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# **TSPSC Degree Lecturer**

**Previous Year Paper  
Chemistry 2018 Paper II**



106224

Hall Ticket Number

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Marks : 100

Time : 120 minutes

**DL-317-CHEM**

Booklet Code :

**A****A***Signature of the Invigilator**Signature of the Candidate***Total No. of Questions : 100****[Total No. of Printed Pages : 36]****INSTRUCTIONS TO THE CANDIDATE***(Read the Instructions carefully before Answering)*

1. Separate Optical Mark Reader (OMR) Answer Sheet is supplied to you along with Question Paper Booklet. Please read and follow the instructions on the OMR Answer Sheet for marking the responses and the required data.
2. The candidate should ensure that the Booklet Code printed on OMR Answer Sheet and Booklet Code supplied are same.
3. **Immediately on opening the Question Paper Booklet by tearing off the paper seal, please check for (i) The same booklet code (A/B/C/D) on each page, (ii) Serial Number of the questions (1-100), (iii) The number of pages and (iv) Correct Printing.** In case of any defect, please report to the invigilator and ask for replacement of booklet with same code within five minutes from the commencement of the test.
4. Electronic gadgets like Cell Phone, Calculator, Watches and Mathematical/Log Tables are not permitted into the examination hall.
5. **There will be 1/4 negative mark for every wrong answer.** However, if the response to the question is left blank without answering, there will be no penalty of negative mark for that question.
6. Record your answer on the OMR answer sheet by using Blue/Black ball point pen to darken the appropriate circles of (1), (2), (3) or (4) corresponding to the concerned question number in the OMR answer sheet. Darkening of more than one circle against any question automatically gets invalidated and will be treated as wrong answer.
7. Change of an answer is **NOT** allowed.
8. Rough work should be done only in the space provided in the Question Paper Booklet.
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DL-317-CHEM

1. The hybridization of orbitals of N atom in  $\text{NO}_3^-$ ,  $\text{NO}_2^+$  and  $\text{NH}_4^+$  are respectively

- (1)  $sp^2$ ,  $sp^3$ ,  $sp$
- (2)  $sp$ ,  $sp^2$ ,  $sp^3$
- (3)  $sp^2$ ,  $sp$ ,  $sp^3$
- (4)  $sp$ ,  $sp^3$ ,  $sp^2$

2. Which of the following is correct order as a result of polarization in (i) melting points of the compounds - NaBr,  $\text{MgBr}_2$  and  $\text{AlBr}_3$  and (ii) solubility of the compounds in polar solvents - AgF, AgCl, AgBr and AgI.

- (1)  $\text{NaBr} > \text{MgBr}_2 > \text{AlBr}_3$  ;  $\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}$
- (2)  $\text{NaBr} < \text{MgBr}_2 < \text{AlBr}_3$  ;  $\text{AgF} < \text{AgCl} < \text{AgBr} < \text{AgI}$
- (3)  $\text{NaBr} < \text{MgBr}_2 < \text{AlBr}_3$  ;  $\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}$
- (4)  $\text{NaBr} > \text{MgBr}_2 > \text{AlBr}_3$  ;  $\text{AgF} < \text{AgCl} < \text{AgBr} < \text{AgI}$

3. Observe the following sets :

|    | Molecule / Ion                   | Geometry  | Hybridisation |
|----|----------------------------------|-----------|---------------|
| A. | $\text{BeCl}_2$ , $\text{ICl}_2$ | Same      | Different     |
| B. | $\text{NF}_3$ , $\text{PF}_3$    | Same      | Same          |
| C. | $\text{CF}_4$ , $\text{SF}_4$    | Different | Different     |
| D. | $\text{XeF}_4$ , $\text{BrF}_5$  | Different | Different     |

Which of the sets are correctly matched?

- (1) A, C & D only.
  - (2) B & D only.
  - (3) A, B, C & D.
  - (4) A, B & D only.
4. Identify the correct statement(s) from the following :
- (i) NO has one unpaired  $e^-$  in its anti bonding molecular orbital.
  - (ii) Bond length of  $\text{O}_2^+ >$  Bond length of  $\text{NO}^+$ .
  - (iii) Magnetic moment of  $\text{N}_2^+$  is 1.73 BM.
- (1) i only.
  - (2) i, ii & iii.
  - (3) i & ii only.
  - (4) ii & iii only.

5. A compound containing halide ion 'A' on complete hydrolysis gives an amphoteric hydroxide 'B'. 'B' on heating gives 'C', which forms 'D' when heated strongly with carbon. D yields methane and 'C' when reacted with water. What is 'C'?
- (1)  $\text{Ca(OH)}_2$
  - (2)  $\text{Be(OH)}_2$
  - (3)  $\text{CaO}$
  - (4)  $\text{BeO}$
6. The compound which hydrolyses easily among the following is
- (1)  $\text{NCl}_3$
  - (2)  $\text{NF}_3$
  - (3)  $\text{BiCl}_3$
  - (4)  $\text{PCl}_3$
7. Choose the correct statement(s) with reference to thorium (Th) and uranium (U).
- (i) Th forms iodides of the type,  $\text{ThI}_2$ ,  $\text{ThI}_3$  and  $\text{ThI}_4$ .
  - (ii) In the solid state, salts of  $[\text{UO}_2]^{2+}$  contain a linear cation.
  - (iii) Reactions of NaOR with  $\text{UCl}_4$  do not yield monomeric  $\text{U(OR)}_4$  complexes.
- (1) i and iii only.
  - (2) ii only.
  - (3) i and ii only.
  - (4) i only.
8. For which of the following transition metals, the difference between the first and second ionization values is more?
- (1) Mn
  - (2) Fe
  - (3) Cr
  - (4) V
9. Which pair of ions exhibit color and possess same number of electrons?
- (1)  $\text{La}^{3+}$ ,  $\text{Ce}^{4+}$
  - (2)  $\text{Eu}^{2+}$ ,  $\text{Gd}^{3+}$
  - (3)  $\text{Eu}^{3+}$ ,  $\text{Sm}^{2+}$
  - (4)  $\text{Lu}^{3+}$ ,  $\text{Yb}^{2+}$

10. Match the following :

| <i>List I</i>  |     | <i>List II</i> |     |
|----------------|-----|----------------|-----|
| <i>Mineral</i> |     | <i>Metal</i>   |     |
| A. Linnaeite   |     | I) Tungsten    |     |
| B. Scheelite   |     | II) Nickel     |     |
| C. Limonite    |     | III) Cobalt    |     |
| D. Pentlandite |     | IV) Titanium   |     |
|                |     | V) Iron        |     |
| (A)            | (B) | (C)            | (D) |
| (1) I          | III | IV             | V   |
| (2) I          | III | II             | V   |
| (3) III        | I   | IV             | II  |
| (4) III        | I   | V              | II  |

11. Which of the following metallurgical processes does **not** involve heating?

- (1) Smelting
- (2) Calcinations
- (3) Roasting
- (4) Leaching

12. Addition of small amount of the following increases the hardness of iron-

- (1) C
- (2) Al
- (3) Zn
- (4) Sn

13. Which of the following methods uses the principle of fractional crystallization?

- (1) Froth floatation
- (2) Roasting
- (3) Zone refining
- (4) Smelting

14. The alloy used in soldering of electric wires contains the following :

- (1) Lead, Tin
- (2) Copper, Zinc
- (3) Zinc, Tin
- (4) Copper, Tin

15. Staggered ethane and staggered dibenzene chromium belong to which of the following point groups.

- (1)  $D_{3d}$  and  $D_{3d}$
- (2)  $D_{3d}$  and  $D_{6d}$
- (3)  $D_{6d}$  and  $D_{3d}$
- (4)  $D_{6d}$  and  $D_{6d}$

16. How many irreducible representations are possible for  $C_{3v}$  point group?

- (1) 5
- (2) 6
- (3) 3
- (4) 4

17. A molecule contains the following symmetry operations :

$E, 2C_6, 2C_3, C_2, 3\sigma_d, 3\sigma_v$ .

