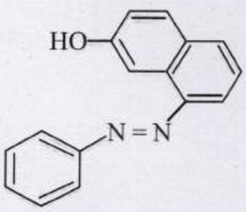
7. In the following reactions, the major product *W* is



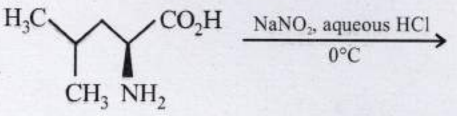
(a)  **[Adv. 2015]**

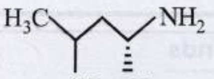
(b) 

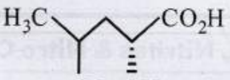
(c) 

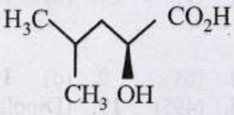
(d) 

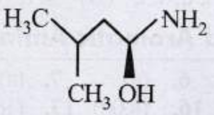
8. The major product of the reaction is **[Adv. 2015]**



(a) 

(b) 

(c) 

(d) 

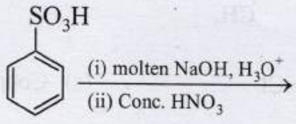
9. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives **[1998 - 2 Marks]**

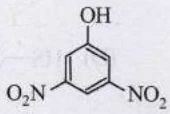
(a) diphenyl ether
(b) *p*-hydroxyazobenzene
(c) chlorobenzene
(d) benzene

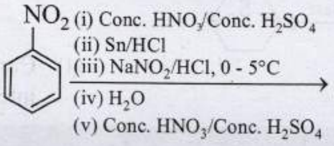
7 Match the Following

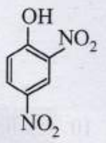
10. **List-I** contains various reaction sequences and **List-II** contains different phenolic compounds. Match each entry in **List-I** with the appropriate entry in **List-II** and choose the correct option. **[Adv. 2024]**

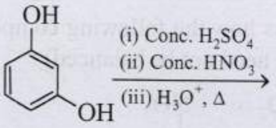
List-I **List-II**

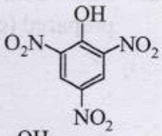
(P) 

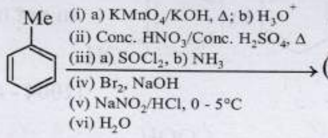
(1) 

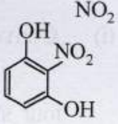
(Q) 

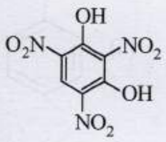
(2) 

(R) 

(3) 

(S) 

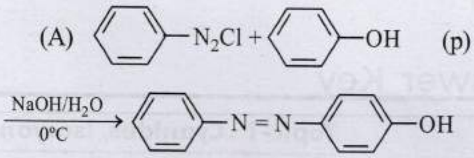
(4) 

(5) 

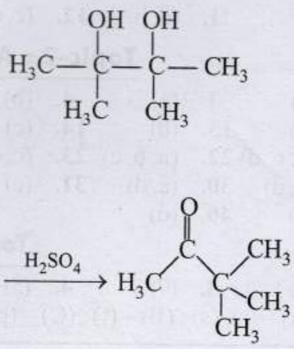
(a) P-2, Q-3, R-4, S-5
(b) P-2, Q-3, R-5, S-1
(c) P-3, Q-5, R-4, S-1
(d) P-3, Q-2, R-5, S-4

11. Match the reaction in Column-I with appropriate options in Column-II. **[2010]**

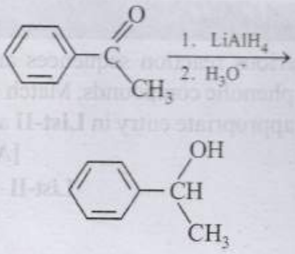
Column-I **Column-II**

(A) 

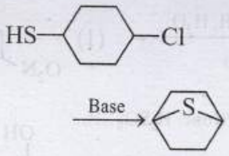
(p) Racemic mixture

(B) 

(q) Addition reaction

(C) 

(r) Substitution reaction

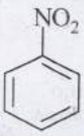
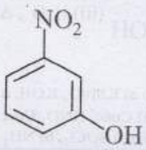
(D) 

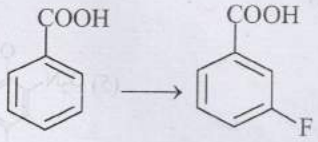
(s) Coupling reaction

(t) Carbocation intermediate

10 Subjective Problems

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

(i) Convert  to  in not more than four steps. **[2004 - 4 Marks]**

(ii)  (in not more than 3 step)

[2003 - 2 Marks]

(iii) Aniline ⟶ Benzylamine (in 3 steps) **[2000 - 3 Marks]**

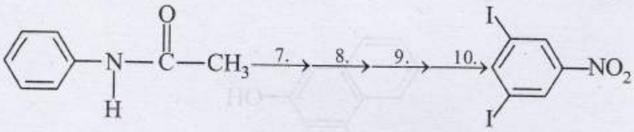
(iv) benzamide from nitrobenzene **[1994 - 2 Marks]**

(v) 4-nitroaniline to 1, 2, 3-tribromobenzene. **[1990 - 2 Marks]**

(vi) benzaldehyde to cyanobenzene. (in not more than 6 steps) **[1986 - 2 Marks]**

13. How would you synthesise 4–methoxyphenol from bromobenzene in NOT more than five steps? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme. **[2001 - 5 Marks]**

14. Complete the following reaction with appropriate reagents:



[1999 - 4 Marks]

15. Complete the following with appropriate structures :

$$\text{2, 4-Dinitroaniline} \xrightarrow[\text{2. anisole}]{\text{1. NaNO}_2 \text{ and HCl at } 5°\text{C}} \underset{-----}{\text{C}}$$

[1995 - 1 Mark]

Answer Key

Topic-1 : Cyanides, Isocyanides, Nitrites & Nitro Compounds

1. (b) **2.** (c) **3.** (N) **4.** (d) **5.** (a) **6.** (c) **7.** (d) **8.** (b) **9.** (a)
10. (Meta isomer) **11.** (a, b, d) **12.** (c, e) **13.** (A)– p, q, s, t; (B) – s, t; (C) – p; (D) – r **14.** (d) **15.** (a)

Topic-2 : Aliphatic and Aromatic Amines

1. (c) **2.** (c) **3.** (a) **4.** (b) **5.** (b) **6.** (a) **7.** (a) **8.** (b) **9.** (d) **10.** (b)
11. (a) **12.** (b) **13.** (b) **14.** (c) **15.** (28) **16.** (4.00) **17.** (18.60) **18.** (495) **19.** (Dipolar ion)
20. (aniline) **21.** (b, c, d) **22.** (a, b, c) **23.** (c, d) **24.** (c, d) **25.** (a) **26.** (a) **27.** (a, b, d)
28. (a,b,c) **29.** (b, d) **30.** (a, d) **31.** (c) **32.** (c) **33.** (a, c) **34.** (c) **35.** (a) **36.** (b) **37.** (d)
38. (d) **39.** (b) **40.** (d)

Topic-3 : Diazonium Salts

1. (c) **2.** (a) **3.** (9) **4.** (51) **5.** (d) **6.** (b) **7.** (a) **8.** (c) **9.** (b)
10. (c) **11.** (A) – (r), (s) ; (B) – (t) ; (C) – (p), (q) ; (D) – (r)

Hints & Solutions

Topic-1: Cyanides, Isocyanides, Nitrites & Nitro Compounds

1. **(b)** $H_2C=N^+=N^- > H_2C^- - N^+\equiv N$

I: Octet complete, 6 covalent bonds, –ve charge on N
III: Octet complete, 6 covalent bonds, –ve charge on C

$> H_2C^+ - N=N^- > H_2C^- - N=N^+$

II: Octet incomplete, 5 covalent bonds, –ve charge on N
IV: Octet incomplete, 5 covalent bonds, –ve charge on C

2. **(c)** $CHCl_3 + RNH_2 + KOH \xrightarrow[\text{reaction}]{\text{Carbylamine}} R-N^+\equiv C^- + 3KCl + 3H_2O$

3. **(N)** None of the given options is correct. Benzene sulphonic acid, being stronger acid than carbonic acid, would liberate CO_2 when treated with sodium bicarbonate, but *p*-nitrophenol, being less acidic than carbonic acid, will not liberate CO_2.

4. **(d)** $POCl_3$ is a dehydrating agent. Hence $C_6H_5CONH_2 \xrightarrow{POCl_3} C_6H_5CN + H_2O$

5. **(a)** Two moles of NH_2^- ions will abstract two moles of most acidic hydrogen out of the four moles of acidic hydrogen present per mole of the compound. The acidic strength is in the order:
–COOH > –OH (phenolic having NO_2 group) > –OH (phenolic) > alkynic H.

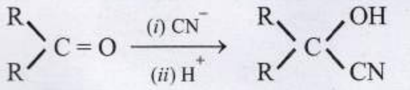
6. **(c)** N can't have more than 8 electrons in its valence shell as it does not have any *d* orbital. In (c), N has 10 electrons.

7 **(d)** In the formation of nitrile, number of carbon atoms in parent chain increases by one.

$CH_3CH_2CH_2Cl + alc.\,KCN \xrightarrow{100^\circ C} CH_3CH_2CH_2CN$

Propyl chloride

8. **(b)** The addition is initiated by the attack of CN^- group which is a nucleophile.



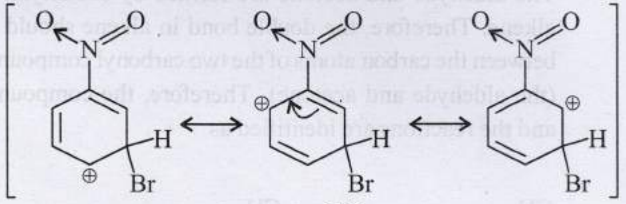
$$R_2C=O \xrightarrow[(ii)\ H^+]{(i)\ CN^-} R_2C(OH)CN$$

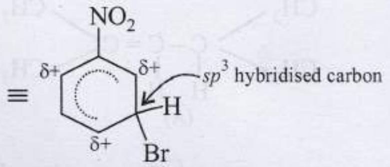
Ketone cyanohydrin

9. **(a)** Toluene has electron-donating methyl group. Hence, reacts fastest while others have either electron withdrawing groups (*i.e.* – COOH or – NO_2 *etc.*) or no substituent.

10. **Meta isomer**

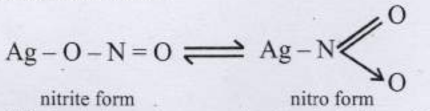
11. **(a, b, d)**
(a) Nitro group decreases the electron density at the *o*- and *p*-positions in comparison to *m*-position due to –M effect.
(b) The below intermediate is a resonance hybrid of three equivalent structures.





Due to –NO_2 group, electron density will decrease more from *o*- and *p*- positions. Hence, the attack of electrophile Br^+ will be favourable at meta position.
In another words, after attack of Br^+ at meta position, intermediate will be least destabilised.
(c) There will be loss of aromaticity when Br^+ attacks at any position because of formation of sp^3 hybridised carbon. Thus, option (c) is incorrect.
(d) Due to more electron density at meta position, heterolytic fission of C – H bond and removal of H^+ will be easy from this position.
Thus, option (d) is correct.

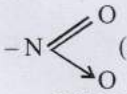
12. **(c, e)** Silver nitrite, being a salt of nitrous acid, occurs in two tautomeric forms.



$$Ag-O-N=O \rightleftharpoons Ag-N(=O)\rightarrow O$$

nitrite form (trivalent nitrogen) — nitro form (pentavalent nitrogen)

NO_2^- ion from $AgNO_2$ may exist in two tautomeric forms, –O – N = O (nitrite ion) forming **alkyl nitrites**, and



$-N(=O)\rightarrow O$ (nitro group) forming **nitroalkanes**.

