# GATE – 2002 – Chemistry

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**Q.1 – Q.50 Multiple Choice Question (MCQ), carry TWO marks each (for each wrong answer: –2/3).**

**1.** **The ground state of aluminium atom is**

(a) $^2P_{1/2}$ (b) $^2P_{3/2}$ (c) $^4D_{5/2}$ (d) $^4S_{3/2}$

**2.** **The point group symmetry of the free nitrate ion is**

(a) $D_{3h}$ (b) $C_{3v}$ (c) $C_{3h}$ (d) $D_3$

**3.** **The total number of vibrational degrees of freedom of $H_2O_2$ is**

(a) 7 (b) 6 (c) 4 (d) 9

**4.** **The velocity of the electron in the hydrogen atom**

(a) increases with increasing principal quantum number

(b) decreases with increasing principal quantum number

(c) is uniform for any value of the principal quantum number

(d) first increases and then decreases with principal quantum number

**5.** **The enthalpy of formation of AgCl is obtained from the enthalpy change from which one of the following processes?**

(a) $Ag^+_{(aq)} + Cl^-_{(aq)} \longrightarrow AgCl_{(s)}$ (b) $Ag_{(s)} + \frac{1}{2}Cl_{2(g)} \longrightarrow AgCl_{(s)}$

(c) $AgCl \longrightarrow Ag_{(s)} + \frac{1}{2}Cl_{2(g)}$ (d) $Ag_{(s)} + AuCl \longrightarrow Au_{(s)} + AgCl_{(s)}$

**6.** **The Nernst equation for the reaction, $A^{2+} + 2e \longrightarrow B$ , in terms of free energy change is**

(a) $\Delta G = \Delta G^0 + 2.303\ RT \ln \frac{[B]}{[A^{2+}]}$ (b) $\Delta G = \Delta G^0 - 2.303\ RT \ln \frac{[B]}{[A^{2+}]}$

(c) $-\Delta G = -\Delta G^0 + 2.303\ RT \ln \frac{[B]}{[A^{2+}]}$ (d) $\Delta G = -\Delta G^0 + 2.303\ RT \ln \frac{[B]}{[A^{2+}]}$

**7.** **0.1M aqueous solution of the following compounds will exhibit the largest depression of freezing point?**

(a) KCl (b) $C_6H_{12}O_6$ (c) $K_2SO_4$ (d) $Al_2(SO_4)_3$

3

**8.** **The vapour pressure of a pure solvent is 0.8 atm. A non-volatile substance-B is added to the solvent and its vapour pressure drops to 0.6 atm. The mole fraction of the component-B in the solution is**

(a) 0.75 (b) 0.50 (c) 0.25 (d) 0.20

**9.** **The existence of two different coloured complexes of $[Co(NH_3)_4Cl_2]$ is due to**

(a) optical isomerism (b) linkage isomerism

(c) geometrical isomerism (d) coordination isomerism

**10. Which of the following species has two nonbonded electron pairs on the central atom?**

(a) $TeCl_4$ (b) $ClF_3$ (c) $ICl_2$ (d) $PCl_3$

**11. The complex which obeys the 18-electron rule is**

(a) $[Fe(CO)_4]$ (b) $[Ni(CO)_3(PPh_3)]$ (c) $[Cr(CO)_5]$ (d) $[Cr(C_5H_5)_2]$

**12. When sodium carbonate is added to an aqueous solution of copper sulfate, which one of the following compounds is precipitated?**

(a) $[Cu(CO_3)_2]$ (b) $[Cu(OH)_2(CO_3)]$ (c) $[Cu(HCO_3)_2]$ (d) $[Cu(OH)_2]$

**13. The complex formed in the brown ring test for nitrates is**

(a) $[Fe(H_2O)_5\,NO]^{3+}$ (b) $[Fe(H_2O)_5\,NO]^{2+}$

(c) $[Fe(H_2O)_4\,(NO)_2]^{2+}$ (d) $Fe(H_2O)_4\,(NO)_2]^{3+}$

**14. The transmittance of an alcoholic solution of a certain compound at 500 nm is 1 percent in a 1 cm cell. Its absorbance is**