The number of classes and order of the symmetry point group is

- (1) 6, 6
- (2) 3, 12
- (3) 6, 12
- (4) 3, 6

18. Character Table for the point group  $C_{2v}$  is given below :

| $C_{2v}$ | E | $C_2$ | $\sigma_{xz}$ | $\sigma_{yz}$ |          |                 |
|----------|---|-------|---------------|---------------|----------|-----------------|
| $A_1$    | 1 | 1     | 1             | 1             | Z        | $z_2, x_2, y_2$ |
| $A_2$    | 1 | 1     | -1            | -1            | $R_z$    | xy              |
| $B_1$    | 1 | -1    | 1             | -1            | x, $R_y$ | xz              |
| $B_2$    | 1 | -1    | -1            | 1             | y, $R_x$ | yz              |

The reducible representation corresponding to the three translational degrees of freedom,  $\Gamma_{tr}$  is

- (1) 3, 1, 1, 1
- (2) 3, -1, 1, 1
- (3) 3, -1, -1, -1
- (4) 3, 1, -1, -1

19. The terms which arise from a  $p^1d^1$  configuration are :

- (1)  $^1F, ^3F$
- (2)  $^1P, ^3P$
- (3)  $^3P, ^3F$
- (4)  $^1P, ^1F$

20. If the Lande splitting factor,  $g$  is  $6/7$  for  $\text{Ce}^{3+}$ , then the effective magnetic moment (in BM) is  
 (1) 2.54  
 (2) 1.73  
 (3) 2.87  
 (4) 3.82
21. The magnitudes of the crystal field splitting ( $\Delta_0$ ) and the mean pairing energy ( $P$ ) for  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  are  $13900$  and  $23500 \text{ cm}^{-1}$ , respectively. The CFSE values for the high-spin and the low-spin states of  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  are respectively.  
 (1)  $8340$  and  $-1260 \text{ cm}^{-1}$   
 (2)  $-1390$  and  $2350 \text{ cm}^{-1}$   
 (3)  $-8340$  and  $1260 \text{ cm}^{-1}$   
 (4)  $1390$  and  $-2350 \text{ cm}^{-1}$
22. The correct order of energy of LMCT bands in  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ,  $[\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$  is :  
 (1)  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+} > [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} > [\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} > [\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$   
 (2)  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+} < [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} < [\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} < [\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$   
 (3)  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+} < [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} < [\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} = [\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$   
 (4)  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+} > [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} > [\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} = [\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$
23. Which of the following statement(s) are correct?  
 (i)  $[\text{Co}(\text{CN})_5\text{I}]^{3-}$  and  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  are stable complexes.  
 (ii)  $\text{LiI} + \text{CsF} \rightarrow \text{LiF} + \text{CsI}$  is a feasible reaction.  
 (iii)  $(\text{SCN})^-$  ligand coordinates through 'S' atom to form the complex  $[\text{Co}(\text{SCN})_4]^{2-}$ .  
 (1) (i) only.  
 (2) (i), (ii) and (iii).  
 (3) (i) and (ii) only  
 (4) (ii) and (iii) only.
24. Pick up the correct order of stabilities of the complexes formed by  $\text{Ni}^{2+}$  with the three chelating agents (i) 8-hydroxy quinoline, (ii) 2-methyl-8-hydroxy quinoline, (iii) 4-methyl-8-hydroxy quinoline.  
 (1)  $\text{i} > \text{ii} > \text{iii}$   
 (2)  $\text{ii} > \text{iii} > \text{i}$   
 (3)  $\text{iii} > \text{i} > \text{ii}$   
 (4)  $\text{iii} > \text{ii} > \text{i}$

25. Which of the following statements is correct for base hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ?
- (1) The base hydrolysis does not depend on the concentration of the base.
  - (2) The rate determining step does not involve dissociation of  $\text{Cl}^-$  and  $\text{NH}_3$  in  $[\text{Co}(\text{NH}_3)_4\text{NH}_2\text{Cl}]^{2+}$ .
  - (3) It involves both associative and dissociative types of substitution.
  - (4) It is a first order reaction involving the conjugate base of the complex.
26. Among the following, the correct set of inert complexes is :  
 $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- (1)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$
  - (2)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
  - (3)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
  - (4)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$
27. Consider the second order rate constants for the following outer-sphere electron transfer reactions -
- | reaction  | rate constant                                     |
|---|---|
| $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} / [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | $4.0 \text{ M}^{-1} \text{ sec}^{-1}$             |
| $[\text{Fe}(\text{Phen})_3]^{3+} / [\text{Fe}(\text{Phen})_3]^{2+}$               | $3.0 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ |
- The reason for the enhanced rate constant for the second reaction is -
- (1) 1, 10 - phenanthroline is a  $\pi$ -acceptor ligand that allows mixing of electron donor and acceptor orbitals that enhance the rate of electron transfer.
  - (2) 1, 10 - phenanthroline is a  $\pi$  donor ligand that enhances the rate of electron transfer.
  - (3) 1, 10 - phenanthroline forms charge transfer complex with iron and facilitates the electron transfer.
  - (4) 1, 10 - phenanthroline forms kinetically labile complex with Fe and facilitates the electron transfer.
28. Choose the correct statements on ferrocene from the following :
- (a) It undergoes electrophilic substitution on the cyclopentadienyl ring.
  - (b) It reacts with iodine to form a paramagnetic species.
  - (c) It can be prepared by treating iron(II) chloride with cyclopentadiene and diethylamine.
- (1) a and b only.
  - (2) b and c only.
  - (3) a, b and c.
  - (4) a and c only.

29. Which of the following complexes does **not** obey the 18-electron rule?
- (1)  $[\text{Fe}(\text{CO})_4]^{2-}$
  - (2)  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$
  - (3)  $[\text{Mn}(\text{CO})_5]^-$
  - (4)  $[\text{V}(\text{CO})_6]^-$
30. The active site of metalloprotein, oxyhemocyanin contains
- (1) two Fe(II) and one  $\text{O}_2^{2-}$ .
  - (2) two Cu(II) and one  $\text{O}_2^{2-}$ .
  - (3) two Cu(II) and one  $\text{O}_2^-$ .
  - (4) two Fe(III) and one  $\text{O}_2^{2-}$ .
31. Which of the following statements about haemoglobin is correct?
- (1) 2, 3 - Bisphosphoglycerate (BPG) increases the affinity of haemoglobin for oxygen.
  - (2) Deoxygenated haemoglobin has higher binding affinity for protons than oxyhaemoglobin.
  - (3) Haemoglobin has higher affinity for oxygen than myoglobin.
  - (4) One molecule of haemoglobin binds sixteen molecules of oxygen.
32. If the retention time of the sample is 9.34 min with a base width of 0.43 min in column length of 18.3, then the total number of plates in the column is approximately -
- (1)  $7.55 \times 10^3$
  - (2) 471.79
  - (3) 21.72
  - (4) 359.52
33. In the analysis of an organic compound by paper chromatography, the solvent front was 18 cm while the front due to compounds A, B, C and D was 16.5, 14.3, 9.5 and 5.7 cm respectively. If the  $R_f$  value of one of these compounds was 0.794, then the compound corresponds to
- (1) A
  - (2) D
  - (3) C
  - (4) B