$2\,C_2H_5Br + 2AgNO_2 \rightarrow C_2H_5NO_2 + C_2H_5ONO + 2\,AgBr$

13. **(A)– p, q, s, t; (B) – s, t; (C) – p; (D) – r**
(A) $CH_3CH_2CH_2CN \xrightarrow[\text{DIBAL–H}]{\text{Pd–C/H}_2\text{ or}} CH_3CH_2CH_2CH_2NH_2$

$$CH_3CH_2CH_2CN \xrightarrow[\text{(Stephen reduction)}]{SnCl_2/HCl} CH_3CH_2CH_2CHO$$

$$CH_3CH_2CH_2CN \xrightarrow[H_2O]{OH^-} CH_3CH_2CH_2COO^-$$

(B) $CH_3CH_2OCOCH_3 \xrightarrow{DIBAL-H} CH_3CH_2OH$

$$CH_3CH_2OCOCH_3 \xrightarrow[H_2O]{OH^-} CH_3CH_2OH + CH_3COO^-$$

(C) $CH_3CH=CHCH_2OH \xrightarrow{Pd-C/H_2} CH_3CH_2CH_2CH_2OH$

(D) $CH_3CH_2CH_2CH_2NH_2 \xrightarrow[KOH]{CHCl_3} CH_3CH_2CH_2CH_2NC$
Isonitrile (foul smelling)

14. (d) Chlorobenzene is resonance stabilized. Thus aryl halides (chlorobenzene) do not undergo nucleophilic substitution. Reason is correct.

15. (a) In *o*-nitrophenol, intramolecular H-bonding is possible because OH and NO_2 groups are close to each other. This makes the *ortho* isomer less acidic as its capacity to donate a proton (H-atom) decreases. There is no such intramolecular H–bonding in the *p*-isomer.

16. (*i*) (a) $-\ddot{N}=O$ group is electron releasing, hence *o*-, *p*-directing

(b) $-NO_2$ group is electron withdrawing, hence *m*-directing

(*ii*) $-NO_2$ group is electron withdrawing, hence *m*-directing, whereas $-CH_2NO_2$ is not.

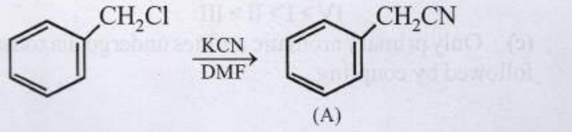
(a) Given compound is an aryl fluoride having electron-withdrawing $-NO_2$ group at *para* position of fluoride atom which activates the fluoride due to – M and – E effects for nucleophilic substitution (S_NAr), hence reaction with NaOH will liberate F^- as NaF.

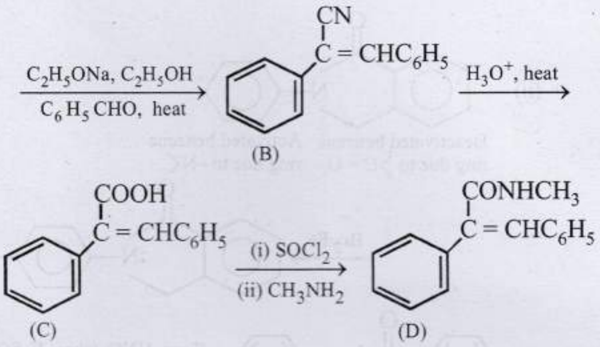
(b) The given compound is an aryl fluoride having $-CH_2NO_2$ group in the *meta* position which is not capable of activating aryl fluoride (absence of –M and –E effects because NO_2 group is not conjugated to benzene ring) for nucleophilic substitution, hence aq. NaOH will not displace fluorine here, *i.e.* no F^- will be formed.

(*iii*) The nitro group in nitrobenzene strongly deactivates the benzene ring due to – I and – M effects. This decreases the reactivity of benzene ring towards Friedel - Crafts alkylation.

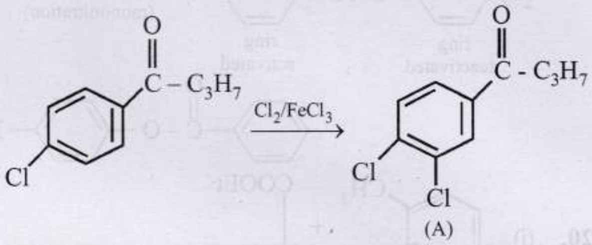
(*iv*) *o*-Nitrophenol shows intramolecular H-bonding and exists as a single molecule, while *p*-nitrophenol shows intermolecular H- bonding and thus its several molecules associate with each other. The *ortho* isomer goes with the steam due to its low boiling point.

17.

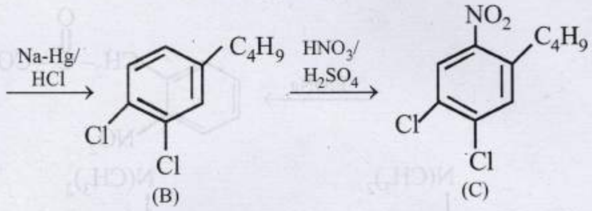




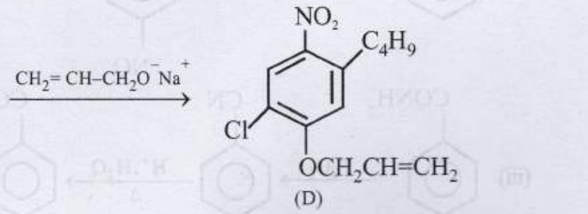
18.



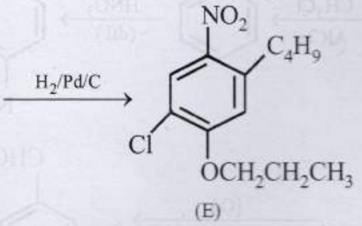
(–COR is a meta directing group)



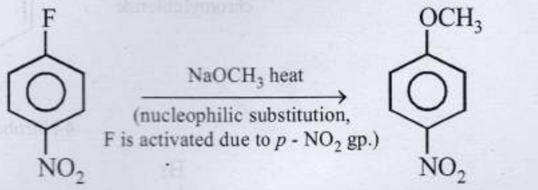
(–R activates the ring at *o*- and *p*-positions for electrophilic aromatic substitution)



($-NO_2$ decrease the e^- density at *o*- and *p*-positions for $Nu^{\ominus}$ aromatic substitution)

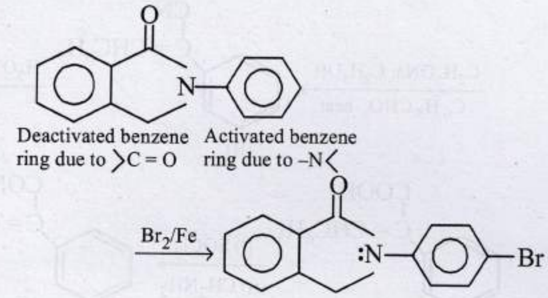


19. (*i*)

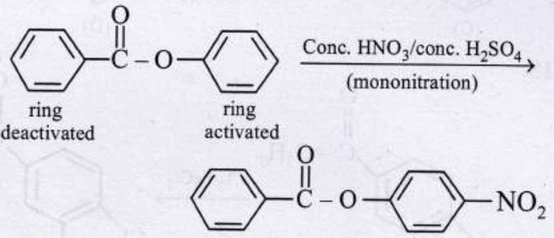


NO_2 group deactivates the ring and thus, decreases the electron density at *o*- and *p*-positions. This makes it for nucleophilic attack at these positions.

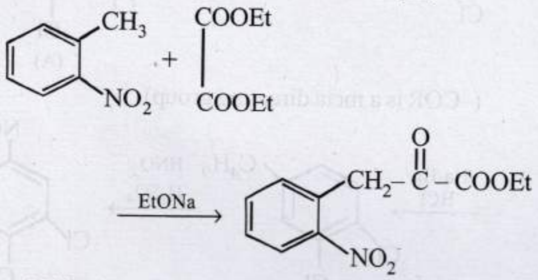
(ii)



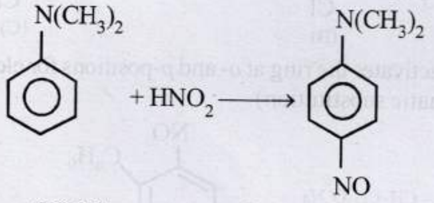
(iii)



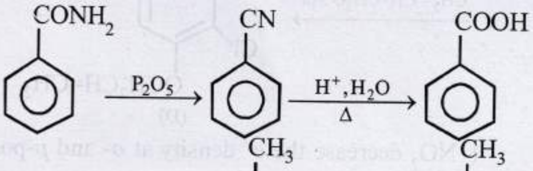
20. (i)



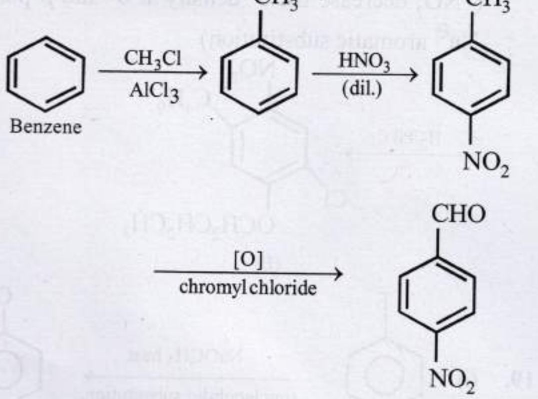
(ii)



(iii)

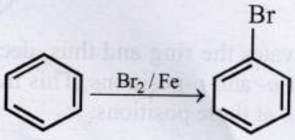


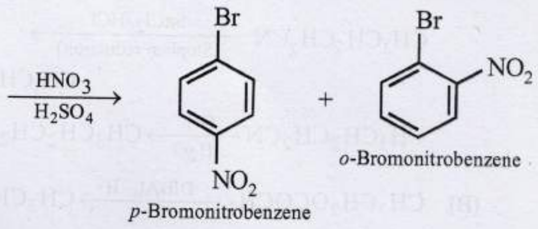
21. (i)



4-Nitrobenzaldehyde

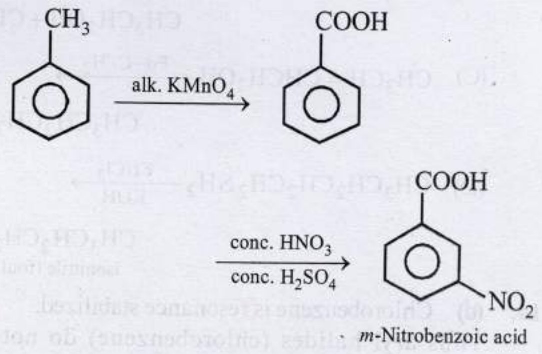
(ii)





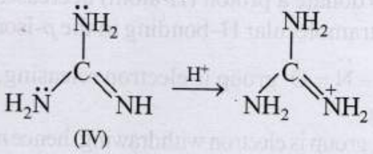
On fractional crystallization, para isomer crystallizes first.

(iii)



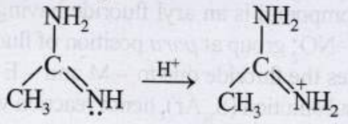
Topic-2: Aliphatic and Aromatic Amines

1. (c) Higher the stability of the conjugate acid, more is the basic character of the parent amine.



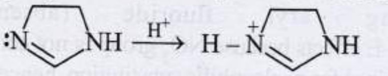
(IV)

The conjugate acid is stabilized by resonance with two different –NH_2 groups.



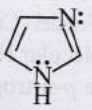
(I)

The conjugate acid is stabilized by resonance with one –NH_2 group. Hence, as compared to IV it is less basic.



(II)

Lone pair is not involvd in aromaticity. Hence, more available than III.



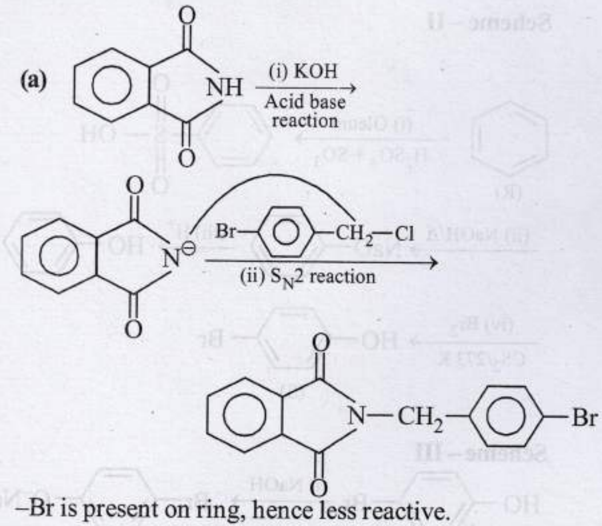
(III)

Lone pair is involved in aromatic sextet. Hence, not available. Hence, the correct order of basic strength is

IV > I > II > III

2. (c) Only primary aromatic amines undergo diazotisation followed by coupling.