(a) 1.0 (b) 2.0 (c) 2.5 (d) 4.0

**15. The species which has a square planar structure is**

(a) $BF_4$ (b) $[FeCl_4]^-$ (c) $SF_4$ (d) $XeF_4$

**16. Electron transfer from $[Fe(H_2O)_6]^{2+}$ to $[Fe(H_2O)_6]^{3+}$ is likely to occur via**

(a) d-d transition (b) inner sphere electron transfer

(c) $S_N1$ mechanism (d) outer sphere electron transfer

**17. In allene, hybridization of the central and terminal carbons respectively, are**

(a) $sp^2$ and $sp^2$ (b) $sp^2$ and $sp^3$ (c) sp and $sp^2$ (d) sp and $sp^3$

**18. Among the isomers of $C_4H_6$ given below, the compound which exhibits an absorption band at 3300 $cm^{-1}$ in the IR spectrum, is:**

(a) 1,3-butadiene (b) 1-butyne (c) 2-butyne (d) cyclobutene

**19. Among formaldehyde, acetaldehyde and benzaldehyde, the aldehydes which undergo Cannizaro's reaction are**

(a) All the three (b) formaldehyde and acetaldehyde

(c) acetaldehyde and benzaldehyde (d) formaldehyde and benzaldehyde

**20. Reaction of benzyl benzoate with an excess of methylmagnesium bromide generates a mixture of**

(a) benzyl methyl ether and 2-phenylpropan-2-ol (b) benzyl alcohol and benzoic acid

(c) benzyl alcohol and 2-phenylpropan-2-ol (d) ethyl benzene and benzoic acid

**21.** **Benzaldehyde can be prepared by reacting phenylmagnesium bromide with**

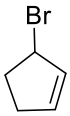
(a) N, N-dimethylformamide (b) carbon dioxide (c) formaldehyde (d) ethyl chloroformate

**22.** **Proteins are biopolymers. The monomer units present in them are**

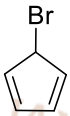
(a) carbohydrates (b) amino acids (c) fatty acids (d) alkenes

**23.** **Among the bromides I-III given below, the order of their reactivity in the $S_N1$ reaction is**

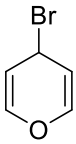
**I**




**II**




**III**




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

**24.** **Reaction of phenyl acetate with anhydrous aluminium chloride generates a mixture of**

(a) ortho-, meta- and para-hydroxyacetophenones

(b) meta- and para-hydroxyacetophenones

(c) ortho- and meta-hydroxyacetophenones

(d) ortho- and para-hydroxyacetophenones

**25.** **The major product formed in the reaction of anisole with lithium in liquid ammonia and t-butanol is**

(a) 1-methoxycyclohexa-1,4-diene (b) 2-methoxycyclohexa-1,3-diene

(c) 1-methoxycyclohexa-1,3-diene (d) 3-methoxycyclohexa-1,4-diene

**26.** **Consider an orthorhombic unit cell of dimensions $a = 450\ pm, b = 650\ pm$ and $c = 400\ pm$. The perpendicular distance between the (110) planes is**

(a) 650 pm (b) 450 pm (c) 370 pm (d) 500 pm

**27.** **The spacing between the rotational lines of the HF is 40 $cm^{-1}$. The corresponding spacing between the rotational lines in DF is approximately.**

(a) 20 $cm^{-1}$ (b) 30 $cm^{-1}$ (c) 60 $cm^{-1}$ (d) 7.5 $cm^{-1}$

**28.** **The activation energy for the decomposition of $H_2O_2$ is 76 kJ/mol at room temperature and the decomposition is very slow. When a little iodide is added, the activation energy decreases to 57 KJ/mol. The rate coefficient increases approximately by a factor of**

(a) 500 (b) 1000 (c) 2000 (d) 50

**29.** **The probability of finding a free particle inside the left half of a 1-dimensional box of length L is**

(a) $L/2$ (b) $\sqrt{(2/L)}$ (c) $2/L$ (d) ½

**30.** **The force between two electrons separated by 0.1 nm in vacuum is**

$(\varepsilon_0 = 8.854 \times 10^{-12}\ J^{-2}\ C^{-2}\ m^{-1})$

(a) $2.31 \times 10^{-8}$ N (b) $-2.31 \times 10^{-8}$ N (c) $-1.15 \times 10^{-8}$ N (d) $1.155 \times 10^{-8}$ N