34. The vapour pressure of acetone at  $20^{\circ}\text{C}$  is 185 torr. When 1.2g of non-volatile substance was dissolved in 100g of acetone at  $20^{\circ}\text{C}$ , its vapour pressure was 183 torr. The molar mass of the substance in  $\text{g mol}^{-1}$  is approximately -
- (1) 32
  - (2) 64
  - (3) 128
  - (4) 488
35. The freezing point of benzene decreases by  $0.45^{\circ}\text{C}$  when 0.2g of acetic acid is added to 20g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be -
- ( $K_f$  for benzene =  $5.12 \text{ K kg mol}^{-1}$ )
- (1) 64.6%
  - (2) 80.4%
  - (3) 74.6%
  - (4) 94.6%
36. At  $20^{\circ}\text{C}$ , the vapour pressure of benzene and methyl benzene are 76 torr and 22 torr respectively. One mole of benzene and one mole of methyl benzene are mixed to form an ideal solution. The mole fractions of benzene and methyl benzene in vapour pressure are respectively
- (1) 0.1 and 0.9
  - (2) 0.78 and 0.22
  - (3) 0.38 and 0.11
  - (4) 0.38 and 0.22
37. The elevation in boiling point of a dilute aqueous solution is 0.4 K. What is its  $\Delta T_f$ ?
- (For water  $K_b = 0.52 \text{ K kg mol}^{-1}$ ;  $K_f = 1.86 \text{ K kg mol}^{-1}$ )
- (1) 0.77 K
  - (2) 0.208 K
  - (3) 1.43 K
  - (4) 2.86 K

38. To a 1L solution of 0.1M acetic acid, solid NaOH is added such that (i)  $\frac{1}{4}$  th of acetic acid is neutralized ( $\text{pH}_1$ ) and (ii)  $\frac{3}{4}$  th of acetic acid is neutralized ( $\text{pH}_2$ ).

What is  $\Delta\text{pH}$  ( $\text{pH}_1 - \text{pH}_2$ )?

- (1)  $2 \log 2$
  - (2)  $2 \log 3$
  - (3)  $2 \log 5$
  - (4)  $2 \log 4$
39. What is pH of  $10^{-3}$  M sodium acetate solution? ( $\text{pK}_a$  of acetic acid = 4.8)
- (1) 13.9
  - (2) 9.4
  - (3) 6.4
  - (4) 7.9
40. The dissociation constants of  $\text{HAsO}_4$ ,  $\text{HAsO}_3$  and  $\text{HAsO}_2$  are  $2 \times 10^{-2}$ ,  $3 \times 10^{-3}$  and  $3 \times 10^{-6}$  respectively. The relative basic strengths of  $\text{AsO}_4^-$ ,  $\text{AsO}_3^-$  and  $\text{AsO}_2^-$  follow the order -
- (1)  $\text{AsO}_2^- > \text{AsO}_4^- > \text{AsO}_3^-$
  - (2)  $\text{AsO}_4^- > \text{AsO}_3^- > \text{AsO}_2^-$
  - (3)  $\text{AsO}_2^- > \text{AsO}_3^- > \text{AsO}_4^-$
  - (4)  $\text{AsO}_3^- > \text{AsO}_4^- > \text{AsO}_2^-$
41. A typical resting person transfers 8640 kJ of heat to the surroundings at  $27^\circ\text{C}$ , the increase in entropy of surroundings is -
- (1)  $28.8 \text{ kJ K}^{-1}$
  - (2)  $28.8 \text{ J K}^{-1}$
  - (3)  $2.88 \text{ kJ K}^{-1}$
  - (4)  $0.288 \text{ kJ K}^{-1}$

42. The correct equation for variation of free energy with pressure at constant T for an ideal gas is

- (1)  $\left(\frac{dG}{dP}\right)_T = S$   
 (2)  $\left(\frac{dG}{dP}\right)_T = -S$   
 (3)  $\left(\frac{dG}{dP}\right)_T = -V$   
 (4)  $\left(\frac{dG}{dP}\right)_T = V$

43. For an ideal gas reaction,  $A \rightarrow P$ ,  $\Delta H = +24 \text{ kJ mol}^{-1}$  and  $\Delta S = 12 \text{ J K}^{-1}$ . The reaction becomes spontaneous at

- (1) above 1000 K  
 (2) above 1500 K  
 (3) above 2000 K  
 (4) above 500 K

44. The transport numbers of a few 1:1 electrolytes are given below :

| Electrolyte | transport | number |
|-------------|-----------|--------|
|             | $t_+$     | $t_-$  |
| AB          | 0.5       | 0.5    |
| CD          | 0.8       | 0.2    |
| EF          | 0.2       | 0.8    |
| GH          | 0.1       | 0.9    |
| IJ          | 0.51      | 0.49   |

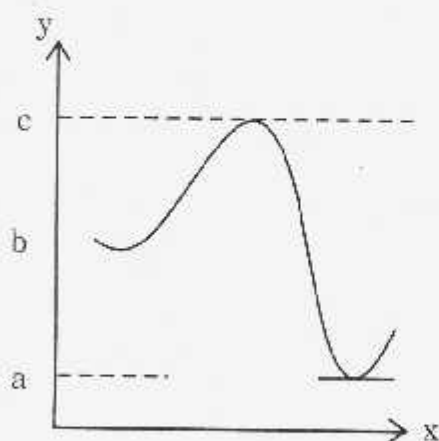
The electrolytes which can be used in salt bridge are

- (1) AB, CD, EF  
 (2) EF, GH  
 (3) EF, GH, IJ  
 (4) AB, IJ

45. A plot of molar conductance ( $\Lambda_m$ ) (on y-axis) versus square root of concentration ( $\sqrt{C}$ ) (on x-axis) of KCl gave a straight line with negative slope. The intercept is -
- (1) Debye Huckel constants (A and B) of KCl.
  - (2) Degree of dissociation of KCl.
  - (3) Molar conductance at infinite dilution of KCl.
  - (4) Specific conductance of KCl.
46. For the following cell
- $$\text{Zn(s)} | \text{Zn}^{2+}_{(\text{aq})} || \text{Cu}^{2+}_{(\text{aq})} | \text{Cu(s)}$$
- When the concentration of  $\text{Zn}^{2+}$  is 10 times to the concentration of  $\text{Cu}^{2+}$ , the expression for  $\Delta G$  (in  $\text{J mol}^{-1}$ ) is
- (1)  $\Delta G = 3.303 RT + 1.1 F$
  - (2)  $\Delta G = 1.1 F$
  - (3)  $\Delta G = 2.303 RT - 2.2 F$
  - (4)  $\Delta G = -2.2 F$
47. At  $25^\circ\text{C}$ , the resistance of a 1:1 electrolyte of concentration  $0.01 \text{ mol dm}^{-3}$  is  $400 \Omega$ . What is its molar conductance (in  $\text{S m}^2 \text{ mol}^{-1}$ ) at  $25^\circ\text{C}$ ?  
(Cell constant =  $100 \text{ m}^{-1}$ )
- (1) 0.25
  - (2) 0.025
  - (3) 0.0025
  - (4) 2.5
48. The operators  $\hat{A}$  &  $\hat{B}$  do not commute with each other. Then  $(\hat{A} + \hat{B})^2$  is
- (1)  $\hat{A}^2 + \hat{B}^2 + \hat{A}\hat{B} + \hat{B}\hat{A}$
  - (2)  $\hat{A}^2 + \hat{B}^2 + 2\hat{A}\hat{B}$
  - (3)  $\hat{A}^2 + \hat{B}^2 - 2\hat{A}\hat{B}$
  - (4)  $\hat{A}^2 + \hat{B}^2$