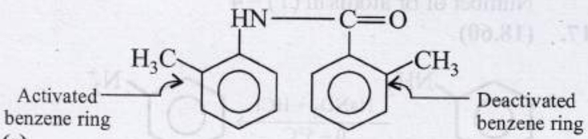
3. **(a)**



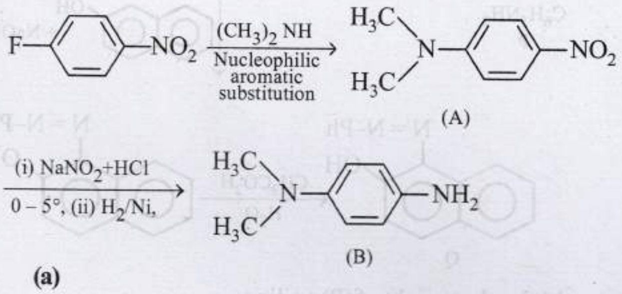
–Br is present on ring, hence less reactive.

4. **(b)** (i) Position (X) is most acidic due to – COOH group.
(ii) $-NH_3^+$ group at position Y is more acidic than at Z because of presence of electron withdrawing – COOH group in close proximity. Hence $-NH_3^+$ group at position Z is least acidic.

5. **(b)** NH is more activating than $-CH_3$ group, whereas C = O group is a deactivating group. Hence, electrophilic substitution at para-position will be governed by the ring having >NH group.



6. **(a)**



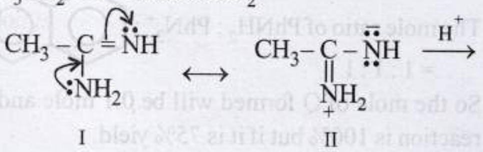
7. **(a)**

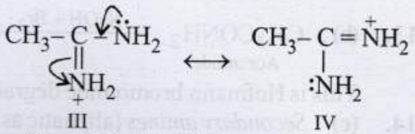
$$\underset{(A)}{C_3H_8O} \xrightarrow{K_2Cr_2O_7/H^+} \underset{(B)}{C_3H_6O} \xrightarrow{\text{amm. } AgNO_3} \text{Silver mirror}$$

$$(B) \xrightarrow{H_2NCONHNH_2.HCl} (C)$$

Reaction of (B) indicates that it is an aldehyde which thus should be C_2H_5CHO or CH_3CH_2CHO, hence (C) should be $CH_3CH_2CH=NNHCONH_2$

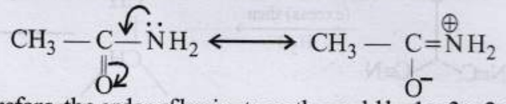
8. **(b)**





The protonated form of II would be III which is more stable because here the contributing structures (III) and (IV) are equivalent.

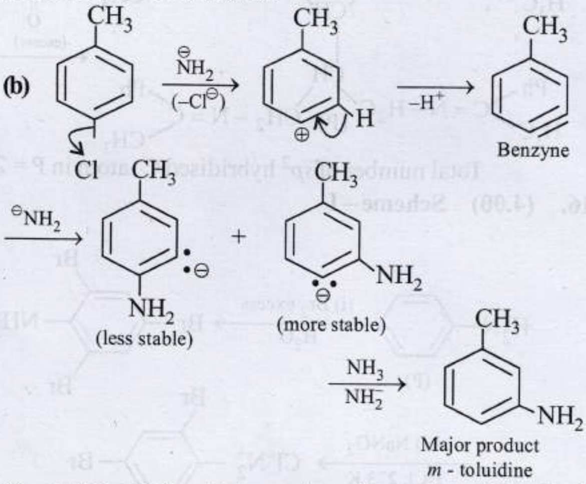
In $CH_3-\ddot{N}H-CH_3$, the availability of electron pair increases due to the +I effect of two CH_3 groups while in $CH_3CH_2NH_2$, +I effect of only one ethyl group is operative. In $CH_3-CO-NH_2$, the electron availability on nitrogen decreases due to resonance as shown below



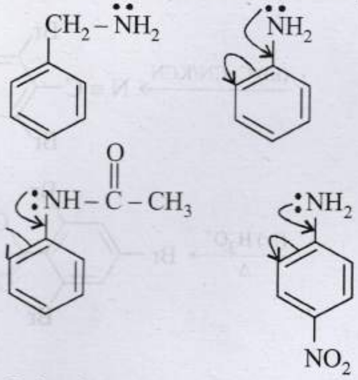
Therefore, the order of basic strength would be 1 > 3 > 2 > 4.

9. **(d)** Aliphatic amines are more basic than aromatic amines because in aliphatic amines electron pair on nitrogen is not involved in resonance.

10. **(b)**



11. **(a)** In benzylamine, electron pair on nitrogen is not delocalised due to lack of conjugation; while in all other compounds it is delocalised and hence, lesser available for protonation.



12. **(b)** Only primary aliphatic and aromatic amines give this test.

$CHX_3 + RNH_2 + 3KOH \rightarrow RNC + 3KX + 3H_2O$

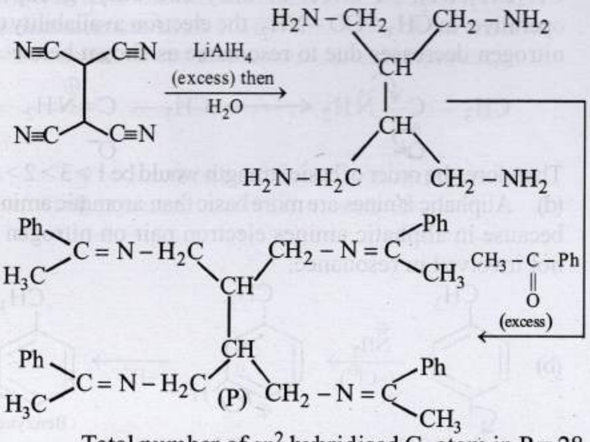
13. **(b)** $\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{NaOH + Br_2} \underset{\text{Methylamine}}{CH_3NH_2}$

This is Hofmann bromomide degradation reaction.

14. **(c)** *Secondary amines* (aliphatic as well as aromatic) *react with nitrous acid to form* **N-nitrosoamines.**

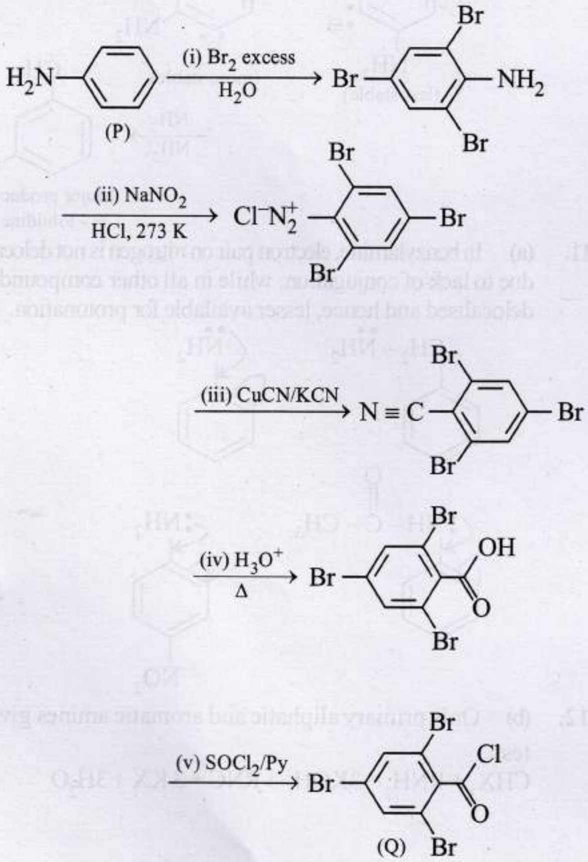
$(C_2H_5)_2NH + HONO \longrightarrow \underset{\text{N-Nitrosodiethylamine}}{(C_2H_5)_2N-N=O} + H_2O$

15. **(28)**

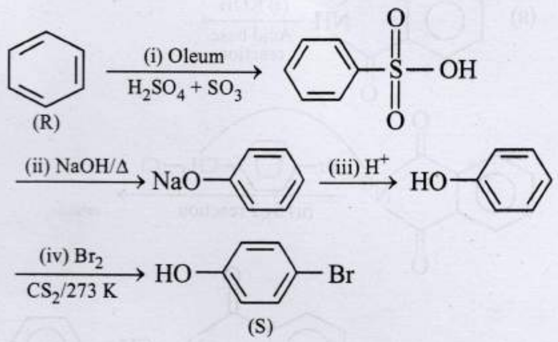


Total number of sp^2 hybridised C–atom in P = 28

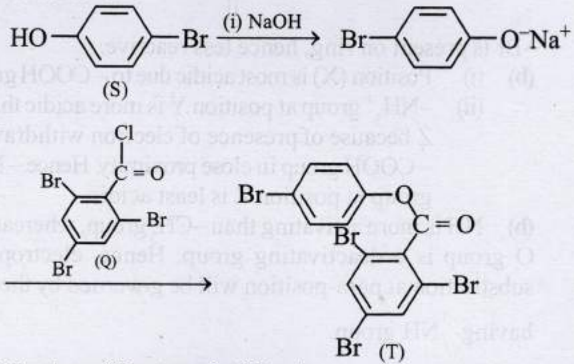
16. **(4.00)** **Scheme – I**



Scheme – II

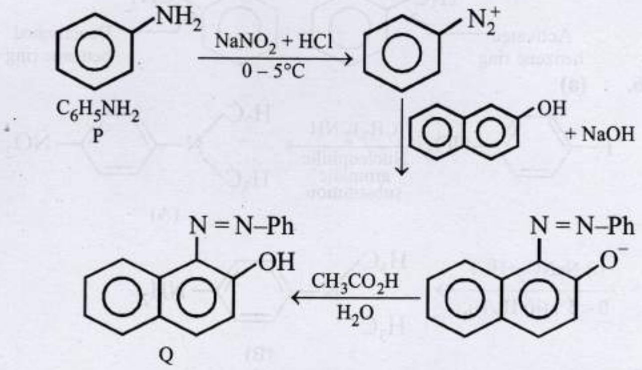


Scheme – III



Number of Br atoms in (T) = 4

17. **(18.60)**



Molecular weight of (P) aniline

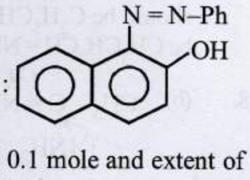
$= \text{M.wt. of } C_6NH_7 = 72 + 7 + 14 = 93$

Density of P = 1 g mL^{-1}

$\therefore$ 9.3 mL of P = 9.3 g P

$= \dfrac{9.3}{9.3} = 0.1$ mole P

The mole ratio of $PhNH_2 : PhN_2^+$:



= 1 : 1 : 1

So the mole of Q formed will be 0.1 mole and extent of reaction is 100% but if it is 75% yield.

Then amount of Q $= 0.1 \times \frac{75}{100} = 0.075$ mol

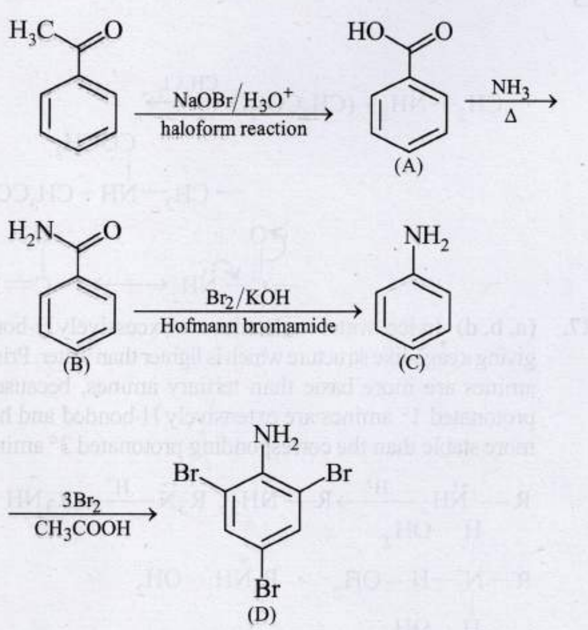
The molecular formula of Q $= C_{16}H_{12}ON_2$

So M.wt. of Q $= 16 \times 12 + 12 \times 1 + 16 + 2 \times 14$

$= 192 + 12 + 16 + 28 = 248$ g

So amount of Q $= 248 \times 0.075 = 18.6$ g

18. **(495)**



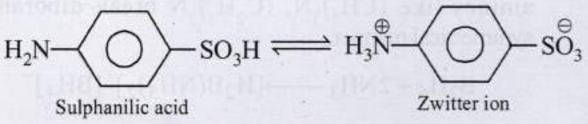
Molecular mass of (D) $= (6 \times 12) + (4 \times 1) + (1 \times 14) + (3 \times 80)$