**31.** **Assuming that there is no chemical reaction, the change in entropy when 2 mole of $N_2$, 3 mols of $H_2$ and 2 mols of $NH_3$ are mixed at constant temperature is**

(a) $-62.79\ JK^{-1}$ (b) $62.79\ JK^{-1}$ (c) $125.58\ JK^{-1}$ (d) $-125.58\ JK^{-1}$

**32.** **The half-life of a first order reaction varies with temperature according to**

(a) $\ln t_{1/2} \propto 1/T$ (b) $\ln t_{1/2} \propto T$ (c) $t_{1/2} \propto 1/T^2$ (d) $t_{1/2} \propto T^2$

**33.** **The ionization constant of formic acid, which ionizes to an extent of 4.2%, in 0.1 M aqueous solution is**

(a) $0.92 \times 10^{-2}$ (b) $1.84 \times 10^{-2}$ (c) $1.84 \times 10^{-4}$ (d) $0.92 \times 10^{-4}$

**34.** **Radiation of $10^{14}$ Hz falls in the region of**

(a) Radio frequency (b) Microwave (c) Visible (d) X-rays

**35.** **The bond order for $N_2$, $O_2$, $N_2^-$, $O_2^-$ varies as**

(a) $N_2 > N_2^- > O_2 > O_2^-$ (b) $N_2 > O_2 > N_2^- > O_2^-$

(c) $O_2 > N_2 > O_2^- > N_2^-$ (d) $N_2^- > N_2 > O_2^- > O_2$

**36.** **Sodium metal crystalizes in the body centered cubic lattice with cell edge "a". The radius of the sodium atom is**

(a) $a/\sqrt{2}$ (b) $a\sqrt{3}/2$ (c) $a\sqrt{3}/4$ (d) $a/2\sqrt{2}$

**37.** **The metals involved in nitrogenase are**

(a) Fe and Mg (b) Mo and K (c) Mo and Fe (d) Fe and K

**38.** **The complexes $V(C_6H_6)_2$ and $Cr(C_6H_6)_2$ are both readily oxidized in air to their respective cations. The number of unpaired electrons, respectively, in each are**

(a) 0, 0 (b) 1, 0 (c) 0, 1 (d) 1,1

**39.** **The lowest energy d-d transition in the Cr(III) complexes varies in the order**

(a) $[CrCl_6]^{3-} < [Cr(H_2O)_6]^{3+} < [Cr(en)_3]^{3+} < [Cr(CN)_6]^{3-}$

(b) $[CrCl_6]^{3-} < [Cr(en)_3]^{3+} < [Cr(H_2O)_6]^{3+} < [Cr(CN)_6]^{3-}$

(c) $[Cr(CN)_6]^{3-} < [CrCl_6]^{3-} < [Cr(H_2O)_6]^{3+} < [Cr(en)_3]^{3+}$

(d) $[Cr(H_2O)_6]^{3+} < [Cr(en)_3]^{3+} < [CrCl_6]^{3-} < [Cr(CN)_6]^{3-}$

**40.** **The bonding of cyclopentadienyl in $Ti(Cp)_4$ is such that**

(a) all Cp rings are pentahapto

(b) one Cp ring is pentahapto and the other three rings are monohapto

(c) two Cp rings are monohapto and the other two rings are pentahapto

(d) all Cp rings are monohapto

**41.** **The structures of $O_3$ and $N_3^-$ are**

(a) linear and bent, respectively (b) both linear

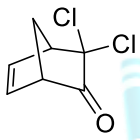
(c) both bent (d) bent and linear, respectively

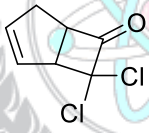
**42.** **Lability of the ions $Cr^{2+}$, $Mn^{2+}$ and $V^{2+}$ should follow the order**