49. The eigen value of  $\frac{d^2}{dx^2}(\sin x + \cos x)$  is
- (1) 1
  - (2) 0
  - (3) -1
  - (4) 2
50. One of the following statements is correct about the eigen function
- (1) Eigen functions need not be finite and continuous.
  - (2) Two eigen functions of a Hermitian operator that correspond to different eigen values are orthogonal.
  - (3) Eigen values of Hermitian operator are never real.
  - (4) An eigen function is normalised if  $\int_0^1 \psi_1 \psi_2 dx = 0$ .
51. Two reactions  $R_1$  and  $R_2$  have identical pre-exponential factors and activation energy of  $R_1$  exceeds that of  $R_2$  by  $10 \text{ kJ mole}^{-1}$ . If  $k_1$  and  $k_2$  are rate constants for reactions  $R_1$  and  $R_2$  respectively at 300 K, then  $\ln\left(\frac{k_2}{k_1}\right)$  is
- ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )
- (1) 8
  - (2) 12
  - (3) 6
  - (4) 4
52.  $A \rightarrow \text{Product}$ , is a first order reaction. In the reaction, concentration of A changes from 0.1 M to 0.025 M in 40 min. Find the rate of reaction when concentration of A is 0.01 M.
- (1)  $3.47 \times 10^{-4} \text{ M min}^{-1}$
  - (2)  $3.47 \times 10^{-5} \text{ M min}^{-1}$
  - (3)  $1.73 \times 10^{-4} \text{ M min}^{-1}$
  - (4)  $1.73 \times 10^{-5} \text{ M min}^{-1}$

53. The energy (on y-axis) as a function of reaction co-ordinate on x-axis is shown below :



The activation energy  $E_a$  and  $\Delta E$  of the reaction are respectively

- (1)  $(c - b), (c - a)$
  - (2)  $(b - a), (c - b)$
  - (3)  $(b - a), (c - a)$
  - (4)  $(c - b), (b - a)$
54. For  $\text{NO}_2$  group the substituent constant ( $\sigma$ ) in para position is 0.78. If  $K_a$  &  $K_{a0}$  are dissociation constants of para nitro benzoic acid and benzoic acids respectively, which one of the following is correct?

- (1)  $\frac{K_a}{K_{a0}} = 0.78$
- (2)  $\frac{K_{a0}}{K_a} = 0.78$
- (3)  $\log \frac{K_a}{K_{a0}} = 0.78$
- (4)  $\log \frac{K_{a0}}{K_a} = 0.78$

55. For the reaction  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2 \text{HBr}$   
the rate follows

$$\frac{d[\text{HBr}]}{dt} = k[\text{Br}_2]^{\frac{1}{2}} [\text{H}_2]$$

This equation is derived assuming

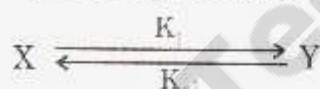
(1)  $\frac{d[\text{H}]}{dt} = 0; \frac{d[\text{Br}]}{dt} \neq 0$

(2)  $\frac{d[\text{H}]}{dt} \neq 0; \frac{d[\text{Br}]}{dt} \neq 0$

(3)  $\frac{d[\text{H}]}{dt} = 0; \frac{d[\text{Br}]}{dt} = 0$

(4)  $\frac{d[\text{H}]}{dt} \neq 0; \frac{d[\text{Br}]}{dt} = 0$

56. For the opposing reaction,



a plot of  $\ln\left(\frac{x_e}{x_e - x}\right)$  (on y-axis) versus time (on x-axis) gave straight line. The intercept of the straight line is equal to : ( $x_e$  = concentration of Y at equilibrium)

(1)  $(k_1 + k_{-1})$

(2)  $\frac{k_1}{k_{-1}}$

(3) Zero

(4) 1

57. The fact that the fluorescence wavelength ' $\lambda$ ' is often much longer than the irradiation wavelength is a consequence of the phenomenon.
- (1) low molar extinction coefficient.
  - (2) high inter system crossing (ISC) rates.
  - (3) quantum yield values.
  - (4) Franck-Condon principle.
58. When Chlorophyll is irradiated with light it exhibits fluorescence, with rate constant  $k_1$  equal to  $10^8 \text{ s}^{-1}$ . Addition of oxygen quenches fluorescence and then the rate constant  $k_2$  is equal to  $10^{10} \text{ s}^{-1}$ .  
The life time ( $\tau$ ) of fluorescence in the absence of quencher is
- (1)  $0.1 \times 10^{-9} \text{ s}$
  - (2)  $10.1 \times 10^{-9} \text{ s}$
  - (3)  $0.01 \times 10^{-9} \text{ s}$
  - (4)  $1.01 \times 10^{-9} \text{ s}$
59. One of the following is **not** correct about photochemical reactions -
- (1)  $\Delta G$  for photo chemical reactions is always negative.
  - (2) Photochemical reactions are highly selective.
  - (3) Temperature 'T' has no effect on the rate of reaction.
  - (4) These reactions occur only in presence of light.
60. Observe the following reactions.
- (i)  $A \xrightarrow{h\nu} A^*$
  - (ii)  $A^* + B \rightarrow (AB)^* \rightarrow A + B + h\nu'$
  - (iii)  $A^* + A \rightarrow (AA)^* \rightarrow 2A + h\nu''$
  - (iv)  $A^* + D \rightarrow A + D^* \rightarrow A + P$
  - (v)  $A^* \rightarrow P$
- Identify the reactions belonging to photo-sensitization.
- (1) i, iii, v
  - (2) i, iv, v
  - (3) i, iv
  - (4) i, ii, v

61. The molecular formula of solid having cubic close packing is  $X_3Y_4Z_6$ . Anions (Z) occupy all the corners of cubic unit cell, Cations (X) and cations (Y) occupy some octahedral and some tetrahedral voids respectively. The fractions of octahedral voids and tetrahedral voids occupied are respectively-

(1)  $\frac{1}{4}, \frac{1}{3}$

(2)  $\frac{1}{3}, \frac{1}{3}$

(3)  $\frac{1}{2}, \frac{1}{2}$

(4)  $\frac{1}{2}, \frac{1}{3}$

62. The density of an element (atomic weight =  $200 \text{ g mol}^{-1}$ ) is  $5.21 \text{ g cm}^{-3}$ . It crystallizes in cubic lattice. What is its approximate unit cell length? (Take  $N = 6 \times 10^{23} \text{ mol}^{-1}$ )