$= 330$ g/mol

Moles of (D) formed $= 10 \times 0.6 \times 0.5 \times 0.5 \times 1 = 1.5$

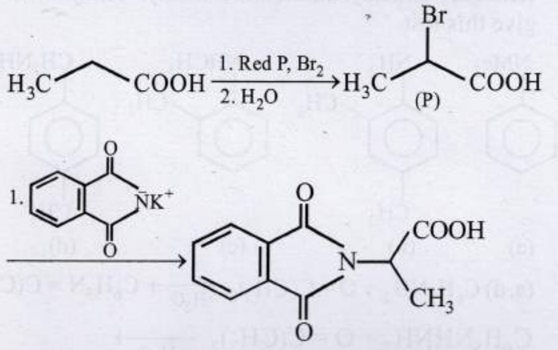
Mass of (D) formed $= 1.5 \times 330 = 495$ g

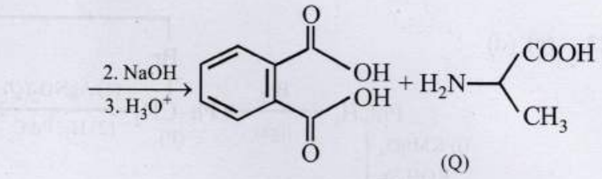
19. **Dipolar ion.** (Salt like)

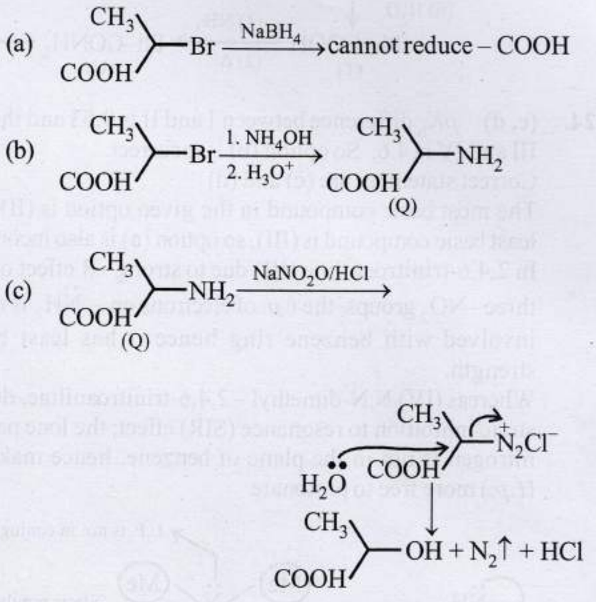


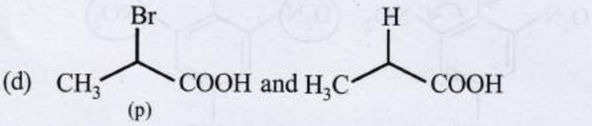
20. **aniline.**

21. **(b, c, d)**



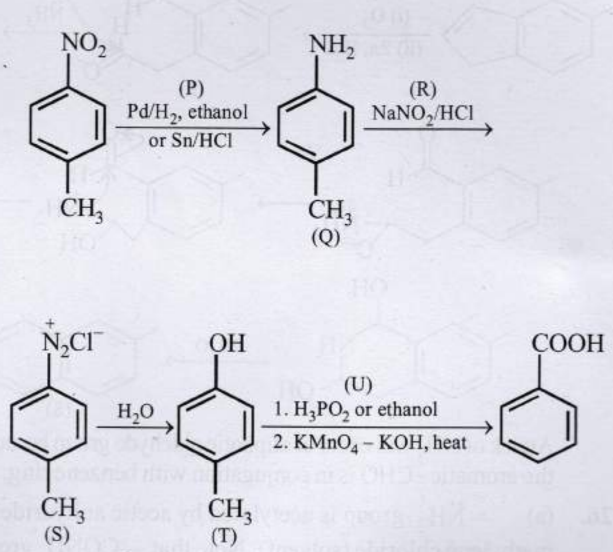




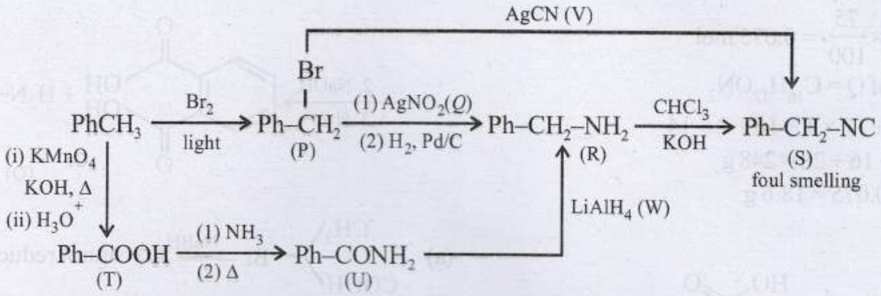


(P) is more acidic than CH_3CH_2COOH as –Br has (–I) effect.

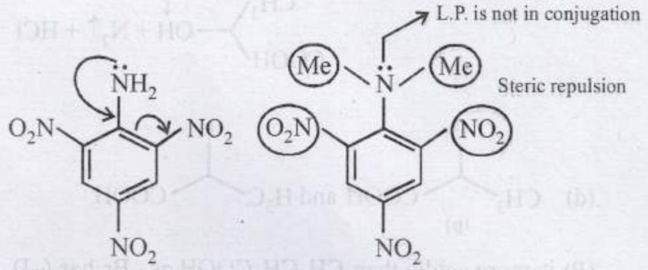
22. **(a, b, c)**



23. **(c) (d)**

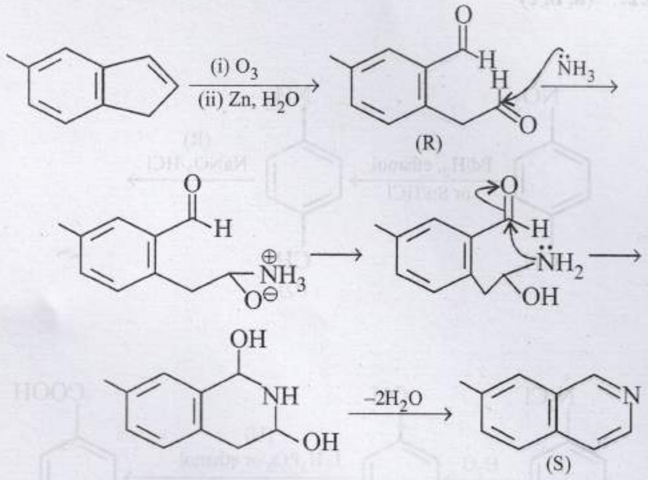


24. **(c, d)** pK_b difference between I and II is 0.53 and that of III and IV is 4.6. So option (b) is incorrect
Correct statement are (c) and (d)
The most basic compound in the given option is (II) and least basic compound is (III), so option (a) is also incorrect. In 2,4,6-trinitroaniline (III) due to strong –R effect of the three $–NO_2$ groups, the ℓ.p. of electrons on $-\ddot{N}H_2$ is more involved with benzene ring hence it has least basic strength.
Whereas (IV) N,N-dimethyl – 2,4,6-trinitroaniline, due to steric inhibition to resonance (SIR) effect; the lone pair of nitrogen is not in the plane of benzene, hence makes it (ℓ.p.) more free to protonate



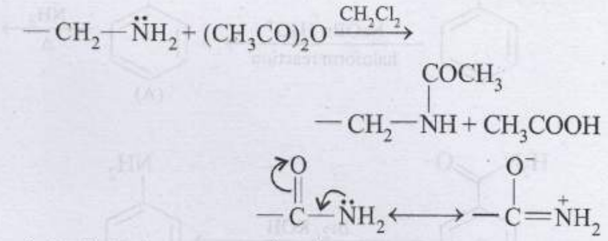
More effective resonance

25. **(a)**

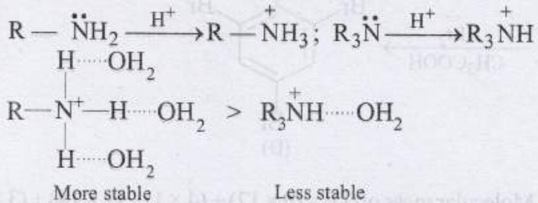


Attack of NH_3 will occur at aliphatic aldehyde group because the aromatic –CHO is in conjugation with benzene ring.

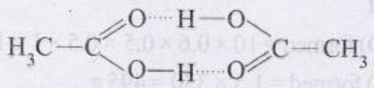
26. **(a)** $-\ddot{N}H_2$ group is acetylated by acetic anhydride in methylene chloride (solvent). Note that $-CONH_2$ group does not undergo acetylation because here lone pair of electrons is delocalised.



27. **(a, b, d)** In ice, water molecules are excessively H-bonded giving a cage-like structure which is lighter than water. Primary amines are more basic than tertiary amines, because the protonated 1° amines are extensively H-bonded and hence more stable than the corresponding protonated 3° amines.



Acetic acid undergoes dimerisation in benzene.

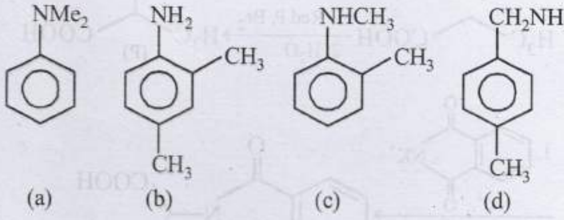


28. **(a,b,c)** Lower amines like NH_3, CH_3NH_2 and $(CH_3)_2NH$ break diborane molecule unsymmetrically, while larger amines like $(CH_3)_3N$, $(C_2H_5)_3N$ break diborane in symmetrical manner.

$$B_2H_6 + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+[BH_4]^-$$

$$B_2H_6 + 2(CH_3)_3N \longrightarrow 2H_3B \leftarrow N(CH_3)_3$$

29. **(b,d)** Only primary amines give carbylamine test. Hence 2,4-dimethylaniline and P-methyl–benzylamine both give this test.



30. **(a, d)** $C_6H_5NH_2 + O=C(CH_3)_2 \xrightarrow[-H_2O]{} C_6H_5N=C(CH_3)_2$

$C_6H_5NHNH_2 + O=C(CH_3)_2 \xrightarrow[-H_2O]{}$

$C_6H_5NHN=C(CH_3)_2$

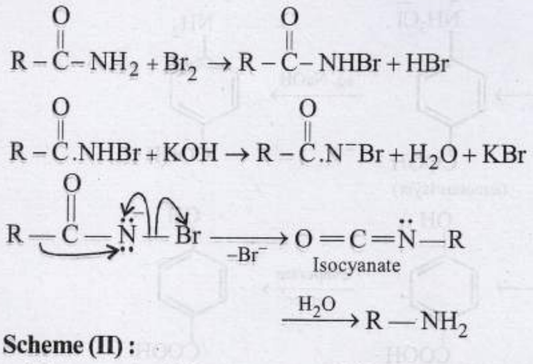
31. **(c)** Anilinium hydrochloride has ionisable chlorine, whereas p-chloro-aniline has non ionizable chlorine. Thus, anilinium hydrochloride gives white precipitate of AgCl with $AgNO_3$.

$$C_6H_5NH_3^+Cl^- + AgNO_3 \rightarrow C_6H_5NH_3^+NO_3^- + AgCl\downarrow$$

In chloroaniline, –Cl is directly attached to benzene ring, hence it is non-reactive.

32. **(c)** In I^st^ structure N has complete octet, whereas in II^nd^ structure N has 10 electrons in its valence shell, which is not possible.

33. **(a, c)** This is an example of Hofmann degradation of amides.

