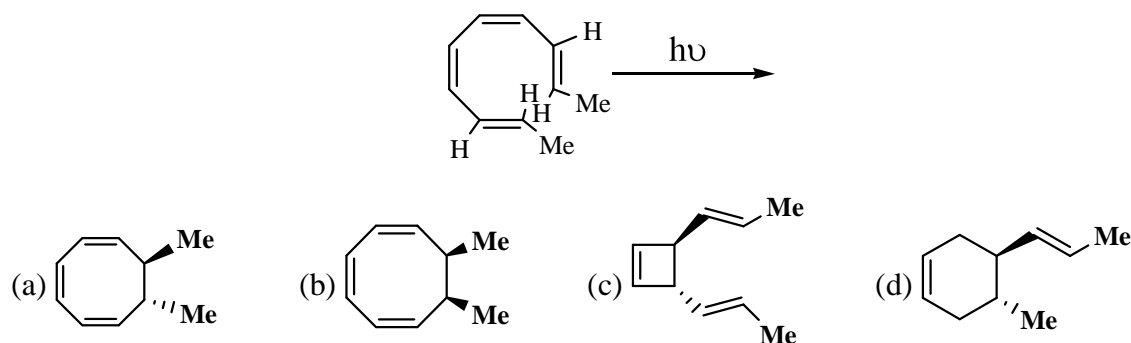## SECTION-A

1.   *This question consists of TWENTY FIVE sub-questions (1.1 to 1.25) of ONE mark each. For each of these sub-questions, four possible answers (a, b, c and d) are given, out of which only one is correct.*   **[25×2 = 50]**

1.1.   Which among the following molecules belong to point group C_{4v}?
(a) $[BF_4]Na^+$ (b) $XeOF_4$ (c) XeF_4 (d) $[PtCl_4]^{2-}$

1.2.   The ^{19}F NMR spectrum of PCl_2F_3 (I for $^{31}P = ½$, I for $^{19}F = ½$) shows
(a) two triplets and two doublets   (b) two triplets and one doublet
(c) two doublets and one triplet   (d) three triplets and one doublet

1.3.   The compound $(SiH_3)_3N$ is expected to be
(a) pyramidal and more basic than $(CH_3)_3N$
(b) planar and less basic than $(CH_3)_3N$
(c) pyramidal and less basic than $(CH_3)_3N$
(d) planar and more basic than $(CH_3)_3N$

1.4.   The infrared and Raman spectrum BF_3 are expected to show
(a) the same number of peaks
(b) more absorption peaks in IR in comparison to Raman
(c) more absorption peaks in Raman in comparison with IR
(d) absorption peaks present in Raman are absent in R

1.5.   The complex with maximum CFSE is
(a) $\left[CoCl_4\right]^{2-}$ (b) $\left[Co\left(H_2O\right)_6\right]^{3+}$ (c) $CoF_3\left(H_2O\right)_3$ (d) $\left[CoF_6\right]^{3+}$

1.6.   The compound which has four metal-metal bonds is
(a) $Fe_2\left(CO\right)_9$ (b) $Co_2\left(CO\right)_8$ (c) $\left[Re_2Cl_8\right]^{2-}$ (d) $\left[Ru_3\left(CO\right)\right]_{12}$

1.7.   The complex with spin-only magnetic moment of ~ 4.9 B.M. is
(a) $\left[Fe\left(H_2O\right)_6\right]^{2+}$ (b) $\left[Fe\left(CN\right)_6\right]^{3-}$ (c) $\left[Fe\left(CN\right)_6\right]^{4-}$ (d) $\left[Fe\left(H_2O\right)_6\right]^{3+}$

1.8.   The complex with exhibits lowest energy electronic absorption band is
(a) $\left[NiCl_4\right]^{2-}$ (b) $\left[Ni\left(H_2O\right)_6\right]^{2+}$ (c) $\left[Ni\left(CN\right)_4\right]^{2-}$ (d) $\left[Ni\left(CO\right)_4\right]$

1.9.   The system for which energy (E) increases quadratically with the quantum number (n) is
(a) particle-in-a-one dimensional box   (b) hydrogen atom
(c) one dimensional harmonic oscillator   (d) rigid rotor

1.10.   Among the following orbitals of a diatomic molecule, the bonding one is
(a) $1\sigma_u$ (b) $2\sigma_u$ (c) $1\pi_u$ (d) $1\pi_g$

1.11.   The population (N) distribution over states (n) of a diatomic molecule corresponds to   **[GATE 2000]**
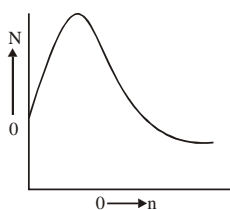

(a) Translation   (b) Vibration   (c) Rotation   (d) Electronic.

1.12. $^2P_{3/2}$ is the ground state of

   (a) H   (b) Li   (c) B   (d) F

1.13. The vapour pressure of pure components 'A' and 'B' are 200 torr and 100 torr respectively. Assuming a solution of these components obeys Raoult's law, the mole fraction of component 'A' in vapour phase in equilibrium with a solution containing equimoles of 'A' and 'B' is

   (a) 0.33   (b) 0.66   (c) 0.80   (d) 0.50

1.14. The half-life time for a reaction at initial concentrations of 0.1 and 0.4 mol^{-1} are 200s and 50s respectively. The order of the reaction is

   (a) 0   (b) 1   (c) 2   (d) 3

1.15. The pH of a buffer solution containing 4×10^{-3} and 0.4 moles of acetic acid $(pK_a = 4.76)$ and sodium acetate respectively will be

   (a) 6.76   (b) 4.76   (c) 2.76   (d) 0.76

1.16. Under the equilibrium conditions for the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the total pressure is 12 atm. The value of K_p is

   (a) 16   (b) 0.5   (c) 2   (d) 32

1.17. An aqueous solution containing m moles of non-volatile solute freeezes at –0.186ºC. The elevation in the boiling point of the same aqueous solution $(K_f = 1.86°, K_b = 0.512°)$ would be

   (a) 0.186   (b) 0.512   (c) 0.0512   (d) 0.512/1.86

1.18. The two H's at C-2 and C-3 in (2R, 3S) tartaric acid

   (a) enantiotopic   (b) diastereotopic   (c) homotopic   (d) constitutionally heterotopic

1.19. Oxymercuration-demercuration reaction of 1-methylcyclohexene gives

   (a) cis-2-methylcyclohexanol   (b) trans-2-methylcyclohexanol

   (c) 1-methylcyclohexanol   (d) mixture of cis and trans-2-methylcyclohexanol

1.20. Bromination of (E)-2-butenedioic acid gives

   (a) (2R, 3S)-2, 3-diboromosccinic acid   (b) (2R, 3R)-2, 3-dibromosuccinic acid

   (c) 5-iodo-tetrahydropyran-2-one   (d) 4-pentenoyliodide

1.21. 4-Pentenoic acid when treated with I_2 and $NaHCO_3$ gives

   (a) 4, 5-diiodopentanoic acid   (b) 5-iodomethyl-dihydrofuran-2-one

   (c) 5-iodo-tetrahydropyran-2-one   (d) 4-pentenoyliodide

1.22. The following tetraene upon photolysis gives

1.23. The product formed upon heating camphene with HCl is

(Camphene)