(1)  $6 \times 10^{-8} \text{ cm}$

(2)  $5 \times 10^{-9} \text{ cm}$

(3)  $4 \times 10^{-8} \text{ cm}$

(4)  $4 \times 10^{-9} \text{ cm}$

63. Observe the following defects.

(i) Schottky defects

(ii) Frenkel defects

(iii) Metal deficiency defects

The density of the solid decreases due to the presence of

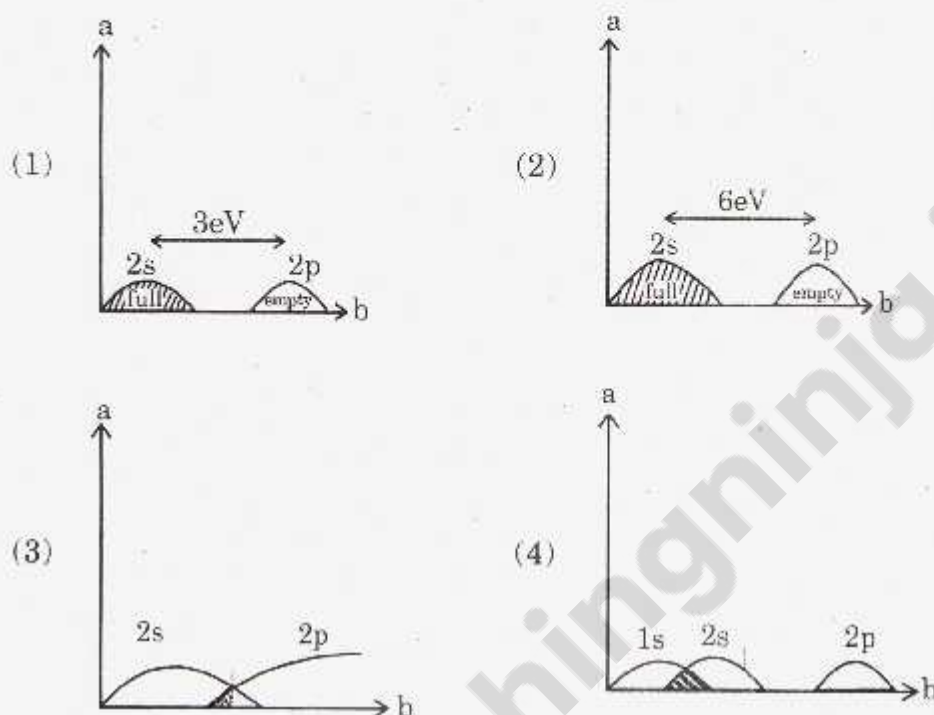
(1) i, ii, iii

(2) i, ii

(3) i, iii

(4) ii, iii

64. Which one of the following figures correctly represents the band structure of beryllium? ( $a = N(E)$ ;  $b = E$ ).



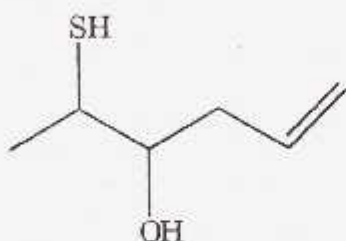
65. The structure of high temperature superconductor (HTSC) is related to

- (1) Garnet structure
- (2) Perovskite structure
- (3) NaCl structure
- (4) Diamond structure

66. Which one of the following is generally referred as "123" superconductor? ( $x < 1$ )

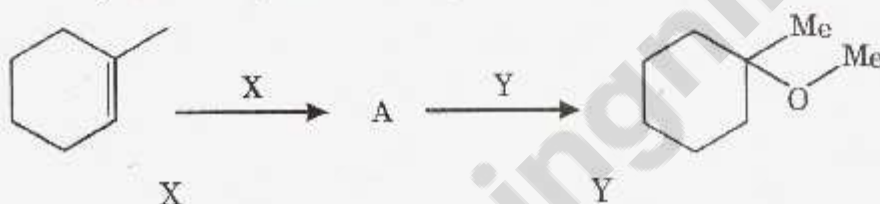
- (1)  $\text{YBa}_2\text{Cu}_2\text{O}_6$
- (2)  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$
- (3)  $\text{BaY}_2\text{Cu}_3\text{O}_{7-x}$
- (4)  $\text{BaCu}_2\text{Y}_3\text{O}_{7-x}$

67. The IUPAC name of the following compound is



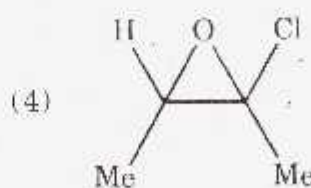
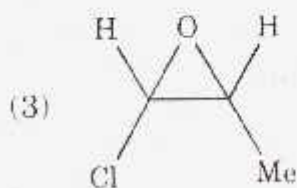
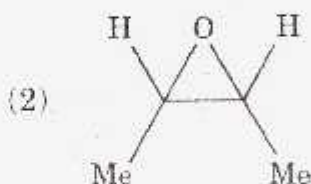
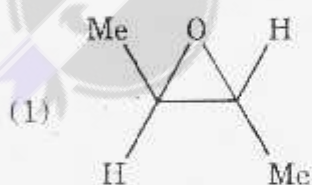
- (1) 3-Hydroxy - 5 - hexen - 2 - thiol
- (2) 4 - Hydroxy - 1 - hexen - 5 - thiol
- (3) 2 - Mercapto - 5 - hexen - 3 - ol
- (4) 5 - Mercapto - 1 - hexen - 4 - ol

68. Identify the most preferred reagents X and Y in the following reaction sequence.

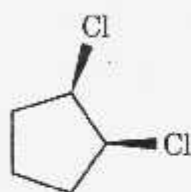


- |   |                       |
|---|-----------------------|
| (1) HBr   | NaOMe / MeOH          |
| (2) (i) Hg (OAc) <sub>2</sub> / H <sub>2</sub> O      | NaH / MeI             |
| (ii) NaBH <sub>4</sub> / <sup>-</sup> OH              |                       |
| (3) (i) Hg (OAc) <sub>2</sub> / H <sub>2</sub> O      | NaH / MeI             |
| (ii) NaBH <sub>4</sub> / <sup>-</sup> OH              |                       |
| (4) H <sub>2</sub> O / H <sub>2</sub> SO <sub>4</sub> | MeOH / H <sup>+</sup> |

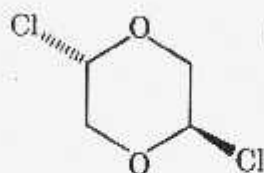
69. Which of the following compounds possess enantiotropic groups / atoms?



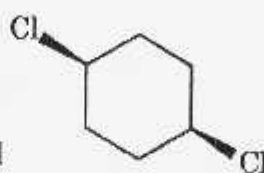
70. Group the following compounds into chiral and achiral



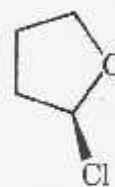
(i)



(ii)



(iii)



(iv)

Chiral

Achiral

(1) ii & iii

i & iv

(2) i, ii, iii

iv

(3) ii & iv

i & iii

(4) i & iii

ii & iv

71. Match the following two tables with correct answer

Table 1

Table 2

(i) Meso compound

(a) An equimolar mixture of enantiomers.

(ii) Enantiomers

(b) Stereo isomers that are not enantiomers.

(iii) Diastereomers

(c) Non-super imposable mirror images.

(iv) Racemate

(d) An optically inactive compound containing chiral centers.