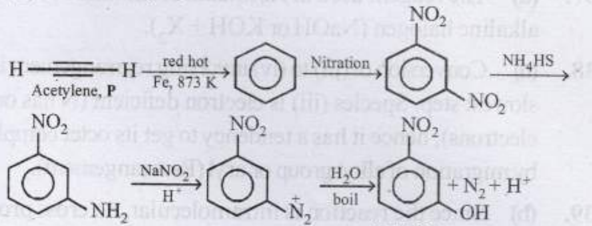


$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 \rightarrow R-\overset{O}{\overset{\|}{C}}-NHBr + HBr$$

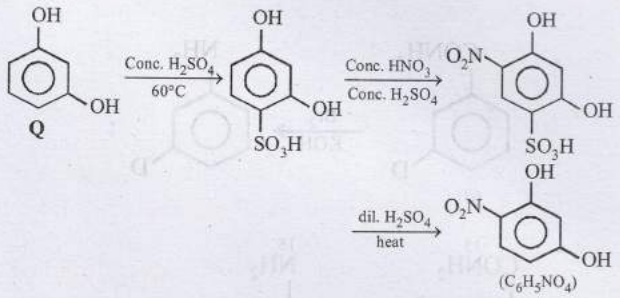
$$R-\overset{O}{\overset{\|}{C}}.NHBr + KOH \rightarrow R-\overset{O}{\overset{\|}{C}}.N^-Br + H_2O + KBr$$

$$R-\overset{O}{\overset{\|}{C}}-\ddot{N}^--Br \xrightarrow[-Br^-]{} O=C=\ddot{N}-R \xrightarrow{H_2O} R-NH_2$$

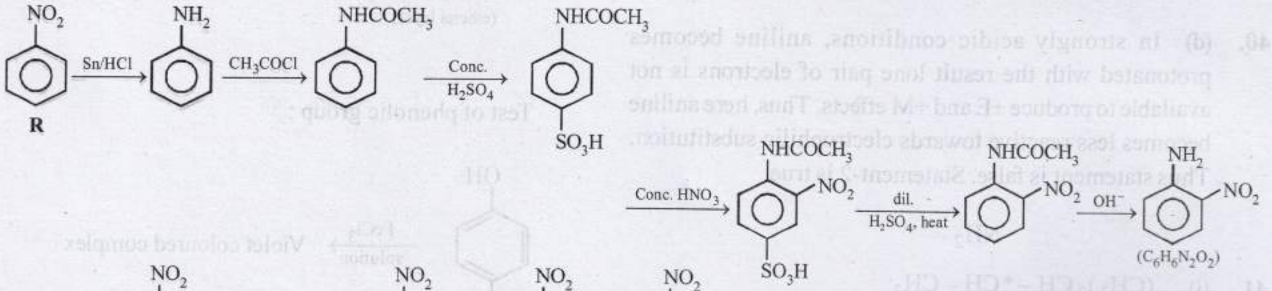
34. **(c)** **Scheme (III) :**



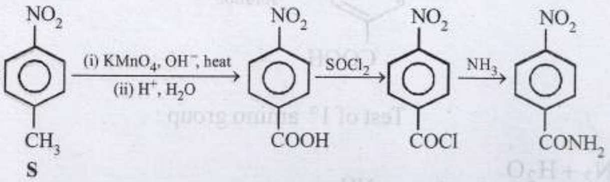
Scheme (IV) :



Scheme (II) :

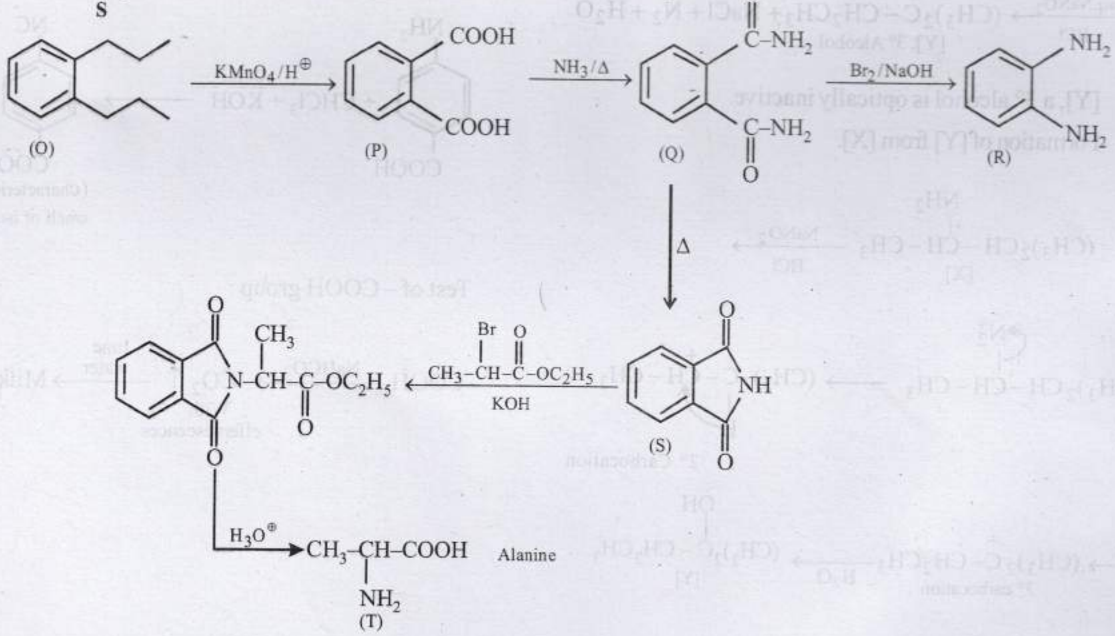


Scheme (I) :



35. **(a)**

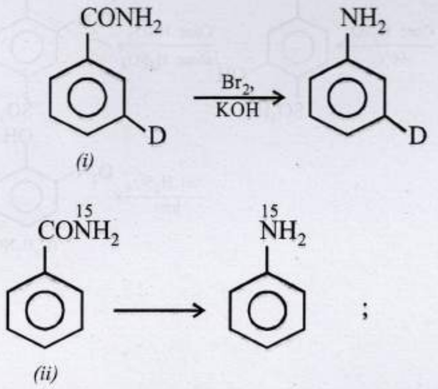
36. **(b)**



37. **(d)** The reagent used in Hoffmann bromamide reaction is alkaline halogen (NaOH or KOH + X_2).

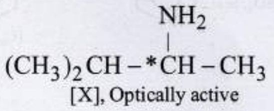
38. **(d)** Conversion of (iii) to (iv) involving rearrangement is the slowest step. Species (iii) is electron deficient (N has only 6 electrons), hence it has a tendency to get its octet completed by migration of alkyl group or aryl (Rearrangement).

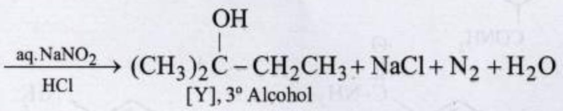
39. **(b)** Since the reaction is intramolecular, no cross product will be formed.



40. **(d)** In strongly acidic conditions, aniline becomes protonated with the result lone pair of electrons is not available to produce +E and +M effects. Thus, here aniline becomes less reactive towards electrophilic substitution. Thus statement is false. Statement-2 is true.

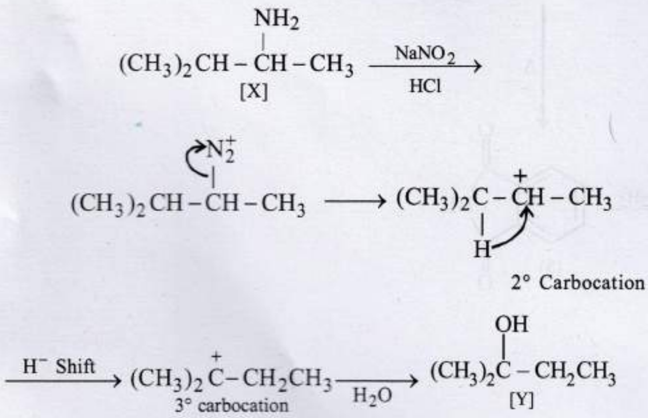
41. (i)


$$\underset{\text{[X], Optically active}}{(CH_3)_2CH-\overset{\overset{NH_2}{|}}{{}^{*}CH}-CH_3}$$


$$\xrightarrow[HCl]{aq.NaNO_2} \underset{\text{[Y], 3° Alcohol}}{(CH_3)_2\overset{\overset{OH}{|}}{C}-CH_2CH_3}+NaCl+N_2+H_2O$$

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

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

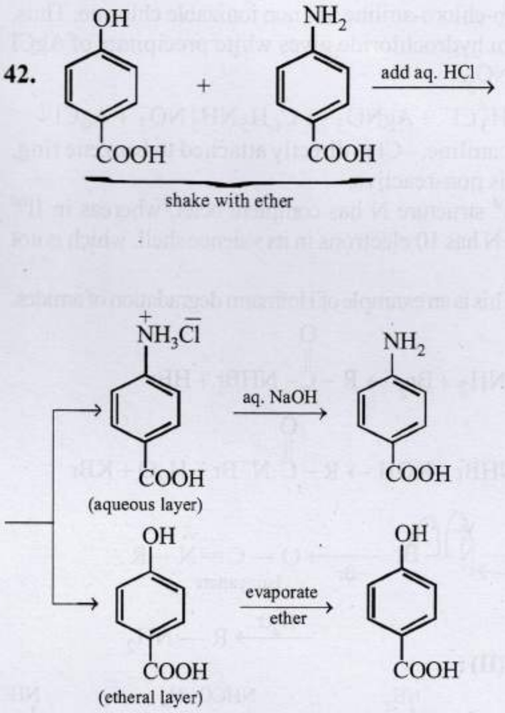

$$\underset{[X]}{(CH_3)_2CH-\overset{\overset{NH_2}{|}}{CH}-CH_3}\xrightarrow[HCl]{NaNO_2}$$

$$(CH_3)_2CH-\overset{\overset{N_2^+}{|}}{CH}-CH_3\longrightarrow(CH_3)_2\underset{\underset{H}{|}}{C}-\overset{+}{C}H-CH_3$$

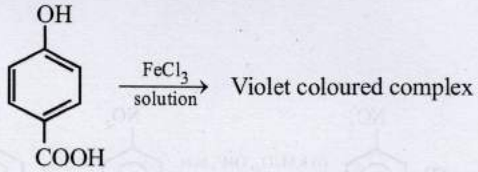
2° Carbocation

$$\xrightarrow{H^-\text{ Shift}}\underset{\text{3° carbocation}}{(CH_3)_2\overset{+}{C}-CH_2CH_3}\xrightarrow[H_2O]{}\underset{[Y]}{(CH_3)_2\overset{\overset{OH}{|}}{C}-CH_2CH_3}$$

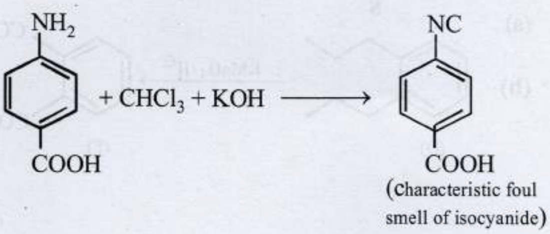
42.



Test of phenolic group :



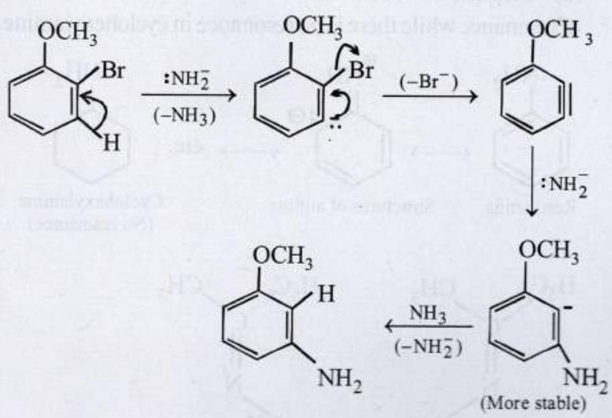
Test of 1° amino group :



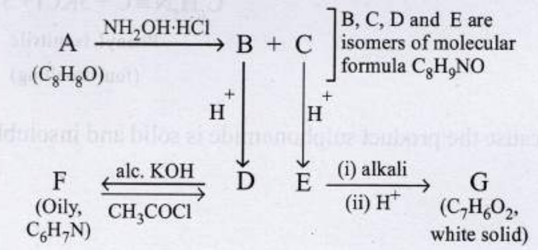
Test of – COOH group :

$$-COOH\xrightarrow{NaHCO_3}\underset{\substack{\text{With}\\\text{effervescences}}}{CO_2\uparrow}\xrightarrow{\substack{\text{lime}\\\text{water}}}\text{Milky solution}$$

43. The reaction proceeds via benzyne formation



44. Summary of the given facts.



From the above set, following conclusions can be drawn.