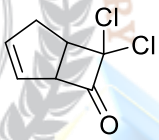
(a) $Cr^{2+} > Mn^{2+} > V^{2+}$ (b) $Mn^{2+} > Cr^{2+} > V^{2+}$

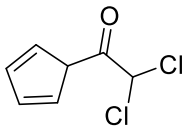
(c) $Mn^{2+} > V^{2+} > Cr^{2+}$ (d) $V^{2+} > Cr^{2+} > Mn^{2+}$

**43.** **The major product formed in the reaction of cyclopentadiene with a mixture of dichloroacetyl chloride and triethylamine is**

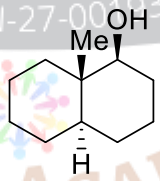
(a) 


(b) 


(c) 

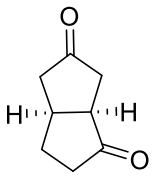

(d) 

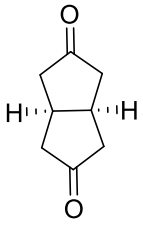

**44.** **The configurations at the three chiral centres in the bicyclodecanol given below, are**

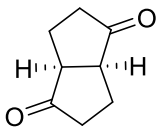


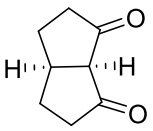

(a) 1S, 2S, 6R (b) 1S, 2S, 6S (c) 1R, 2S, 6R (d) 1R, 2R, 6R

**45.** **Among the bicyclo-[3,3,0]-octanediones given below, which one will exhibit FIVE signals in the broad band decoupled $^{13}C$ NMR spectrum?**

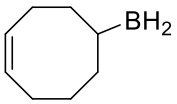
(a) 

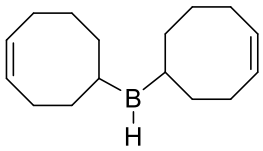

(b) 

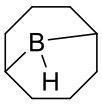

(c) 

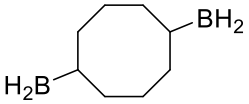

(d) 


**46.** **The major product formed in the reaction of 1,5-cyclooctadiene with 0.5 equivalent of diborane is**

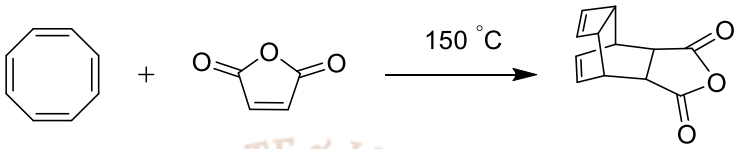
(a) 


(b) 


(c) 


(d) 


**47. The two pericyclic reactions successively involved in the thermal transformation given below are**



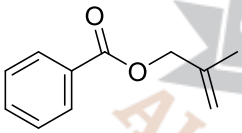

(a) 6 π-electrocyclization followed by [4 + 2] π -cycloaddition

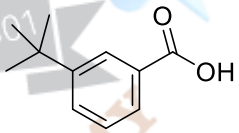
(b) 8 π -cycloaddition followed by [2 + 2] π -electrocyclization

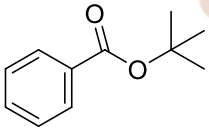
(c) 6 π -cycloaddition followed by [2 + 2] π -electrocyclization

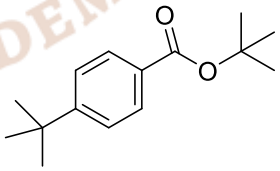
(d) 4 π -electrocyclization followed by [ 4 + 2] π -cycloaddition

**48. The major product formed in the reaction benzoic acid with isobutylene in the presence of a catalytic amount of sulfuric acid is:**

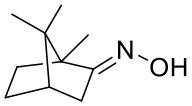
(a) 

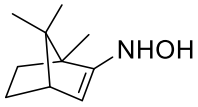

(b) 

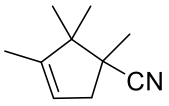

(c) 

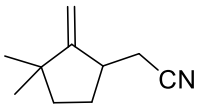

(d) 