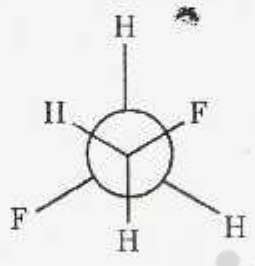

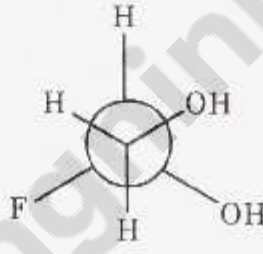
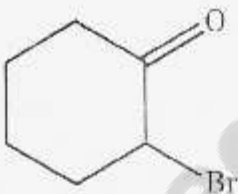
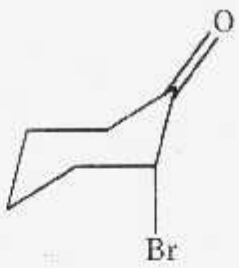
(1) i-b, ii-c, iii-a, iv-d

(2) i-c, ii-a, iii-d, iv-b

(3) i-d, ii-c, iii-a, iv-b

(4) i-d, ii-c, iii-b, iv-a

72. Which of the following pairs are correctly matched?

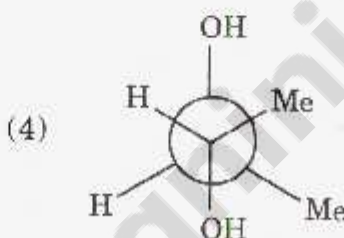
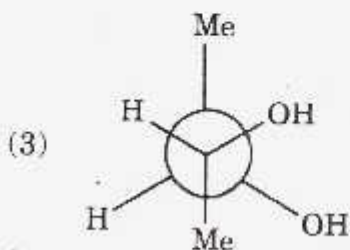
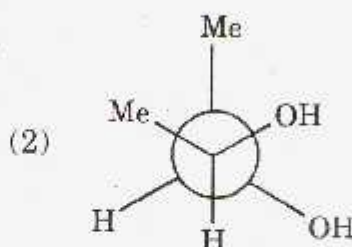
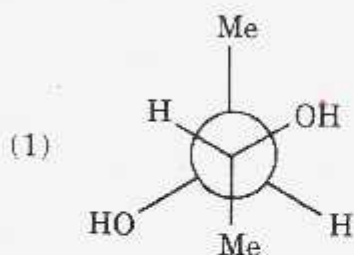
| Compound  | most preferred conformation  |
|---|--|
| (i)      |    |
| (ii)    |   |
| (iii)  |  |

- (1) i & iii  
 (2) i & ii  
 (3) i, ii & iii  
 (4) ii & iii

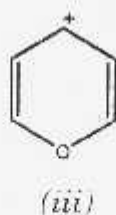
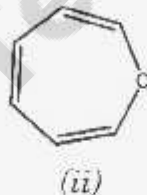
73. Which of the following represents correct order of the relative energies of conformations of cyclonhexane?

- (1)  $E(\text{chair}) < E(\text{boat}) < E(\text{twist-boat})$ .  
 (2)  $E(\text{twist-boat}) < E(\text{boat}) < E(\text{chair})$ .  
 (3)  $E(\text{boat}) < E(\text{twist-boat}) < E(\text{chair})$ .  
 (4)  $E(\text{chair}) < E(\text{twist-boat}) < E(\text{boat})$ .

74. The most stable conformational isomer of (2S, 3R)-2, 3-butane diol is

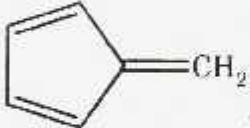
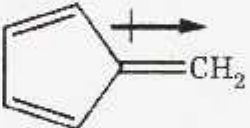

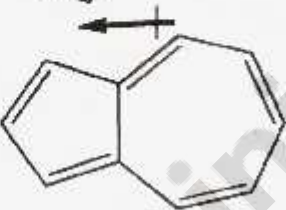
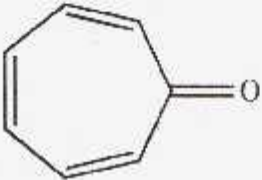
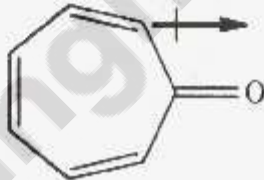




75. Which of the following are aromatic?



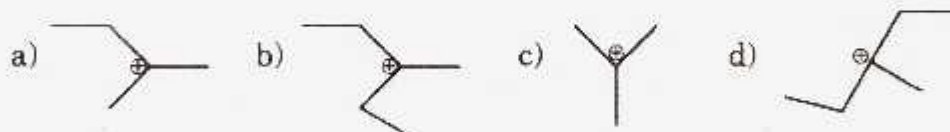
- (1) i, ii and iii.  
 (2) ii and iii.  
 (3) i and iv.  
 (4) ii and iv.

76. Which of the following pairs are correctly matched?

| Compound  | Dipole moment  |
|---|--|
| (i)      |    |
| (ii)     |    |
| (iii)  |  |
| (iv)   |  |

- (1) i, ii, iii  
 (2) i, iii, iv  
 (3) i, ii, iv  
 (4) ii, iii, iv

77. The decreasing order of stability of the following carbocations is




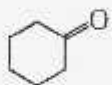
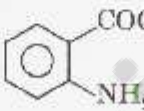
- (1)  $a > d > c > b$   
 (2)  $b > c > a > d$   
 (3)  $c > a > b > d$   
 (4)  $a > b > c > d$

78. Match the following

List-I

- (I) Carbene  
(II) Benzyne  
(III) Nitrene  
(IV) Free radical

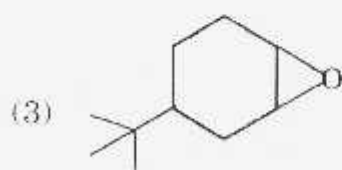
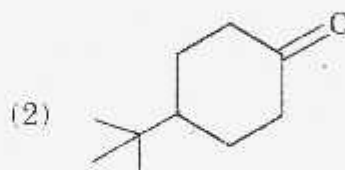
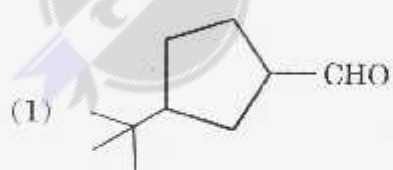
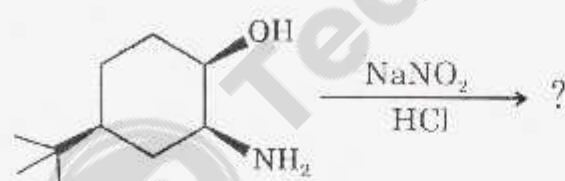
List-II

- (a)  $\text{H}_3\text{CCON}_3 \xrightarrow{\Delta}$   
(b)   $\xrightarrow[\text{h}\nu]{\text{NBS / CCl}_4}$   
(c)  $\text{H}_3\text{CCOCHN}_2 \xrightarrow{\text{Rh}_2(\text{OAc})_4}$   
(d)   $\xrightarrow{\text{NaOEt}}$   
(e)   $\xrightarrow[\text{iii. } \Delta]{\text{i. RONO, ii. OH}}$

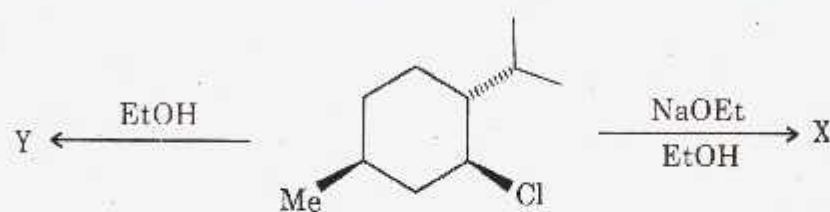
The correct answer is

- |     | I | II | III | IV |
|-----|---|----|-----|----|
| (1) | c | e  | a   | d  |
| (2) | c | e  | a   | b  |
| (3) | a | e  | c   | d  |
| (4) | a | b  | c   | e  |