(a)   (b)   (c)   (d)
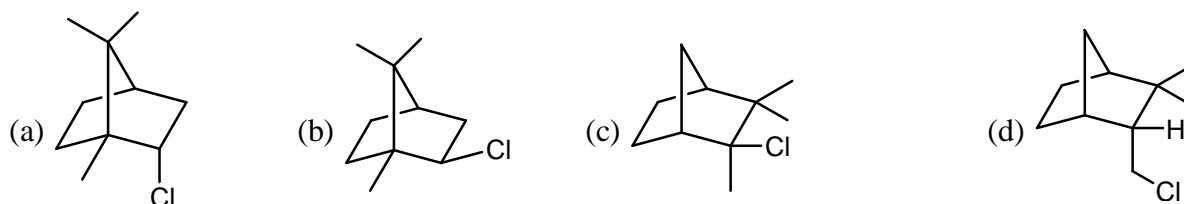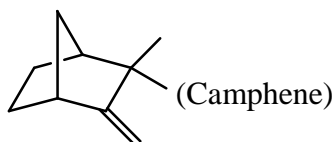
1.24. Pyridine undergoes electrophilic nitration at elevated temperature to give the following as a major product:

(a)   (b)   (c)   (d)
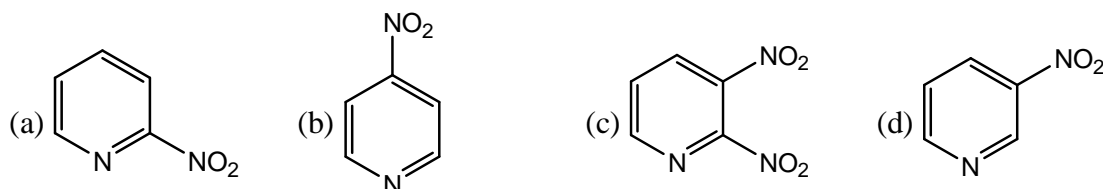
1.25. Among the following, the acid which undergoes fastest decarboxylation is

(a)   (b)

(c) PhCOOH   (d)

2. *This question consists of TWENTY FIVE sub-questions (2.1 to 2.25) of ONE mark each. For each of these sub-questions, four possible answers (a, b, c and d) are given, out of which only one is correct.*   **[25×2 = 50]**

2.1. Which of the following statements about the molecule NOCl is correct?
   (a) It has a linear structure   (b) It belongs to the point group C_s
   (c) It does not have a dipole moment   (d) It is a chiral molecule

2.2. Which of the following is an *arachno* borane?

   (a) $\left[B_6H_6\right]^{2-}$ (b) $\left[B_5H_9\right]$ (c) $\left[B_2H_6\right]$ (d) $\left[B_8H_{14}\right]$

2.3. C_{60} has
   (a) 14 pentagons and 18 hexagons   (b) 12 pentagons and 20 hexagons
   (c) 10 pentagons and 20 hexagons   (d) 12 pentagons and 18 hexagons

2.4. The order of acidity in boron trihalides is

   (a) $BF_3 > BCl_3 > BBr_3$ (b) $BBr_3 > BCl_3 > BF_3$

   (c) $BF_3 > BBr_3 > BCl_3$ (d) $BBr_3 > BF_3 > BCl_3$

2.5. The compound which obeys 18-electron rule is:

   (a) $Mn(CO)_3$ (b) $Fe(CO)_4$ (c) $V(CO)_6$ (d) $Cr(CO)_6$

2.6. The Si–O–Si bond angle in $Me_3SiOSiMe_3$ is
   (a) ~ 120º   (b) ~ 180º   (c) ~ 90º   (d) ~ 109º

2.7. The compound which exhibits Jahn-Teller distortion is:

   (a) $\left[Mn(H_2O)_6\right]^{2+}$ (b) $\left[Mn(H_2O)_6\right]^{3+}$ (c) $\left[Cr(H_2O)_6\right]^{3+}$ (d) $\left[Fe(CN)_6\right]^{4-}$

2.8. The orange colour of $Cr_2O_7^{2-}$ is due to
(a) metal to ligand charge transfer transition   (b) ligand to metal charge transfer transition
(c) crystal-field transition   (d) charge-transfer complex formation

2.9. Among the following diatomic molecules, the shortest bond length is to be found in

(a) C_2 (b) N_2 (c) O_2 (d) F_2

2.10. Among the following diatomic molecules, the one that shows EPR signal is
(a) Li_2 (b) B_2 (c) C_2 (d) N_2

2.11. Among the following elements, the one that acts as the major component in a semiconductor is
(a) C   (b) Si   (c) Ga   (d) As

2.12. Among the singlet (S), doublet (D) and triplet (T) electronic states, phosphorescence involves transition between
(a) S and S   (b) D and D   (c) T and T   (d) S and T

2.13. In a system, when the chemical potential of each component is the same for all the phases, the equilibrium is said to be
(a) metastable equilibrium   (b) thermal equilibrium
(c) composition equilibrium   (d) mechanical equilibrium

2.14. The number of molecules of an ideal gas in a 8.21 container at 380 torr and 27ºC will be

(a) 1.0×10^{23} (b) 1.0×10^{22} (c) 6.02×10^{23} (d) 12.04×10^{23}

2.15. The criterion for the spontaneity of a process is:

(a) $\Delta S_{sys} > 0$ (b) $\Delta S_{surr} > 0$ (c) $\Delta S_{sys} + \Delta S_{surr} > 0$ (d) $\Delta S_{sys} - \Delta S_{surr} > 0$

2.16. ΔH and ΔE for the reaction $Fe_2O_3(s) + 3H_2(s) \longrightarrow 2Fe(s) + 3H_2O(\ell)$ at constant temperature are related as

(a) $\Delta H = \Delta E$ (b) $\Delta H = \Delta E + RT$ (c) $\Delta H = \Delta E + 3RT$ (d) $\Delta H = \Delta E - 3RT$

2.17. For an ideal gas following adiabatic reversible expansion, plot of $\log P$ versus $\log V$ is linear with a slope equal to $(\gamma = C_P / C_V)$:

(a) $1/\gamma$ (b) $-1/\gamma$ (c) γ (d) $-\gamma$

2.18. Toluene when refluxed with Br_2 in the presence of light mainly gives
(a) o-bromotoluene   (b) p-bromotoluene
(c) mixture of o- and p-bromotoluene   (d) benzyl bromide

2.19. Optically active 2-octanol rapidly loses its optical activity when exposed to
(a) dilute acid   (b) dilute base   (c) light   (d) humidity

2.20. 1-Hexyne upon treatment with disiamylborane followed by oxidation with H_2O_2 gives
(a) hexanoic acid   (b) hexenol   (c) hexanal   (d) hexanol