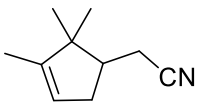

**49. The major product formed in the reaction of the oxime given below with sulfuric acid is**



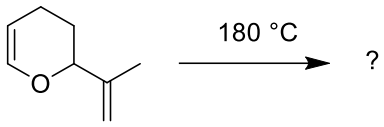

(a) 

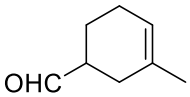

(b) 

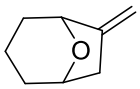

(c) 

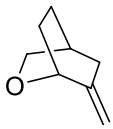

(d) 


**50. The major product formed in the thermal reaction given below, is**




(a) 4(H)-Furan (b) 

(c) 

(d) 


**Questions 51 – 88 (subjective questions) carry five marks each (Answer any twenty).**

**51.** **For the reaction, trans-$[PtL_2Cl_2] + Y \longrightarrow$ trans-$[PtL_2ClY] + Cl^-$ the rate constant K varies as follows:**

| | Y | L | K ($10^3$ $M^{-1}$ $S^{-1}$) |
|---|---|---|---|
| **(i)** | $PPh_3$ | Py | 249,000 |
| **(ii)** | SCN | Py | 180 |
| **(iii)** | $I^-$ | Py | 107 |
| **(iv)** | SCN | $PEt_3$ | 371 |

**(a) What is the mechanism of the reaction?**

**(b) Explain the variations observed.**

**52.** **Calculate the number of theoretical plates for a column where the retention time for a compound is two minutes and the width of the peak at the base is 10s.**

**53.** **Why is the thermal conductivity detector unsuitable for the gas chromatographic detection of hexachlorobenzene?**

**54.** **What types of HPLC columns are suitable for the analysis of organic compounds such as**

**(a) cyclohexene, cyclohexane, methylcyclohexane**

**(b) glycerol, 1,2-dihydroxy propane, 1,3 dihydroxy propane**

**55.** **Write down the products formed in each of the following reactions.**

(A) $P_2S_5 + PCl_5 \longrightarrow$

(B) $S + NH_{3(l)} \leftrightharpoons$

(C) $NaBH_4 + I_2 \longrightarrow$

(D) $XeO_3 + OH^- \rightleftharpoons$

(E) $SiO_2 + HF_{(aq)} \longrightarrow$

56. Draw the structures of the Wilkinson's catalyst and the product formed on its reaction with hydrogen.

57. What is the product formed in the reaction of $[RCo(CO)_4]$ with CO in the presence of hydrogen? Indicate clearly the intermediates involved.

58. Distinguish between limiting current and residual current in a polarogram.

59. What is the separation between the anodic and cathodic waves in a cyclic voltammetry experiment for the reversible one-electron and two-electron processes?

60. How does the separation vary with the scan rate for a quasi-reversible process?

61. Give the structures of (a) $[(CH_3)PF_3]^+$ and (b) $XeO_2F_2$

62. MgO and NaF are isoelectronic and crystallize in NaCl structure. Why MgO is twice as hard as NaF and has a much higher melting point than NaF?

63. Why does the lowest energy charge transfer band shifts from 18,000 $cm^{-1}$ in $KMnO_4$ to 26,000 $cm^{-1}$ in $K_2CrO_4$?

64. Aqueous solution of $MnCl_2$ exhibits a number of very weak intensity absorption bands ($\varepsilon \sim 0.01$) between 18,000 to 42,000 $cm^{-1}$ while solution of $TiCl_3$ in dilute sulfuric acid exhibits a relatively strong band at 20,000 $cm^{-1}$ with a shoulder at 17,400 $cm^{-1}$ ($\varepsilon \sim 10$) . Account for these observations.

65. Explain the variation of hydration energies of divalent metal ions from calcium to zinc.

66. Calculate the vapour pressure of toluene at 100 °C assuming that Trouton's rule is obeyed. The boiling point of toluene is 110 °C.

67. The vapour pressure of ethanol at 20 °C is 44.5 mm. When 15g of a non-volatile compound-A is dissolved in 500g of ethanol, the vapour pressure decreases to 43.5 mm. Calculate the molecular weight of A.

68. 0.1 M $CuSO_4$ solution is electrolyzed employing Cu electrodes using a current of 10A for 1 h. Calculate the weight of Cu deposited.