79. The major product from the following reaction is



80. The major products 'X' and 'Y' from the following reactions are

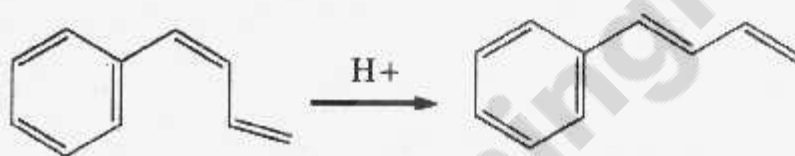


- Four possible products are shown for X and Y:
- (1) X: 4-isopropyl-1-methylcyclohexene; Y: 3-isopropyl-4-methylcyclohexene
- (2) X: 3-isopropyl-4-methylcyclohexene; Y: 4-isopropyl-1-methylcyclohexene
- (3) X: 1-isopropyl-4-methylcyclohexene; Y: 3-isopropyl-4-methylcyclohexene
- (4) X: 3-isopropyl-4-methylcyclohexene; Y: 1-isopropyl-4-methylcyclohexene

81. Identify the correct statement(s) from the following :

- (i) Primary hindered halide on reaction with NaOEt gives major product via  $S_N^2$  mechanism.
  - (ii)  $\beta$  -Haloketones on reaction with NaOEt gives the major product via E1 mechanism.
  - (iii) Primary Unhindered halide on reaction with  $Et_3CONa$  gives the major product via E2 mechanism.
- (1) iii  
 (2) i and iii  
 (3) ii  
 (4) i, ii and iii

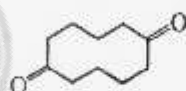
82. Observe the following isomerisation of 1-Phenylbutadiene



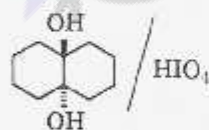
When the same reaction is carried out in  $D^+/D_2O$ , the product obtained is 4-deutero-1-phenylbutadiene, which suggests that the mechanism involves protonation at

- (1) C - 4  
 (2) C - 3  
 (3) C - 2  
 (4) C - 1

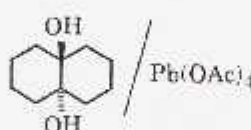
83. The product



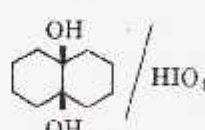
can be obtained from which of the following



(i)



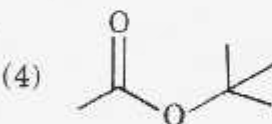
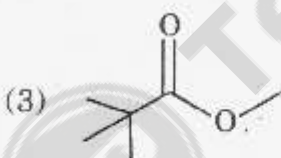
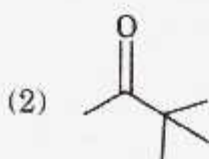
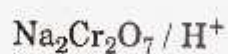
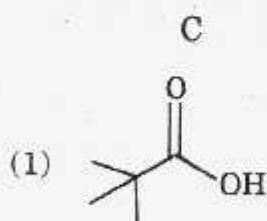
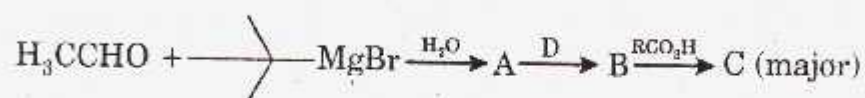
(ii)



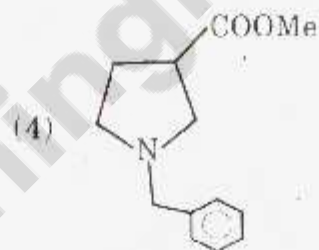
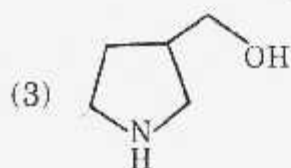
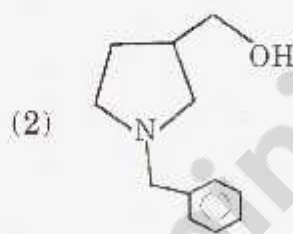
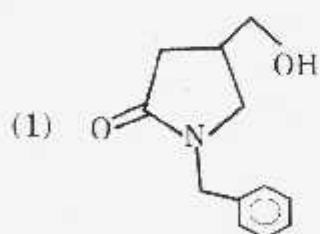
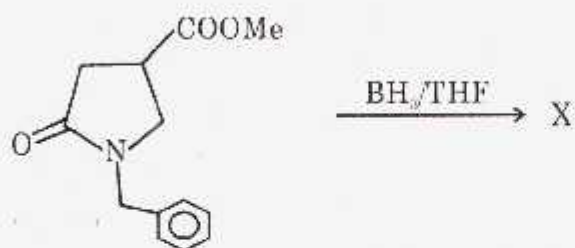
(iii)

- (1) ii and iii  
 (2) i and iii  
 (3) i and ii  
 (4) i, ii and iii

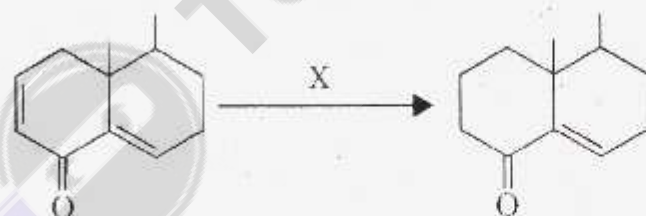
84. Identify 'C' and 'D' in the following reaction sequence.



85. The major product (X) from the following reaction is



86. The reagent (X) in the following conversion is



(1)  $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{AcOH}$ .

(2)  $(\text{Ph}_3\text{P})\text{RhCl}$ .

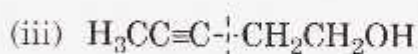
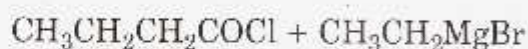
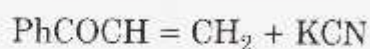
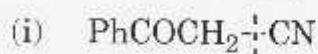
(3)  $\text{H}_2$  /  $\text{Ni}$ .

(4)  $\text{H}_2$  /  $\text{Pd}$  /  $\text{BaSO}_4$ .

87. Which of the following is / are correctly matched?

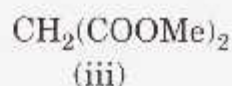
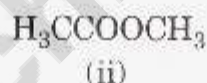
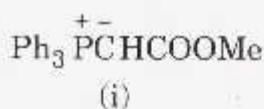
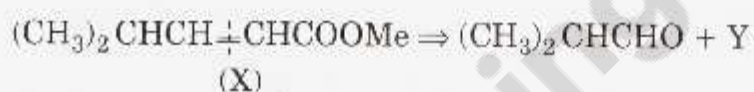
*Disconnection*

*Synthetic equivalents*



- (1) i and ii
- (2) i and iii
- (3) i
- (4) ii

88. What is 'Y' in the retrosynthesis of following target compound X.

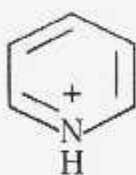


- (1) i and ii
- (2) ii and iii
- (3) i, ii and iii
- (4) i and iii

89. Reaction of ethylacetoacetate on reaction with  $\alpha$ -chloroacetone in pyridine yields

- (1) Pyridine derivative
- (2) Indole derivative
- (3) Pyrole derivative
- (4) Furan derivate

90. Arrange the following in the increasing order of their pKa values.



(i)



(ii)



(iii)

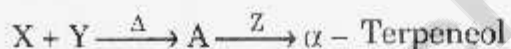
- (1) ii < iii < i  
(3) ii < i < iii

- (2) iii < i < ii  
(4) i < ii < iii

91. Reaction of phenyl hydrazone from cyclohexanone and phenyl hydrazine leads to the formation of

- (1) 2-cyclohexyl Indole.  
(2) 2, 3-Dicyclohexyl Indole.  
(3) Tetrahydrocarbazole.  
(4) 3-Cyclohexyl Indole.