2.21. (E)-3-bromo-3-hexene when treated with CH_3O^- in CH_3OH gives
(a) 3-hexyne   (b) 2-hexyne   (c) 2, 3-hexadiene   (d) 2, 4-hexadiene

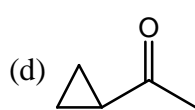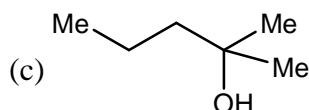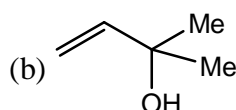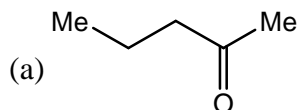2.22. The major product formed in the following reaction is:

(a)

(b)
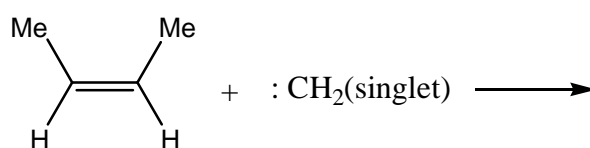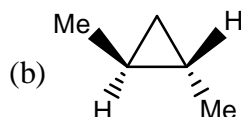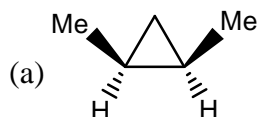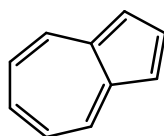
(c) 50 : 50 mixture of above two compounds

(d)
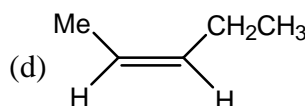
2.23. Methyl vinyl ketone upon reaction with $LiCuMe_2$ gives a major product whose structure is

(a)

(b)

(c)

(d)

2.24. The following hydrocarbon has a dipole moment of 0.8 D because
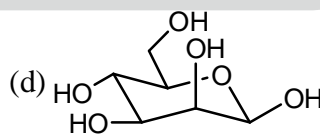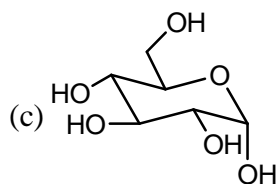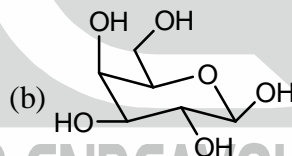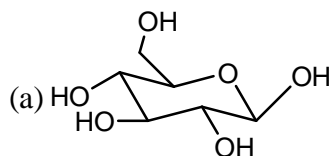

(a) It exist as in which both the rings exhibit aromaticity.

(b) Charge separation permits conformation stability

(c) The two rings are of different size
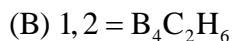
(d) The molecule obeys $4n + 2$ Huckel rule

2.25. β-D-Glucose is represented as

(a)

(b)

(c)

(d)

SECTION-B

This section consists of TWENTY questions of FIVE marks each. ANY FIFTEEN out of these questions have to answered on the Answer Book provided.   **[75 Marks]**

3.1. Write the structures of the following compounds

(A) S_4N_4 (B) $1, 2 = B_4C_2H_6$ (C) SF_4CH_2

3.2. Account in about 10 lines the fact that the IR stretching frequency of the P-O bond increases in the order

$$(CH_3)_3 PO < Cl_3PO < F_3PO$$

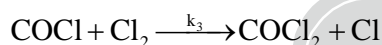4. Complete the following reactions supplying the missing reactant or product

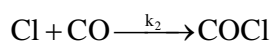(a) $n\left[\left(CH_3\right)_2 SiO_4\right] + \left(CH_3\right)_3 SiOSi\left(CH_3\right)_3 \xrightarrow{H_2SO_4} (A)$

(b) $Al_2\left(CH_3\right)_6 + 6H_2O \longrightarrow (B) + (C)$

(c) $3BCl_3 + 3NH_4Cl \longrightarrow (D)$

(d) $E \xrightarrow[\text{hap}\tan e, 77K]{hv, 270 \text{ nm}} \left(MeS\right)_2 Si = Si\left(MeS\right)_2$ $(MeS = 2, 4, 6\text{-trimethylphenyl})$

(e) $SbF_5 + BrF_3 \longrightarrow (F) + (G)$

5.1.   State whether the following is true or false and explain your choice in about 3 lines. "The Ni-C bond length in nickelocene is longer than the Fe-C bond length in ferrocene".

5.2.   Write the structure of $CO_4\left(CO\right)_{12}$. Using the isolobal analogy show which of the following fragments you would use to replace one of the cobalt fragments in the above cluster? Write the structure of the cluster so formed

(i) CH_2 (ii) CH (iii) NH_2 (iv) CH_3

6.1.   From among the following reactions identify the type of reaction involved viz., oxidative-addition, reductive elimination, insertion or addition. Justify your choice

(i) $\left[RhI_3\left(CO\right)_2\left(CH\right)_3\right]^- \longrightarrow \left[RhI_3CO(\text{solvent})\left(COCH_3\right)\right]^-$

(ii) $\left[Co_2\left(CO\right)_8\right] + H_2 \rightleftharpoons 2\left[CoH\left(CO\right)_4\right]$

(iii) $Mn_2\left(CO\right)_{10} + Br_2 \rightarrow 2MnBr\left(CO\right)_5$

6.2.   Write the structures of the products formed in the following reactions, keeping in view the 18-elecrtron rule

(i) $\eta^4 C_4 H_6 Fe\left(CO\right)_3 + HCl \rightarrow$

(ii) $\left(\eta^5 Cp\right)_2 Fe + HBF_4 \rightarrow$

7.1.   Lower the symmetry of a complex, closer is its magnetic moment, to the spin-only value. Explain in 2-3 sentences.

7.2.   Write the d-orbital splitting diagrams for a square pyramidal and a trigonal bipyramidal complex

8.1.   Draw the active site structure of rubredoxin and two common forms of ferredoxins.

8.2.   Cytochrome C is a redox protein but myoglobin is an oxygen storage protein. Justify in 2-3 sentences.

9.1.   The complex $\left[Fe\left(H_2O\right)_6\right]^{2+}$ displays two overlapping absorption bands at ~1000 nm. Provide an explanation in 2-3 sentences.

9.2.   Comment in 5-6 lines on the metal-olefin bonding in $K\left[PtCl_3\left(C_2H_4\right)\right]$

10. O_3 molecule has bent geometry in its ground electronic state. Using Huckel approximation, derive the eigen values of the π molecular orbitals of O_3 and write down the electronic configuration. Also how schematically all the three π molecular orbitals and label them bonding, non-bonding and antibonding.

11.1.   Show how would you distinguish between propanal and acetone using NMR spectroscopy. Label the axes properly and schematically show all the important features in the spectrum.

11.2.   Using Raman spectrum and IR spectrum, show how you will determine whether a substance is trans-or cis-1, 2-dichloroethylene (without knowing the frequencies at which different vibrational modes occur)

12.1. H_2 has one of the largest rotational constants $\left(B_e = h / 8\pi^2 Ic \sim 60 cm^{-1}\right)$ for a diatomic molecule. Predict the spacing between the lines in the rotational Raman spectrum indicated.