69. A solution contains 0.1 $mol/dm^3$ of $Cl^-$, 0.1 $mol/dm^3$ of $Br^-$and 0.1 $mol/dm^3$ of $I^-$. Solid $AgNO_3$ is gradually added to this solution. Assuming that the volume does not change, answer the following questions.

$$K_{sp}(AgCl) = 1.7 \times 10^{-10}\ (mol/dm^3)^2,$$

$$K_{sp}(AgBr) = 5.0 \times 10^{-13}\ (mol/dm^3)^2,$$

$$K_{sp}(AgI) = 8.5 \times 10^{-17}\ (mol/dm^3)^2$$

(a) **Which salt will precipitate first?**

(b) **What is the concentration of $Ag^+$ ions required to start precipitation?**

(c) **What will be the concentration of the first ion when the second salt begins to precipitate?**

70. **For $BCl_3$ molecule, the Cl atoms are numbered as 1, 2, 3. Examine whether the operations $\sigma_v(1)$ $\sigma_v(2)$ commute. Indicate the symmetry operation equivalent to the binary operations in each case.**

71. **Give the symmetry operation equivalent to** (i) $C_4^6$ (ii) $S_4^2$

72. **Upon absorption of light of 266 nm, ozone dissociates in the following way**

$$O_3(g) \longrightarrow O_2(g) + O(g)$$

**The power of the incident radiation is 20 mW and the sample of ozone is exposed for a period of 3 hrs. The amount of ozone that is photolysed in 10 μ mol. Calculate the quantum yield for the ozone photolysis reaction.**

73. **Acetic acid show two signals "a" and "b" at $\delta = 8.0$ ppm and 3.8 ppm, respectively in a 50 MHz NMR spectrometer. Calculate the separation in frequency between the two signals on a 300 MHz spectrometer.**

74. **The 1s wavefunction for the hydrogen atom is $R_{1s}(r) = (1/\sqrt{\pi})(1/a_0)^{\frac{3}{2}} \exp(-r/a_0)$ Calculate the probability that the electron will be found within the first Bohr radius.**

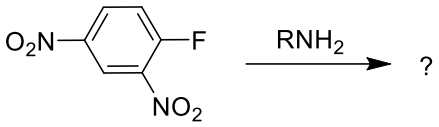
75. **A substance is four times more soluble in $CHCl_3$ than in $H_2O$. If 10 g of the substance is dissolved in 500 ml of water, how much of it will be removed by extraction with 500 ml of $CHCl_3$?**

76. **The root mean square velocity of $O_2$ molecules is 575 $ms^{-1}$. Find out the temperature of $O_2$ gas.**

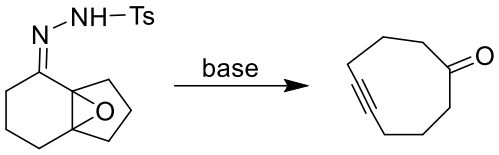
77. **Set up the Huckel determinant for methyleneimine ($H_2C{=}HN$) taking $\beta_{C\text{-}N}$ as 1.0 β and $\alpha_N$ as α + 0.5 β, where α and β represent the usual Coulomb and resonance integrals respectively, and obtain the Huckel molecular orbital energy levels.**

78. **Explain, why the $^1H$ NMR spectrum of p-dichlorobenzene shows a singlet, whereas p-difluorobenzene shows a multiplet.**

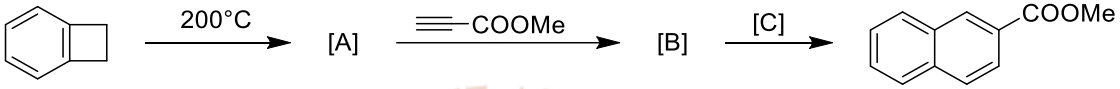
79. **Identify the structure of the major product formed in the following reaction, and give a mechanism of its formation.**