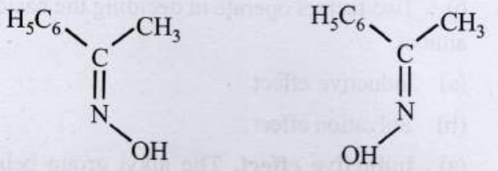
(i) Since the oily compound *F* (C_6H_7N) reacts with acetyl chloride, it must have $-NH_2$ or $>NH$ group. Thus, (*F*) can be written as $C_6H_5NH_2$ and hence, *D* is $C_6H_5NHCOCH_3$.

$$\underset{(F)}{C_6H_5NH_2} \underset{\text{alc. KOH}}{\overset{CH_3COCl}{\rightleftharpoons}} \underset{(D)}{C_6H_5NHCOCH_3}$$

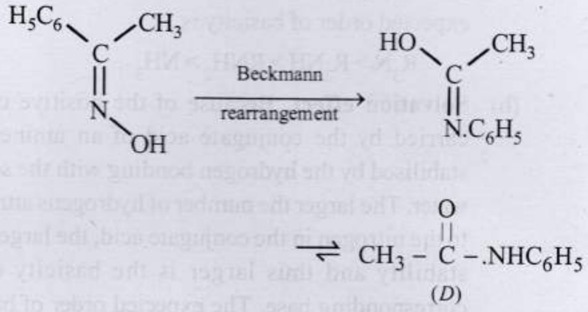
(ii) Compound (*E*) on treatment with alkali followed by acidification gives a white solid compound (*G*), $C_7H_6O_2$. Thus, (*G*) seems to be an acid, hence it is C_6H_5COOH.

(iii) Since (*D*) and (*E*) are isomers of the formula C_8H_9NO, and give $C_6H_5NH_2$ and C_6H_5COOH respectively, both should be amides having different alkyl or aryl group. Thus, (*D*) should be $C_6H_5NHCOCH_3$, and (*E*) must be $CH_3NHCOC_6H_5$.

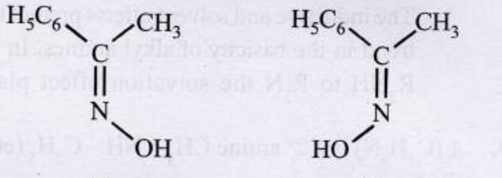
(iv) Since compounds (*D*) and (*E*) are formed by the rearrangement of compounds (*B*) and (*C*) respectively. Compounds (*B*) and (*C*) should be oximes $>C=NOH$ (recall that oximes rearrange to amides - **Beckmann rearrangement**). Further oximes having different alkyl (aryl) groups show geometrical isomerism (*syn* and *anti*), compounds (*B*) and (*C*) must have following structures.



Recall that Beckmann rearrangement involves migration of *anti* -alkyl or aryl group, *i.e.*,

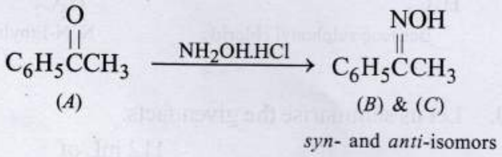


Since (*D*) is formed from (*B*), and (*E*) from (*C*), (*B*) and (*C*) should have following structures.



(*B*) (*C*)

(v) Lastly, oximes (*B*) and (*C*) are formed from (*A*), the latter should be a ketone of the formula $C_6H_5COCH_3$,

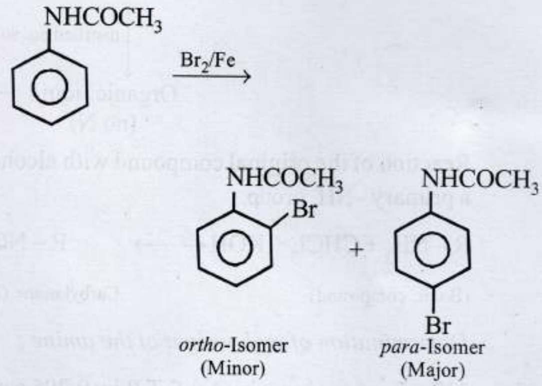


$$\underset{(A)}{C_6H_5\overset{O}{\overset{\|}{C}}CH_3} \xrightarrow{NH_2OH.HCl} \underset{(B)\ \&\ (C)}{C_6H_5\overset{NOH}{\overset{\|}{C}}CH_3}$$

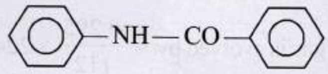
syn- and *anti*-isomors

45. (i) $CH_3-CH_2-NH_2 \xrightarrow{(CH_3CO)_2O} CH_3-CH_2-NH-COCH_3+CH_3COOH$

(ii)



(iii)



46. (i) Two factors operate in deciding the basicity of alkyl amines.

(a) Inductive effect

(b) Solvation effect

(a) **Inductive effect.** The alkyl group being electron releasing, increases the charge density on nitrogen. This in turn increases the basicity of amines. The expected order of basicity is

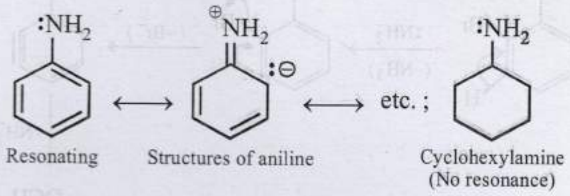
$$R_3N > R_2NH > RNH_2 > NH_3$$

(b) **Solvation effect.** Because of the positive charge carried by the conjugate acid of an amine, it is stabilised by the hydrogen bonding with the solvent water. The larger the number of hydrogens attracted to the nitrogen in the conjugate acid, the larger is its stability and thus larger is the basicity of the corresponding base. The expected order of basicity of the alkylamines will be

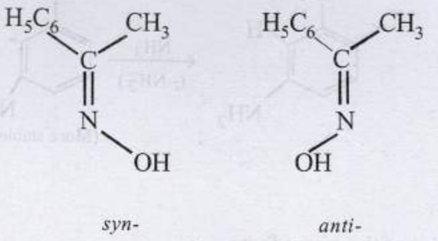
$$NH_3 > RNH_2 > R_2NH > R_3N$$

The inductive and solvent effects predict the opposite trend in the basicity of alkyl amines. In going from R_2NH to R_3N the solvation effect plays a more dominating role as compared to the inductive effect making R_2NH more basic than R_3N.

(ii) Aniline is weak base than cyclohexylamine because of resonance while there is no resonance in cyclohexylamine.



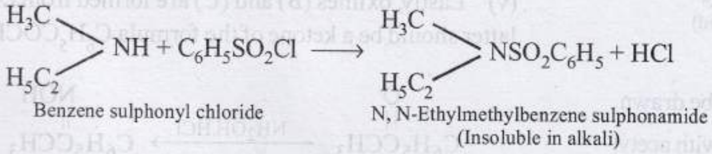
47.



48. $C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_6H_5N{\equiv}C + 3KCl + 3H_2O$

Phenyl isonitrile (foul smelling)

49. *A* (C_3H_9N) is a 2° amine $CH_3-NH-C_2H_5$ (ethylmethylamine) because the product sulphonamide is solid and insoluble in alkali.



$$(H_3C)(H_5C_2)NH + C_6H_5SO_2Cl \longrightarrow (H_3C)(H_5C_2)NSO_2C_6H_5 + HCl$$

Benzene sulphonyl chloride

N, N-Ethylmethylbenzene sulphonamide (Insoluble in alkali)

50. Let us summarise the given facts.

$$\begin{tikzcd}
\text{112 mL of colourless, odourless gas at S.T.P. + Residue} \arrow[d, "\text{distilled aq. sol.}"] & \text{Basic nitrogen compound (0.295 g)} \arrow[l, phantom] \arrow[r, "CHCl_3", "KOH"'] & \text{Foul smelling gas} \\
\text{Organic liquid (no N)} \arrow[r, "OH^-/I_2"] & \text{Yellow ppt.} &
\end{tikzcd}$$

(i) aq. HCl (ii) $NaNO_2$, 0°C

Reaction of the original compound with alcoholic potash and chloroform to give foul smelling gas indicates that it contains a primary $-NH_2$ group.

$$R-NH_2 + CHCl_3 + KOH \longrightarrow R-NC\uparrow$$

(Basic compound) Carbylamine (foul smelling)

Determination of mol. weight of the amine :

112 mL. of gas is evolved at S.T.P. by 0.295 g of amine

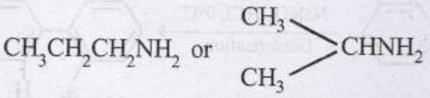
22400 mL. of gas is evolved by $= \frac{0.295}{112} \times 22400 = 59$ g

Hence, the mol. wt. of the amine = 59

$\therefore$ Mol. wt. of the alkyl group = 59 – 16 = 43

Nature of alkyl gp. of mol. wt. 43 = C_3H_7-

Thus, the amine may be either



$$CH_3CH_2CH_2NH_2 \text{ or } \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CHNH_2$$

The reaction of amine with $NaNO_2$ at 0°C and all other reactions may thus be written as below.

$$\underset{n-\text{Propylamine}}{CH_3CH_2CH_2NH_2} \xrightarrow[\text{(ii) } NaNO_2/0°C]{\text{(i) HCl}} CH_3CH_2CH_2OH + N_2\uparrow$$

$$\downarrow \text{aq. sol. distill.}$$

$$CH_3CH_2CH_2OH$$

$$\downarrow OH^-, I_2$$

No yellow ppt.

$$\underset{\text{Isopropylamine}}{(CH_3)_2CHNH_2} \xrightarrow[\text{(ii) } NaNO_2/0°C]{\text{(i) HCl}} (CH_3)_2CHOH + N_2\uparrow$$

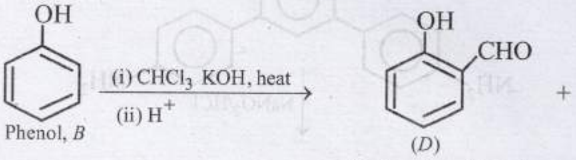
$$\xrightarrow{\text{aq. sol. distill.}} (CH_3)_2CHOH \xrightarrow[\text{(Haloform reaction)}]{OH^-, I_2} \underset{\text{(yellow)}}{CHI_3\downarrow}$$

Since the given reactions correspond to isopropylamine, the original compound is **isopropylamine**, $(CH_3)_2CHNH_2$.

51. Solution of compound *A* in chloroform when treated with alcoholic KOH yields compound *C* (C_7H_5N) having an unpleasant odour which may be due to isocyanide. Hence, the above reaction may be an example of carbylamine reaction. Therefore, compound *A* must be aniline ($C_6H_5NH_2$) and *C* must be phenylisocyanide (C_6H_5NC).

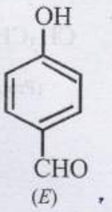
$$\underset{\text{Aniline, } A}{C_6H_5NH_2} + CHCl_3 + 3KOH \rightarrow \underset{\text{Phenyl isocyanide, } C}{C_6H_5NC} + 3KCl + 3H_2O$$

Alkaline aqueous layer of *B* when heated with chloroform and then acidified gives *D* and *E* which are isomeric with each other and have molecular formula $C_7H_6O_2$. This indicates the possibility that Reimer-Tiemann reaction would have taken place. Hence, compound *B* must be phenol and compounds *D* and *E* are *o*- and *p*-hydroxybenzaldehydes.



Phenol, *B*

(*D*)
o- Hydroxybenzaldehyde
(Salicylaldehyde)



(*E*) ,
p-Hydroxybenzaldehyde

52. Carbylamine reaction is a distinction test for primary amines. All primary amines (alphatic or aromatic) on heating with alcoholic KOH and $CHCl_3$ give unpleasant or foul smell of isocyanide which is easily detected.

$$C_2H_5NH_2 + CHCl_3 + 3KOH\,(\text{alc.})$$

$$\longrightarrow \underset{\substack{\text{(foul smell)} \\ \text{Ethyl isocyanide}}}{C_2H_5NC} + 3KCl + 3H_2O$$

Diethylamine, a 2° amine, does not respond this test.

53. Determination of empirical formula :

	C	H	N	O
% age	49.32	9.59	19.18	21.91
mole	$\frac{49.32}{12}$	$\frac{9.59}{1}$	$\frac{19.18}{14}$	$\frac{21.91}{16}$
	=4.11	=9.59	=1.37	=1.37
(Dividing by 1.37)				
Simplest ratio	3	7	1	1

$\therefore$ Empirical formula of A will be C_3H_7NO and empirical formula wt = 73

Calculation of molecular wt. of (B)

We know, meq. of Ag = meq. of Ag salt

$$\text{or } \frac{\text{Wt. of Ag}}{\text{Eq. wt. of Ag}} = \frac{\text{Wt. of salt}}{\text{Eq. wt. of salt}}$$

$$\text{or } \frac{59.67}{108} = \frac{100}{E_{\text{salt}}} \text{ or } E_{\text{salt}} = 181$$

$$E_{\text{salt}} = E_{Ag} + E_{\text{Anion}} \Rightarrow E_{\text{anion}} = 181 - 108 = 73$$

For monobasic acid (B), adding one H,

Mol. wt. = Eq. wt. + 1 = 73 + 1 = 74

B being monobasic can be represented as $C_nH_{2n+1}COOH$

$\Rightarrow 74 = 12n + (2n+1).1 + 12 + 16 + 16 + 1 \Rightarrow n = 2$

$\therefore B = C_2H_5COOH$

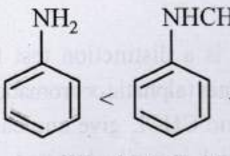
Nature of A : Since B is obtained by the action of A with NaOH followed by hydrolysis, so A is an amide, $CH_3CH_2CONH_2$.