Rayleigh line
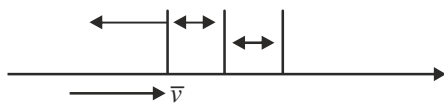
12.2. Predict the spacing between the same set of lines in the rotational Raman spectrum of HD.

13. Two half cells of hydrogen-oxygen fuel cell under basic conditions can be depicted as $OH^-/O_2(g)/Pt$ and $OH^-/H_2(g)/Pt$ and their standard electrode potentials at 25°C are 0.4009 and –0.8279 V respectively. Write the half cell reactions and the complete cell reaction. Depict the complete cell and calculate the emf of the cell.

14. The solubility of Ag_2CrO_4 in water is 8×10^{-5} mol kg^{-1} at 25°C and its solubility in 0.04 mol kg^{-1} NaNO$_3$ solution is 8.84×10^{-5} mol kg^{-1}. What is the mean ionic activity coefficient of Ag_2CrO_4 in 0.04 mol kg^{-1} NaNO$_3$?

15. The formation of phosgene by the reaction $CO + Cl_2 \rightarrow COCl_2$ appears to follow the mechanism:

$$Cl_2 \xrightarrow{k_1} 2Cl$$

$$Cl + CO \xrightarrow{k_2} COCl$$

$$COCl + Cl_2 \xrightarrow{k_3} COCl_2 + Cl$$

$$COCl \xrightarrow{k_4} CO + Cl$$

$$2Cl \xrightarrow{k_5} Cl_2$$
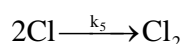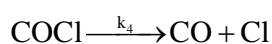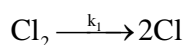
Assuming that the intermediates COCl and Cl are in a steady state, find the rate law for the formation of COCl$_2$.

16.1. Account for the fact that only one of the following compounds A and B give the expected elimination product with KI in acetone


(A)   (B)
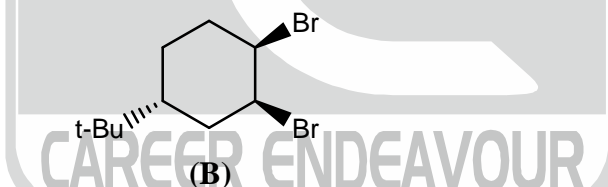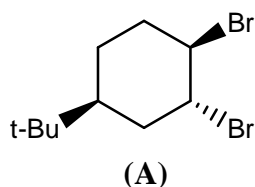
16.2. Account for the fact that aniline is not a suitable substrate in the Friedel-Crafts alkylation reaction

17. Suggest a suitable method and write all the steps for the following transformations
(i) anisole to 2-cyclohexenone
(ii) malonic ester to cyclobutanecarboxylic acid

18.1. An industrial preparation of phenol and acetone makes use of cumene and atmospheric oxygen as starting materials to produce cumene hydroperoxide which is then converted to products. Suggest what steps are involved in the process.

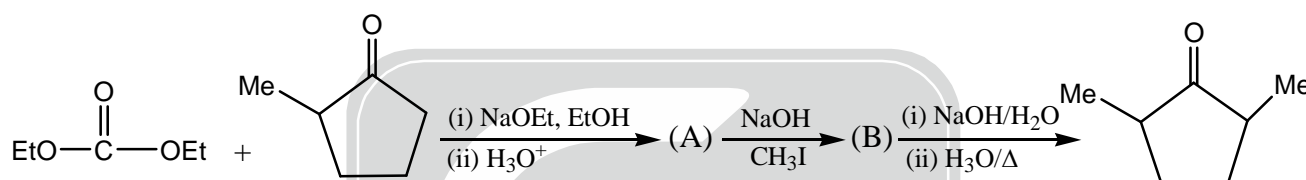18.2. Suggest a plausible mechanism for the following hydrolysis reaction
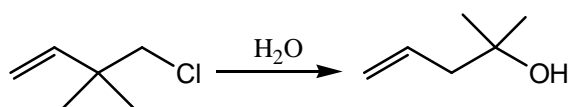
19.1. Explain briefly which nitrogen of the side chain ring of histidine is protonated in the monocationic form?
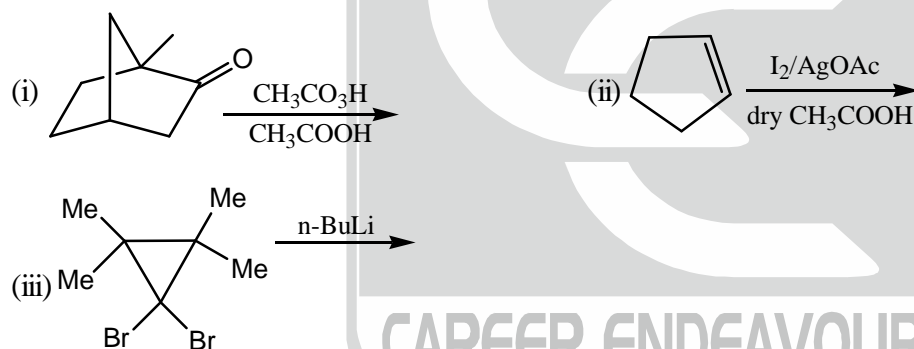
 (Histidine)
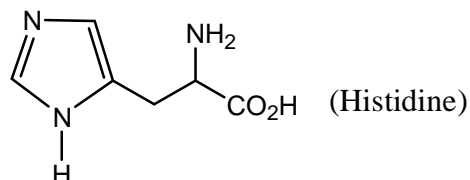
19.2. Optically active ketone A undergoes racemization in basic solution. Suggest a mechanism for this process. Explain whether ketone B would also racemize in basic solution?
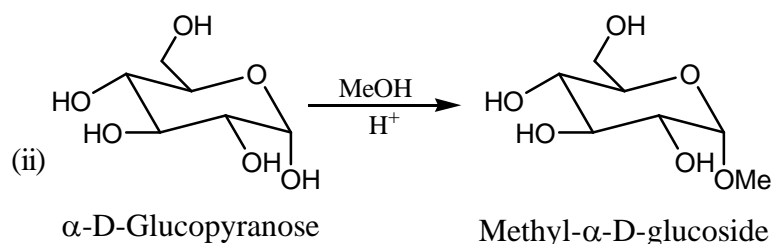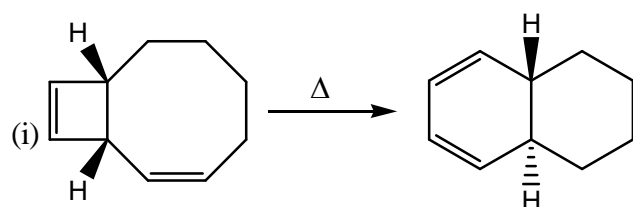

(A)   (B)
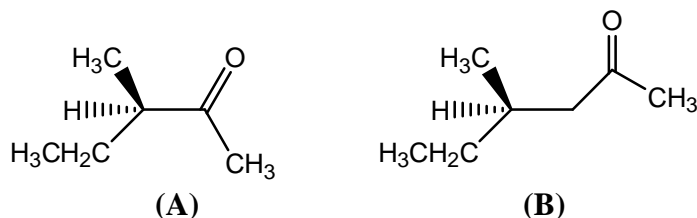
20.1. Write the missing products, A and B in the following reaction scheme

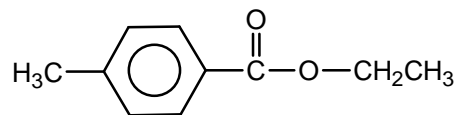20.2. Write the structures of the major product in the following reactions.