92. Identify the X, Y and Z required for the synthesis of  $\alpha$ -terpeneol as given below.

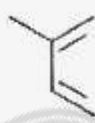


X

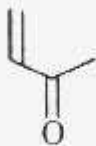
Y

Z

(1)

MeMgBr / H<sub>2</sub>O

(2)



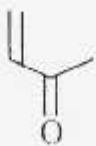
LAH

(3)



LAH

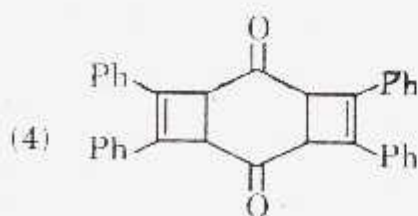
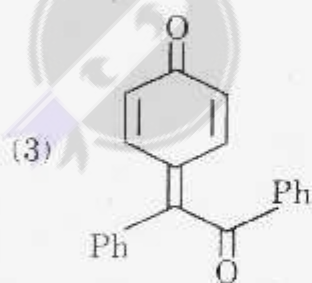
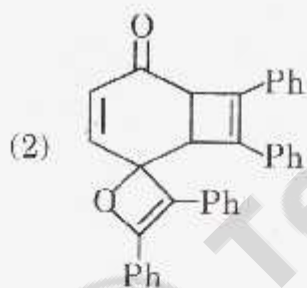
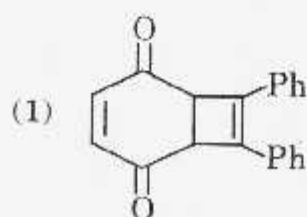
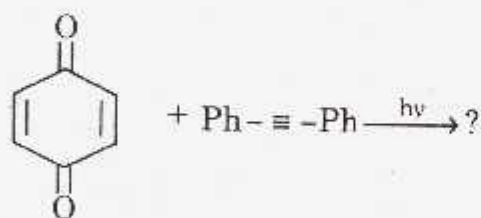
(4)

MeMgBr / H<sub>2</sub>O

93. The two heterocyclic rings present in nicotine are

- (1) Pyridine and Pyrrolidine.
- (2) Pyridine and Peviridine.
- (3) Pyridine and Pyrrole.
- (4) Peviridine and Pyrrole.

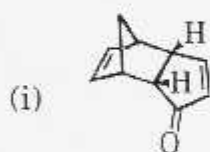
94. The major product from the following reaction is



95. Match the compounds in the column I with the photochemical reaction that they can undergo given in the column II.

I

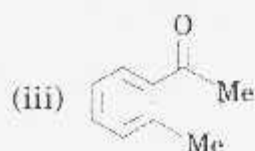
II



(p) oxa di- $\pi$  methane rearrangement.



(q) Paterno-Buchi reaction.



(r) intramolecular [2+2] cycloaddition.

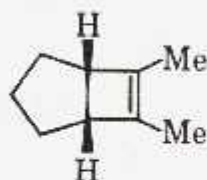
(s) photoenolisation.

- (1) (i)-(q) ; (ii)-(s) ; (iii)-(p).  
 (2) (i)-(r) ; (ii)-(p) ; (iii)-(s).  
 (3) (i)-(r) ; (ii)-(q) ; (iii)-(s).  
 (4) (i)-(q) ; (ii)-(p) ; (iii)-(s).

96. The major product formed when (cR, 4S)-3, 4-dimethyl-hexa-1, 5-diene heated at 240 °C is

- (1) (2Z, 6Z)-octa-2, 6-diene.  
 (2) (2E, 6E)-octa-2, 6-diene.  
 (3) (2E, 6Z)-octa-2, 6-diene.  
 (4) (3Z, 5E)-octa-3, 5-diene.

97. Identify the correct statements regarding the following compound.



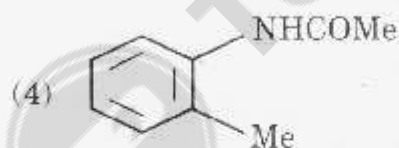
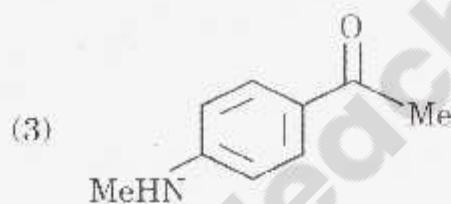
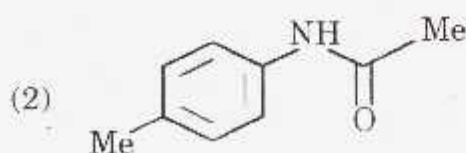
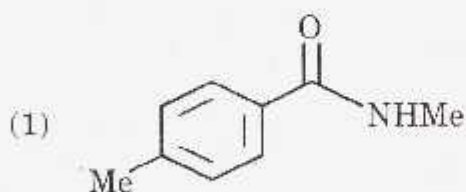
- (i) It will undergo readily thermal electrocyclic ring opening reaction.
  - (ii) It will undergo readily photochemical electrocyclic ring opening reaction.
  - (iii) It will not undergo thermal electrocyclic ring opening reaction.
  - (iv) It will not undergo photochemical electrocyclic ring opening reaction.
- (1) ii and iii.
  - (2) i and iv.
  - (3) i and ii.
  - (4) iii and iv.

98. The characteristic UV absorption bands of acetone at 190 nm and 280 nm respectively correspond to the following transitions

- (i)  $\sigma \rightarrow \sigma^*$     (ii)  $\pi \rightarrow \pi^*$     (iii)  $n \rightarrow \pi^*$     (iv)  $n \rightarrow \sigma^*$
- (1) i and ii.
  - (2) iii and iv.
  - (3) i and iv.
  - (4) ii and iii.

99. An organic compound with the molecular formula  $C_9H_{11}NO$  showed IR absorption peaks at  $3421$  and  $1684\text{ cm}^{-1}$ .

$^1\text{H}$ -NMR spectrum displayed peaks at  $\delta$  2.1 (s, 3H), 2.3 (s, 3H), 7.1 (d, 2H), 7.35 (d, 2H) and 7.6 (br, 1H, exchangeable with  $D_2O$ ). Base peak is at  $m/z = 107$ . The structure of the organic compound is



100. Which of the following are green catalysts?

L-Proline

$\text{CuI}$

Yeast

$\text{Pd}(\text{OAc})_2$

(i)

(ii)

(iii)

(iv)

(1) ii and iv.

(2) i and iii.

(3) ii and iii.

(4) i and iv.

(Space for Rough Work)

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