Reaction :

$$\underset{\substack{(A)\\ \text{(Propanamide)}}}{CH_3CH_2CONH_2} \xrightarrow{NaOH} CH_3CH_2COONa$$

$$\xrightarrow{HOH} \underset{\substack{(B)\\ \text{Ethanoic acid}}}{CH_3CH_2COOH}$$

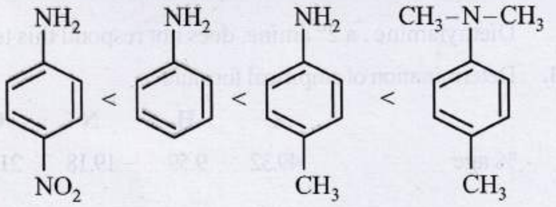
54. (ii)



$< CH_3NH_2 < (CH_3)_2NH$

The ease with which the lone pair of electron (unshared) on the N-atom co-ordinates with a proton determines the relative basic strength of amines.

(i) Presence of +I / +M group increases the basicity whereas presence of –I / –M group decreases the basicity.

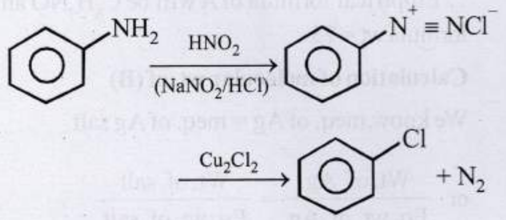


55. Hofmann degradation reaction.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \rightarrow$$

$$\underset{\text{Methyl amine}}{CH_3NH_2} + K_2CO_3 + 2KBr + 2H_2O$$

56. (i)



(ii) $$CH_3CHO \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH \xrightarrow[\text{distill}]{Ca(OH)_2}$$

$$CH_3COCH_3 \xrightarrow{NH_2OH.HCl} \underset{\text{Acetoxime}}{(CH_3)_2C{=}NOH}$$

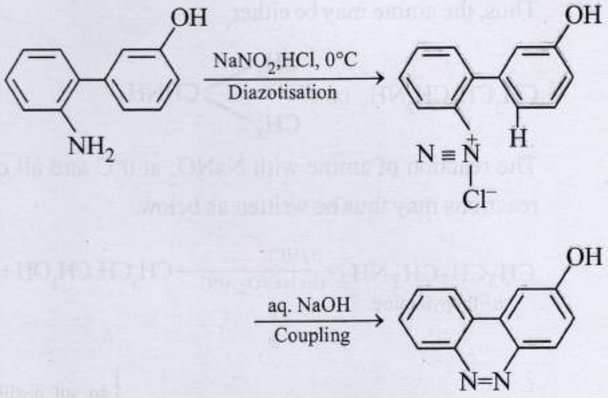
(iii) $$C_6H_6 \xrightarrow[HNO_3\,(\text{conc.})]{H_2SO_4(\text{conc.})} C_6H_5NO_2 \xrightarrow{Sn/HCl} C_6H_5NH_2$$

(iv) $$CH_3CH_2Cl \xrightarrow{\text{alc. KCN}} CH_3CH_2.CN$$

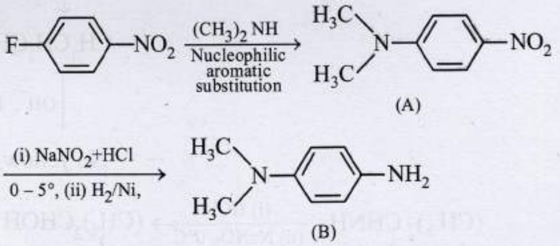
$$\xrightarrow[\text{reduction}]{H_2|Ni} CH_3CH_2CH_2NH_2$$

Topic-3: Diazonium Salts

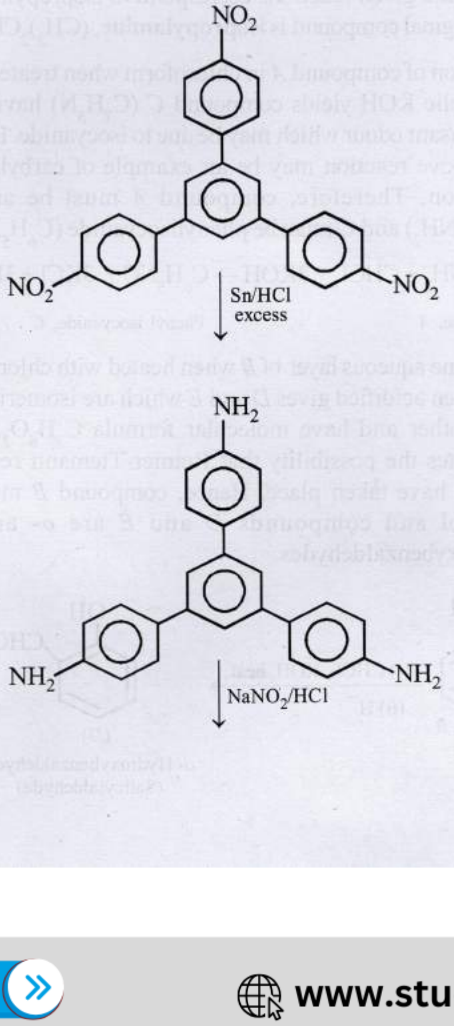
1. (c)

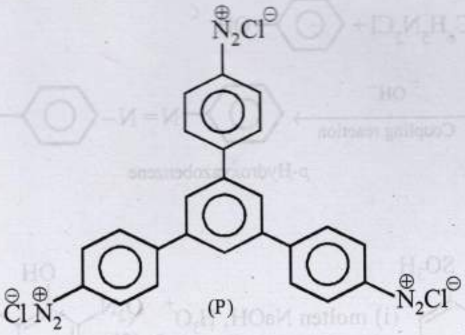


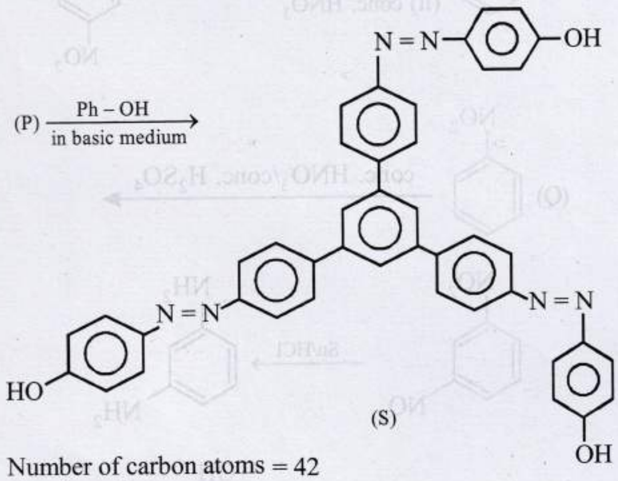
2. (a)



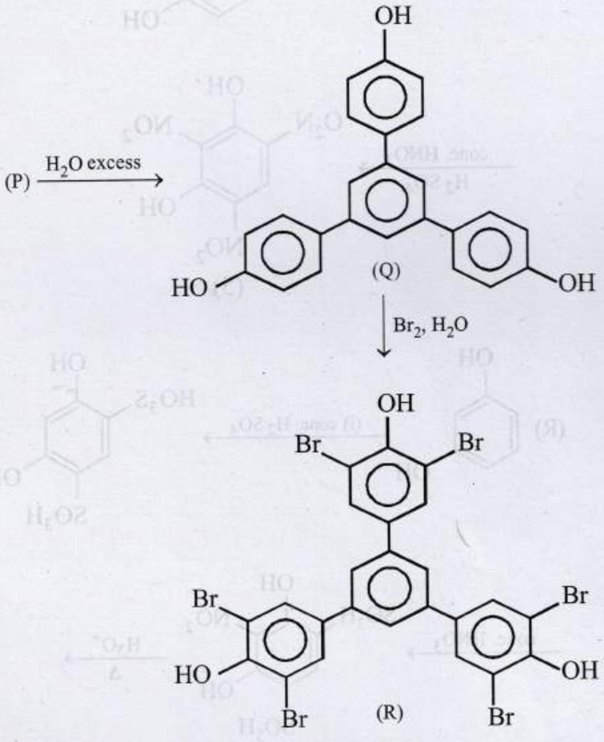
3. (9)
4. (51)
Common solution for Q.no. 3 and 4





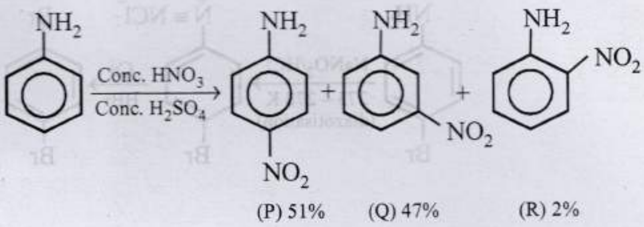


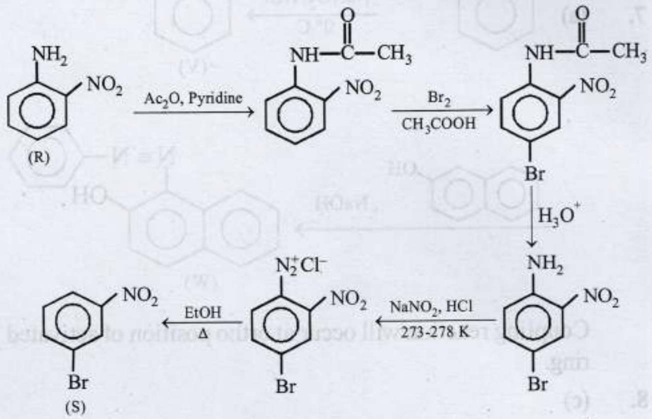
Number of carbon atoms = 42
Number of hetero atoms = 09
Total = 51

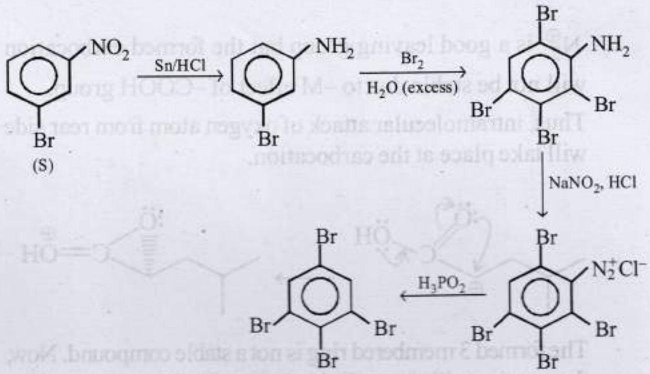


Number of hetero atoms in R is 9.

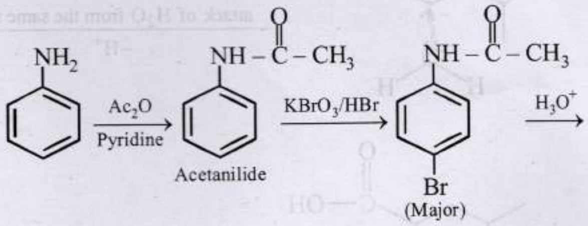
5. (d)

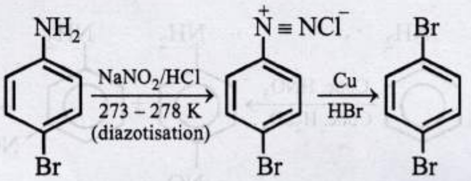




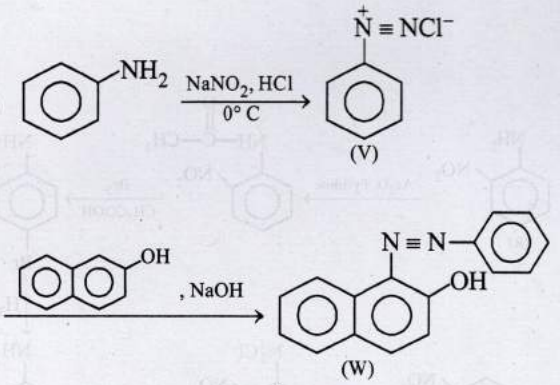


6. (b)



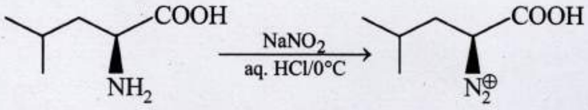


7. **(a)**

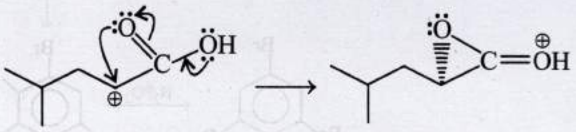


Coupling reaction will occur at ortho position of activated ring.