21. Suggest a suitable mechanism for each of the following reactions

α-D-Glucopyranose   Methyl-α-D-glucoside

22.1. Predict the approximate chemical shifts and multiplicities for the absorptions in the ^{1}H NMR spectrum of the following compound.
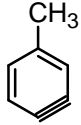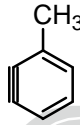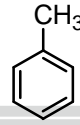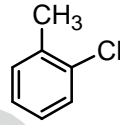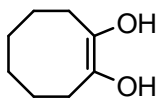

22.2. Explain how the peaks at m/z 115, 101 and 73 arise in the mass spectrum of 3-methyl-3-heptanol.

***** END OF THE QUESTION PAPER *****

SECTION-A

1. *This question consists of TWENTY FIVE sub-questions (1.1 to 1.25) of ONE mark each. For each of these sub-questions, four possible answers (a, b, c and d) are given, out of which only one is correct.*   [25×1 = 25]

1.1. Icosahedral structure is generally exhibited by
     (a) C   (b) Si   (c) Ge   (d) B

1.2. The hybrid orbitals used by bromine atom in BrF_3 are
     (a) sp^2 (b) sp^3 (c) sp^3d (d) sp^3d^2

1.3. The metal ion present in carbonic anhydrase is
     (a) Mn   (b) Zn   (c) Cu   (d) Fe

1.4. The most acidic aqua ion is
     (a) $Fe(H_2O)_6^{3+}$ (b) $Co(H_2O)_6^{3+}$ (c) $Ti(H_2O)_6^{3+}$ (d) $Cr(H_2O)_6^{3+}$
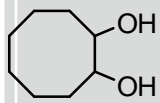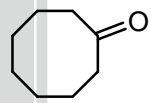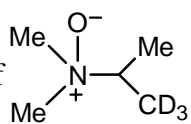
1.5. Which one of the following metal fragments, $d^n - ML_m$, is isolobal with CH?
     (a) $d^7 - ML_5$ (b) $d^8 - ML_4$ (c) $d^9 - ML_3$ (d) $d^5 - ML_6$

1.6. The softest acid amongst the following is:
     (a) Al^{3+} (b) Li^+ (c) Ca^{2+} (d) Ag^+

1.7. The chromium (III) species formed soon after electron transfer between $IrCl_6^{2-}$ and $Cr(H_2O)_6^{2+}$ is:
     (a) $Cr(H_2O)_6^{3+}$ (b) $Cr(H_2O)_5Cl^{2+}$ (c) $CrCl_6^{3-}$ (d) $Cr(H_2O)_3Cl_3$

1.8. The strongest reducing ion of the following is
     (a) U^{3+} (b) Am^{3+} (c) Cm^{3+} (d) Cf^{3+}

1.9. The first ionization potential of Mg, Al, P and S follows the order
     (a) Mg < Al < P < S   (b) Al < Mg < P < S   (c) Al < Mg < S < P   (d) Mg < Al < S < P

1.10. As per the uncertainty principle, $\Delta x \cdot \Delta p_y =$
     (a) h (b) $h/2\pi$ (c) λ (d) zero

1.11. The second lower state of particle in a cubic box is
     (a) non degenerate   (b) doubly degenerate   (c) triply degenerate   (d) six-fold degenerate

1.12. In comparision to the frequency of the EPR transition, the NMR transition frequency is
     (a) much higher   (b) much lower   (c) almost same   (d) none of these

1.13. The symmetry point group of the BF_3 molecule is:
     (a) C_{3v} (b) D_{3h} (c) C_{2v} (d) D_{2h}

1.14. For an irreversible adiabatic expansion of a perfect gas from volume V_i to V_f the change in entropy of the gas is:
     (a) $nR \ln(V_f/V_i)$ (b) Zero   (c) less than zero   (d) greater than zero

1.15. For the cell $Ag(s)|AgCl(satd)$, $NaCl(aq,m_1)|NaCl(aq,m_2)$, $AgCl(satd)|Ag(s)$ where m_1 and m_2 are different molalities $(m_1 > m_2)$, the standard cell potential is:
     (a) $-RT\ln(m_1/m_2)$ (b) Zero   (c) $-RT\ln(a_1/a_2)$ (d) $-FRT\ln(a_1)$

1.16. For an ideal dilute solution, which one of the following statements is correct ? (γ and x are activity coefficient and mole fraction respectively)

(a) $\gamma(\text{solvent}) \to 0$ as x $(\text{solvent}) \to 1$ (b) $\gamma(\text{solvent}) \to 1$ as x $(\text{solvent}) \to 1$

(c) $\gamma(\text{solvent}) \to 1$ as x $(\text{solvent}) \to 1$ (d) $\gamma(\text{solvent}) \to 0$ as x $(\text{solvent}) \to 1$

1.17. For the reaction: $Br_2(g) + BF_2(g) \to 2BrF_3(g)$, the equilibrium constant at 2000 K and 1.0 bar is 5.25.

When the pressure is increased by 8-fold, the equilibrium constant.
(a) Increase by a factor of 1.86   (b) Decreases by a factor of 1.86
(c) Remains same   (d) Increases by a factor of 8

1.18. 2-Phenyl ethanol may be prepared by the reaction of phenyl magnesium bromide with

(a) HCHO   (b) CH_3CHO (c) CH_3COCH_3 (d) ⌀

1.19. o-Chlorotoluene reacts with sodamide in liquid ammonia to give o-toluidine, and m-toluidine. This reaction proceeds through an intermediate

(a) [structure with CH$_3$]   (b) [structure with CH$_3$]   (c) [structure with CH$_3$]   (d) [structure with CH$_3$ and Cl]

1.20. The number of signals observed in ^{1}H NMR spectrum of 3, 5-dibromotoluene is:
(a) 3   (b) 4   (c) 2   (d) 6

1.21. Which one of the following molecules will have $n \to \pi^*$ transition at the longest wavelength ?

(a) HCHO   (b) $CH_3COC_2H_5$ (c) $C_6H_5COC_6H_5$ (d) $CH_3COC_6H_5$

1.22. The reaction of cyclooctyne with $HgSO_4$ in the presence of aqueous H_2SO_4 gives

(a) [cyclooctene with two OH]   (b) [cyclooctane with two OH]   (c) [cyclooctene]   (d) [cyclooctanone]