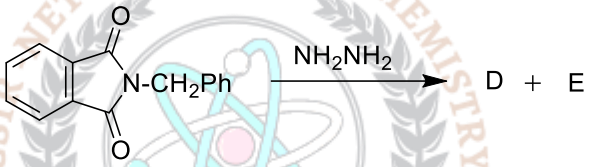

**80. Give a suitable mechanism for the following transformation.**




**81. Identify the products/reagents (A-C) in the following sequence.**

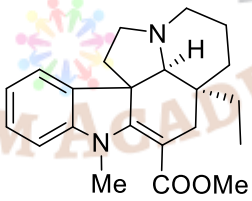



**82. Write structures of the products formed in the following reaction.**

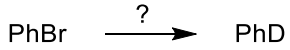


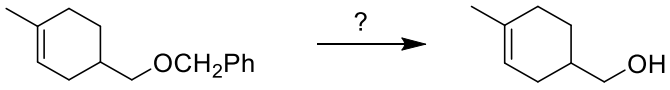

**83. Write the conformational structures of the two cyclic isomers of glucose which are responsible for the phenomenon of mutarotation.**

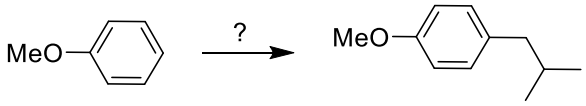
**84. The optically active compound given was found to racemise on heating in a microwave oven. Give a suitable explanation.**

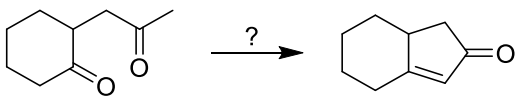


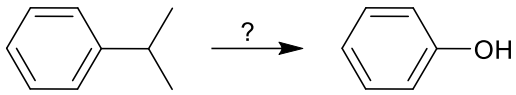

**85. Suggest suitable reagents to bring about the following transformations (may require more than one step).**

I. 

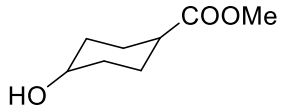

II. 

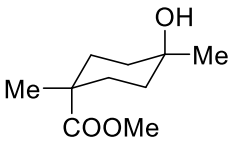

III. 


IV. 

V. 


**86.** **Among the two hydroxyesters given below, which one will readily lactonise on treatment with a mild base. Write the structure of the product and justify your answer briefly.**




**87.** **Identify the reactive intermediate involved in the reaction of furan with a mixture of $HNO_3$ and $H_2SO_4$. Write the mechanism and the structure of the final product.**

**88.** **A sweet-smelling organic compound-A (mol. Formula $C_8H_{16}O_2$) on reaction with lithium aluminium hydride furnishes a single primary alcohol 'B'. Whereas reaction of 'A' with an excess of methylmagnesium bromide furnishes two alcohols 'B' and 'C'.**

**In the $^1H$ NMR spectrum, compound-B exhibits signals at $\delta\ 3.8\ (2H, d, J = 7\ Hz), 1.8\ (1\ H, m), 1.6\ (1\ H,$ brs, exchangeable with $D_2O$) and $0.9\ (6\ H, d, J = 7.2\ Hz)$. Identify the structures of the compounds 'A', 'B' and 'C', and explain the reactions.**

## Answer Key

| Q.No | Ans | | Q.No | Ans | | Q.No | Ans | | Q.No | Ans |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. | a | | 16. | d | | 31. | b | | 46. | c |
| 2. | a | | 17. | c | | 32. | a | | 47. | a |
| 3. | b | | 18. | b | | 33. | c | | 48. | c |
| 4. | b | | 19. | d | | 34. | c | | 49. | d |
| 5. | b | | 20. | c | | 35. | a | | 50. | b |
| 6. | a | | 21. | a | | 36. | c | | | |
| 7. | a | | 22. | b | | 37. | c | | | |
| 8. | c | | 23. | c | | 38. | b | | | |
| 9. | c | | 24. | d | | 39. | a | | | |
| 10. | b | | 25. | a | | 40. | c | | | |
| 11. | b | | 26. | c | | 41. | d | | | |
| 12. | b | | 27. | a | | 42. | a | | | |
| 13. | b | | 28. | c | | 43. | b | | | |
| 14. | b | | 29. | d | | 44. | a | | | |
| 15. | d | | 30. | a | | 45. | d | | | |