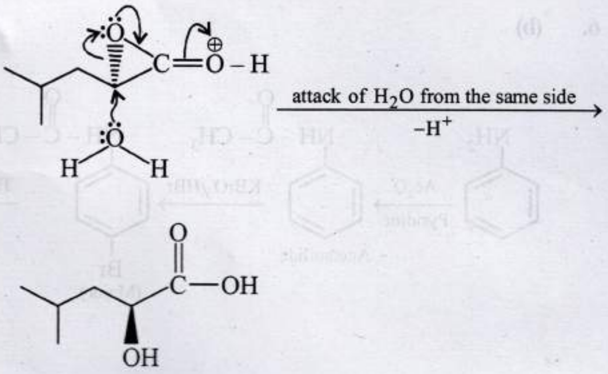
8. **(c)**



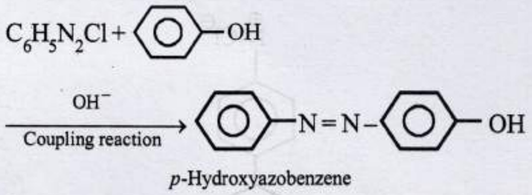
$N_2^{\oplus}$ is a good leaving group but the formed carbocation will not be stable due to –M effect of –COOH group.
Thus, intramolecular attack of oxygen atom from rear side will take place at the carbocation.



The formed 3 membered ring is not a stable compound. Now, the reaction will proceed with the attack of water molecule.

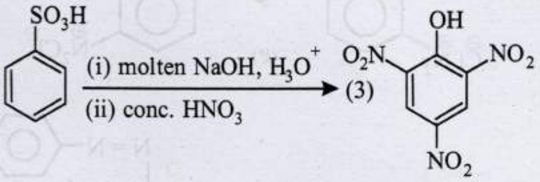


9. **(b)**

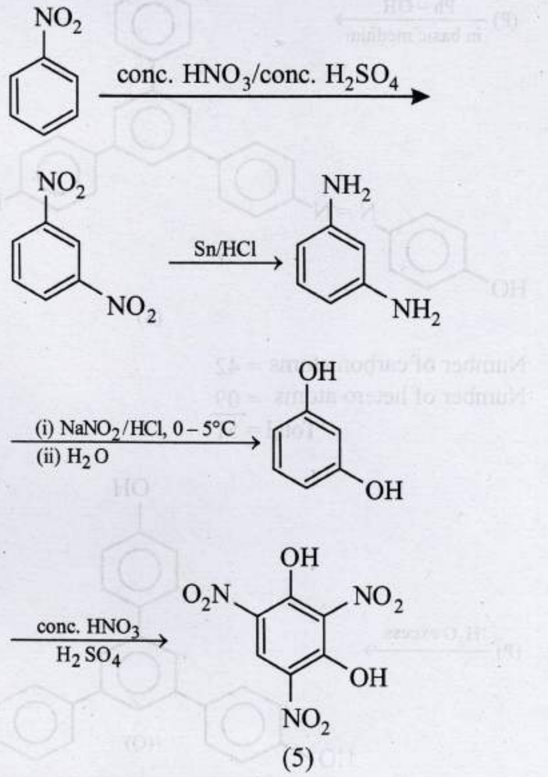


10. **(c)**

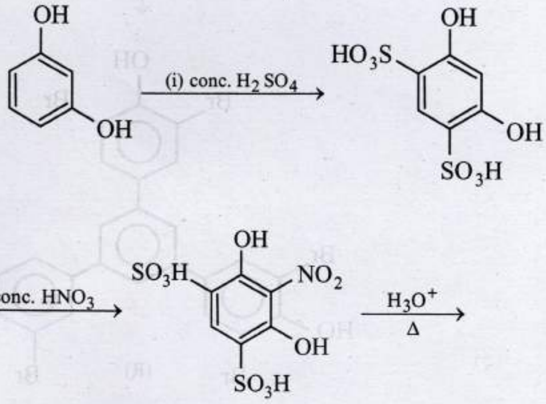
(P)

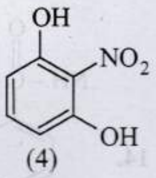


(Q)



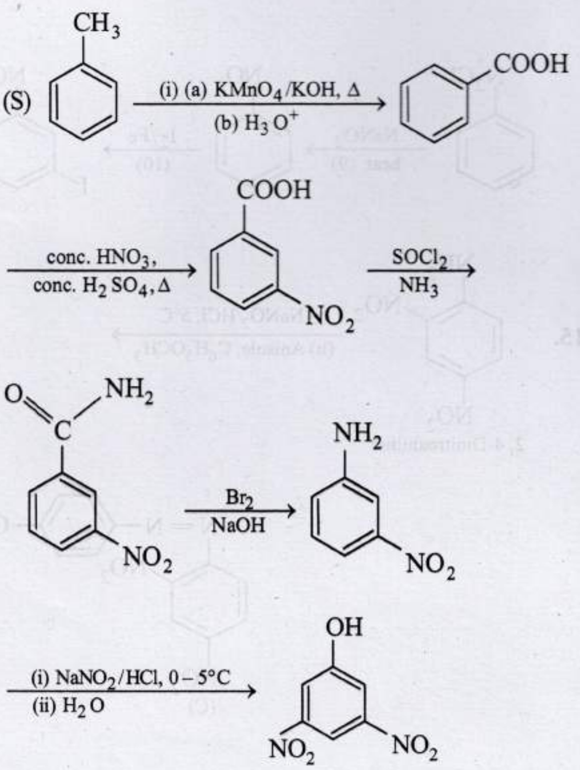
(R)





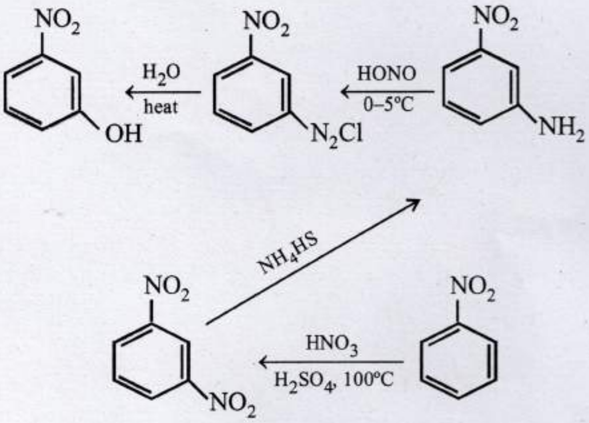
(4)

(S)

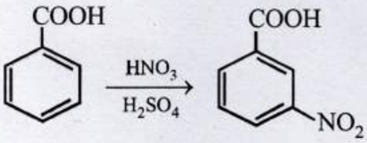


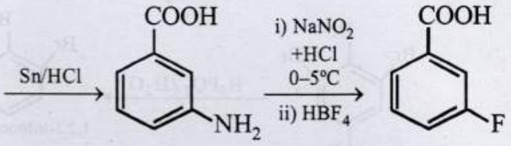
11. **(A) – (r), (s) ; (B) – (t) ; (C) – (p), (q) ; (D) – (r)**

12. (i) Going backward, we can easily solve the problem.

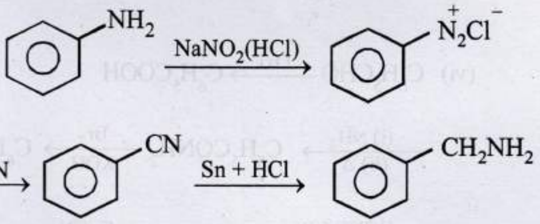


(ii)

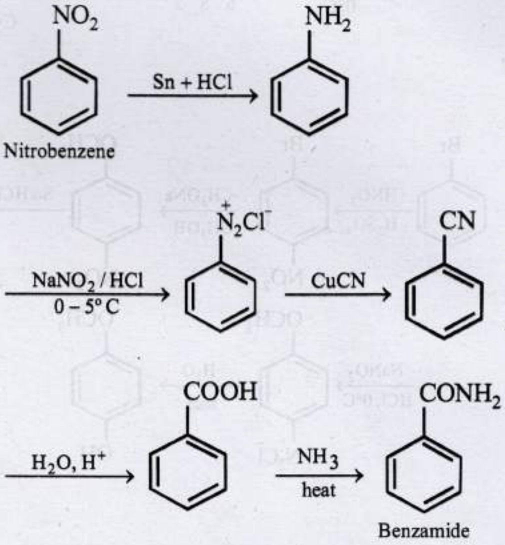




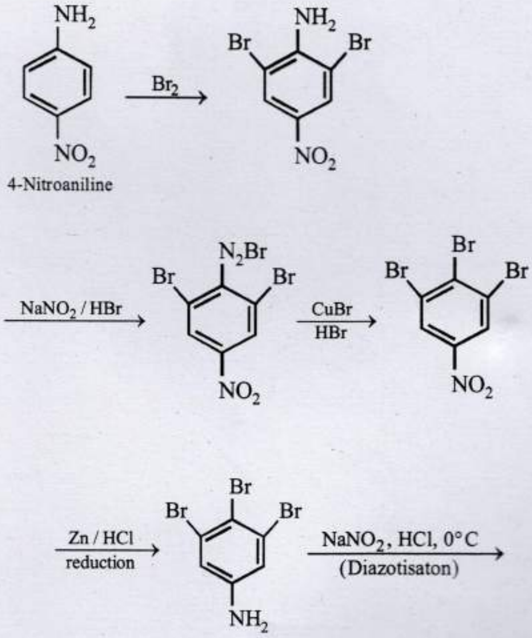
(iii)

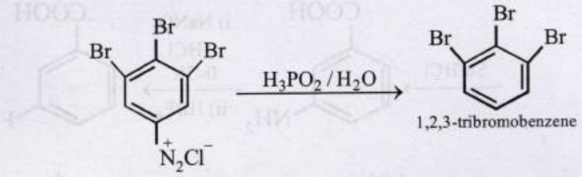


(iv)



(v)



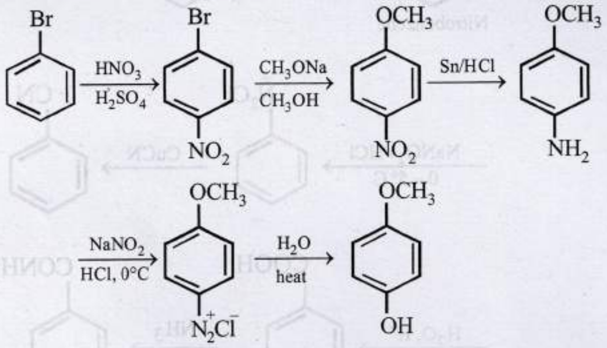


(vi) $C_6H_5CHO \xrightarrow{Oxi.} C_6H_5COOH$

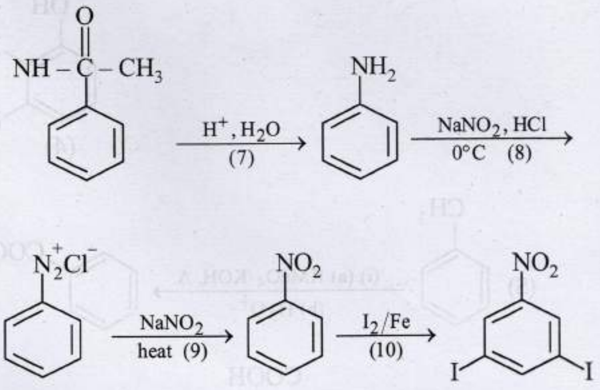
$$\xrightarrow[(ii)\ \Delta]{(i)\ NH_3} C_6H_5CONH_2 \xrightarrow[KOH]{Br_2} C_6H_5NH_2$$

$$\xrightarrow[0°C]{HONO/Cl^-} C_6H_5N_2Cl \xrightarrow{CuCN} \underset{\text{Cyanobenzene}}{C_6H_5CN}$$

13.



14.



15.