1.23. Pyrolysis of [structure: Me−N$^+$(Me)−O$^-$ with CH(Me)CD$_3$] would be

(a) A mixture of $CH_2=CH-CD_3$ and $CH_3-CH=CD_2$

(b) $CH_3-CH=CD_2$

(c) $Me_2N^+=C(CD)_3(CH_3)$

(d) $CH_2=CH-CD_3$

1.24. Amongst the following amino acids, the (R)-enantiomer is represented by

(a) H_2N—[CH$_3$/COOH/H]—COOH   (b) H—[COOH/CH$_3$]—NH$_2$ (c) H_3C—[NH$_2$/COOH]—H   (d) H_3C—[COOH/H]—NH$_2$
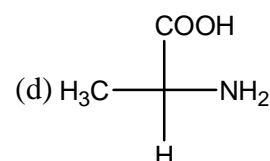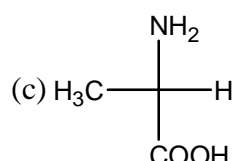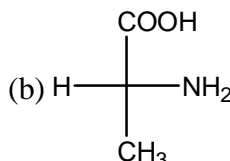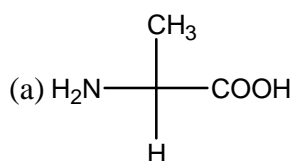
1.25. Arrange the following halides in the decreasing order of SN[1] reactivity

$$CH_3CH_2CH_2Cl, \qquad CH_2=CHCH(Cl)CH_3, \qquad CH_3CH_2CH(Cl)CH_3$$
$$\text{(I)} \qquad\qquad\qquad \text{(II)} \qquad\qquad\qquad \text{(III)}$$

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

2. *This question consists of TWENTY FIVE sub-questions (2.1 to 2.25) of ONE mark each. For each of these sub-questions, four possible answers (a, b, c and d) are given, out of which only one is correct.* **[25×2 = 50]**

2.1. The volume of 1 N $KMnO_4$ required to reach equivalence point in the titration with 0.01 mole of ferrous oxalate dissolved in dilute H_2SO_4 is

(a) $3\,cm^3$ (b) $30\,cm^3$ (c) $10\,cm^3$ (d) $20\,cm^3$

2.2. The number of signals observed in ^{1}H NMR spectrum of 3, 5-dibromotoluene is:

(a) 3   (b) 4   (c) 2   (d) 6

2.3. Among the following, the paramagnetic species among the following is:

(a) B_2 (b) C_2 (c) O_2^{2-} (d) CO

2.4. The purple colour of iodine vapours is due to

(a) d-d transition   (b) $\pi - \sigma*$ transition

(c) charge - transfer transition   (d) $\pi* - \sigma*$ transition

2.5. Amongst the following, the strongest oxidizing anion is:

(a) CrO_4^{2-} (b) VO_4^{3-} (c) FeO_4^{2-} (d) MnO_4^{2-}

2.6. ^{19}F NMR spectrum of meriodional isomer of octahedral $RhCl_3F_3$ complex, [^{103}Rh (I = ½); ^{19}F (I = ½) assuming $J_{Rh-F} > J_{F-F}$, will show

(a) one doublet   (b) two doublets and one triplet

(c) two doublets and two triplets   (d) one singlet and two triplets

2.7. Which one of the following will show closo structure ?

(a) B_5H_9 (b) $B_{12}H_{12}^{2-}$ (c) B_4H_{10} (d) B_5H_{11}

2.8. The correct order of energy level of d-orbitals in ferrocene is:

(a) $dx^2 - y^2, dxy < dz^2 < dxz, dyz$ (b) $dz^2 < dxz, dyz < dx^2 - y^2, dxy$

(c) $dx^2 - y^2, dxy < dxz, dyz < dz^2$ (d) $dyz, dxz < dx^2 - y^2, dxy < dz^2$

2.9. Two moles of a monoatomic perfect gas initially at 4.0 bar and 47°C undergoes reversible expansion in an insulated container. The temperature at which the pressure reduces to 3.0 bar is

(a) 200 K   (b) 285 K   (c) 310 K   (d) 320 K

2.10. The mean ionic activity coefficient of 0.0005 mol kg^{-1} $CaCl_2$ in water at 25°C is:

(a) 0.98   (b) 0.67   (c) 0.81   (d) 0.91

2.11. For the cell : $Cd(Hg)|CdSO_4(8/3)H_2O(s)|CdSO_4(aq, satd.)|Hg_2SO_4(s)|Hg$

The temperature dependence of emf in Volts is given by

$$B = 1.0185 - 4.05 \times 10^{-5}(T - 293) - 9.5 \times 10^{-7}(T - 293)^2$$

The change in entropy at 25°C for the cell reaction is

(a) $-253\,K^{-1}\,mol^{-1}$ (b) $9.65\,J\,K^{-1}\,mol^{-1}$

(c) $8.3 \times 10^{-4}\,J\,K^{-1}\,mol^{-1}$ (d) zero

2.12.   Two separate bulbs contain ideal gases A and B respectively. The density of gas A is twice that of gas B and molecular weight of gas A is half of that of gas B. The ratio of pressure of gas A to that of gas B is

(a) 3   (b) 6   (c) 4   (d) 1

2.13.   Choose the correct criterion of spontaneity in terms of the properties of the system alone.

(a) $(dS)_{U,V} > 0$ (b) $(dS)_{T,P} > 0$ (c) $(dS)_{H,P} < 0$ (d) $(dG)_{T,V} < 0$

2.14.   Compared to C_2H_6, the value of vander waal's constants 'a' and 'b' for He will be

(a) both will be smaller   (b) 'a' will be larger but 'b' will be smaller
(c) 'b' will be larger but 'a' will be smaller   (d) both will be larger

2.15.   The number of hyperfine components observed in the electronic transition $^2 p_{1/2} \rightarrow\ ^2 s_{1/2}$ of an atom with nuclear spin 1/2 is

(a) 3   (b) 4   (c) 6   (d) 5

2.16.   Given than, $\psi_{n,t,m}(r, \theta, \phi) = R_{nt}(r) Y_{tm}(\theta, \phi); R_{20}(r) \propto (2 - r/a_0) e^{-r/ao}, Y_{0,0}(\theta, \phi) = 1/\sqrt{4\pi}$

The position of radial node in the 2s orbital is at

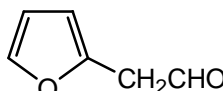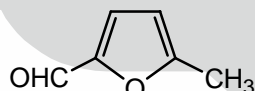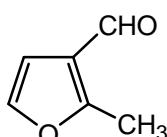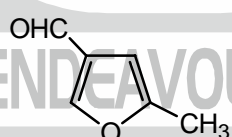(a) $r = a_0$ (b) $r = 2a_0$ (c) $r = a_o/2$ (d) $r = a_o/4$

2.17.   Consider the following reaction and use the data given below   **[GATE 2001]**

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta H^0(25°C) = -92.2 \text{ kJ}$$
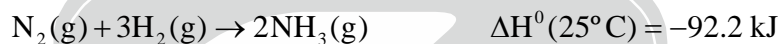
Substance	$N_2(g)$	$H_2(g)$	$NH_3(g)$
$C_P / (J\ K^{-1}\ mol^{-1})$	29.1	28.8	35.1

Assuming C_P to be independent of temperature, the reaction at 100°C compared to that at 25°C will be

(a) Endothermic   (b) Less exothermic   (c) More exothermic   (d) Having $\Delta H^0 = 0$

2.18.   The reaction of 2-methylfuran with DMF–POCl$_3$ would give

(a)   (b)

(c)   (d)

2.19.   The major product formed during the hydroboration-oxidation of 1-methyl cyclopentene is

(a)   (b)   (c)   (d)
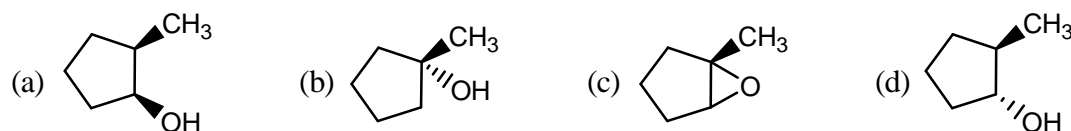
2.20.   Which one of the following carbonyl compounds will give a fragment ion at m/z = 58 in their mass spectra?

(a) $C_2H_5CH(CH_3)CHO$ (b) $CH_3CH_2CH_2CH_2CHO$

(c) $CH_3CH_2CH_2COCD_3$ (d) $(CH_3)_2CHCH_2CHO$

2.21.   The decreasing order of reactivity of meta-nitrobromobenzene (I); 2, 4, 6-trinitrobromobenzene (II); para-nitrobromobenzene (III); and 2, 4-dinitrobromobenzene (IV) towards OH^- ions is
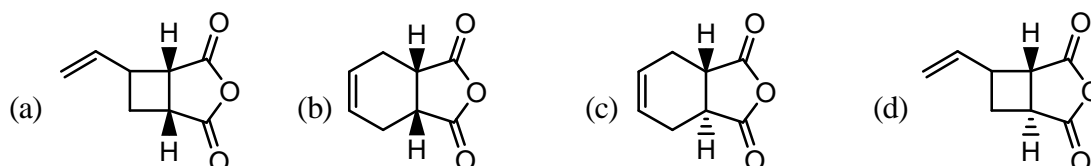
(a) I > II > III > IV   (b) II > IV > III > I   (c) IV > II > III > I   (d) II > IV > I > III

2.22.   Identify the isotactic polypropylene from the following

(a)

(b)

(c)

(d)
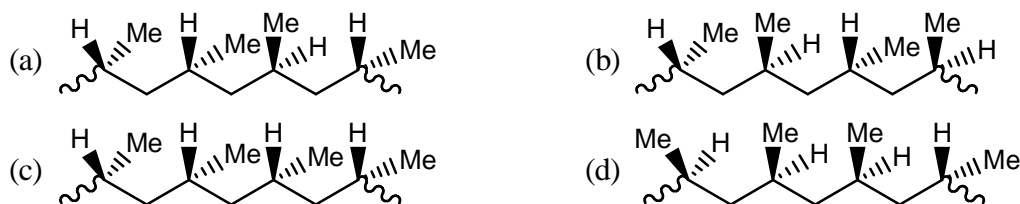
2.23.   Which one of the following compounds will form an osazone derivative?

(a) $CH_3CH_2COCH_2OH$

(b) $CH_3COCH_2CH_2OH$

(c) $CH_3CH_2CHOHCH_2OH$

(d) $CH_3CH_2COCH_2OCH_3$

2.24.   Buta-1, 3-diene on heating with maleic anhydride would give

(a)   (b)   (c)   (d)

2.25.   The product obtained during the following photochemical reaction is
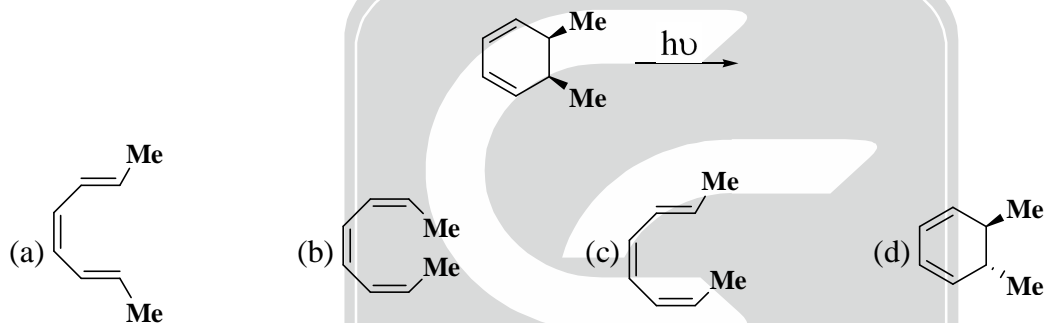

(a)   (b)   (c)   (d)

SECTION-B

This section consists of TWENTY questions of FIVE marks each. ANY FIFTEEN out of these questions have to answered on the Answer Book provided.   **[75 Marks]**

3.1.   There are two isomers of $Pi(NH_3)_2Cl_2$. X and Y. When X is reacted with thiourea(tu). $Pt(tu)_4^{2+}$ is formed while Y on reaction with thiourea yields $Pt(NH_3)_2(tu)_2$. Identify X and Y and explain the reaction.

3.2.   Ligand substitution reaction on metal clusters are often found to occur by associative mechanism by breaking of a M-M bond and thereby providing an open coordination site for the incoming ligand. Which one of the two clusters, $Co_4(CO)_{12}$ of $Ir_4(CO)_{12}$ is expected to undergo faster exchange with ^{13}CO ? Suggest an explanation.

4.1.   Using crystal-field theory, account for the fact that in square - pyramidal $[Ni(CN)_5]^{3-}$ ion, the axial $Ni—C$ bond (217 pm) is longer than $Ni—C$ basal bonds (187 pm), while in trigonal bipyramidal $[CuCl_5]^{3-}$ ion, the axial $Cu–Cl$ bonds (229 pm) are shorter than the $Cu–Cl$ equatorial ones (239 pm).

4.2.   Between complexes $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_3)_5Br]^{2+}$ which one should have a lower energy charge-transfer band and why?

5.   Write the Russell-Saunders terms of the configuration p^1d^1 and identify the ground term. Indicate population of electrons in different d-orbitals corresponding to $^3T_{1g}$ (F), $^3T_{2g}$ (F) and $^3A_{2g}$ (F) states for d^2 configuration in octahedral symmetry.

6.1.   Propose the structure of compounds A, B and C satisfying EAN rule in the following reactions:

$$Fe(CO)_5 + \pentagon \xrightarrow{-nCO} (A) \xrightarrow{-CO} (B) \xrightarrow[\text{dimerisation}]{-H \text{ and}} (C)$$
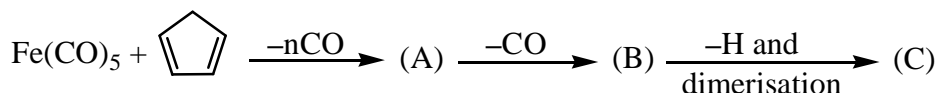
6.2.   Explain why 16- or 14-electron configurations are favoured over 18-electron configurations for the elements at the end of the transition series ?

7.1.   Calculate spin-orbit coupling parameter (λ), for an octahedral nickel (II) complex exhibiting spin allowed d-d bands at 10,750 cm^{-1}, 17,500 cm^{-1} and 28,200 cm^{-1} respectively. The experimentally determined magnetic moment is 3.2 BM.

7.2.   Explain why pKa of $(CH_3)_3SiOH(pKa \approx 11)$ is lower than that of $(CH_3)_3COH(pKa \approx 16)$.

8.1.   Define capacity factor. What is the effect of large capacity factor on the separation of analytes? How can capacity factors be optimized in gas chromatography?

8.2.   What prevents simple iron porphyrins from functioning as O_2 carriers like haemoglobin?

9.   Identify all the symmetry operations for HCHO with rotation axis as the z-axis and plane of the molecule being the yz plane. will the transition from an a_1 to b_1 orbital be allowed in HCHO? What will be the polarization of the corresponding $b_1 \rightarrow a_1$ emission?

10.1.   Using quantization condition for de Broglie wavelength on a ring, derive the expression for rotational energy levels of a rigid homonuclear diatomic rotor of bond length 2r.

10.2.   Given $\psi_n(x) = (2)^{1/2} \sin(n\pi x)$, show that eigen functions $\psi_1(x)$ and $\psi_2(x)$ of a particle in a one dimensional box of length 1 are orthogonal.

11.   The emf of the cell

    $Ag(s) | AgCl(satd), KCl(0.05 \text{ mol dm}^{-3}) | AgNO_3(0.1 \text{ mol dm}^{-3}) | Ag(s)$

    is 0.431 v at 298.15 K. The mean activity coefficient of KCl is 0.817 and that of $AgNO_3$ is 0.723. Calculate the solubility product of AgCl at 25ºC.

12.1.   A paramagnetic substance $(A_2B_3 - 5H_2O)$ initially at T = 0.30 K was magnetized by application of strong magnetic field while the sample was surrounded by helium gas in contact with a cold reservoir. Subsequently, helium gas was pumped away and the magnetic field was slowly reduced to zero. Calculate the change in temperature of the sample using the data given below :

Unmagnetized sample		Magnetized sample	
T/K	S/(J K^{-1} mol^{-1})	T/K	S/(J K^{-1} mol^{-1})
0.30	0.40	0.30	0.19
0.25	0.32	0.25	0.15
0.18	0.19	0.20	0.12
0.15	0.14	0.15	0.10

12.2. When 2 moles of liquid A and 4 moles of liquid B are mixed, experimental measurements give entropy of mixing as 42 J K^{-1}. Show whether the solution AB thus formed is ideal or not.

13.1. The LCAOs : $\phi_1 = \left(1_{sA} + 1_{sB}\right)$ and $\phi_2 = \left(1_{sA} - 1_{sB}\right)$ approximate the lowest σ and $\sigma*$ orbitals of H_2^+ respectively. Show that the σLCAO is of g-type and $\sigma*$ of u type. [1_{s_A} and 1_{s_B} are the 1s orbitals centered on H_A and H_B of $(H_A - H_B)^+$].

13.2. The fundamental vibrational frequency of HCl is 2885 cm^{-1}. Assuming that HCl and DCl may be treated as Simple Harmonic Oscillator, calculate the fundamental frequency of DCl.

14.1. The conversion of A to B and C goes through the following mechanism

$$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 1 \underset{k_4}{\overset{k_2}{\rightleftharpoons}} B + C$$
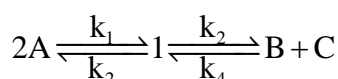
Show that the equilibrium constant (K) of the overall reaction is

$$K = \frac{k_1 k_3}{k_2 k_4}$$

14.2. The rate of the acid catalyzed hydrolysis of ethylacetate in HCl solution obeys the following rate law
$$\text{Rate} = -d[\text{ester}]/dt = k[\text{ester}][\text{HCl}]$$
where $k = 0.1 \text{ mol}^{-1} \text{ dm}^{-3} \text{ h}^{-1}$. Neglecting any back reaction, calculate the time required for half the ester to be hydrolyzed if the initial concentration of ester and HCl are 0.02 mol dm^{-3} and 0.01 mol dm^{-3} respectively.

15.1. Using the data given below, calculate the equilibrium constant and enthalpy of the following reaction at 25°C.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Substance	$\Delta G_f^0 /(\text{kJ mol}^{-1})$	$S^0 /(\text{J K}^{-1} \text{ mol}^{-1})$
$NO_2(g)$	51.31	240.06
$N_2O_4(g)$	97.89	304.29

15.2. When 1.0 mol of $CH_4(g)$ is oxidized to carbon dioxide and water according to the reaction

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

the corresponding thermodynamic parameters are : $\Delta H° = -890 \text{ kJ mol}^{-1}$, and $\Delta S° = -140.3 \text{ JK}^{-1} \text{ mol}^{-1}$. Assuming ideal gas behaviour, calculate the amount of energy that can be extracted as work at 25°C.

16. Acid catalyzed dehydration of a tertiary alcohol $A(C_6H_{14}O)$ gives one major compound B, and one minor compound C both having molecular formula C_6H_{12}. Spectroscopic data of these compounds are as follows:

Compound B : IR : 　　　　1660 cm^{-1}, 3080 cm^{-1}

　　　　^{1}H NMR δ : 0.91(t, J = 7 Hz, 3H), 1.60 (s, 3H). 1.70 (s, 3H), 1.98 (quin, J = 7 Hz, 2H), 5.08 (t, J = 7 Hz, 1H)

Compound C : IR ; 　　　　1640 cm^{-1}, 3090 cm^{-1}

　　　　^{1}H NMR δ : 0.92 (t, J = 7 Hz, 3H), 1.40 (sextet, J = 7Hz, 2H), 1.74 (s, 3H), 2.02 (t, J = 7Hz, 2H), 4.78 (s, 2H)

Deduce the structure of A, B and C.

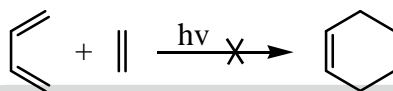17.1. Suggest a plausible mechanism for the following reaction
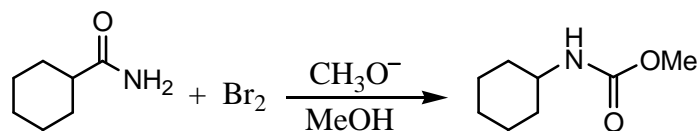
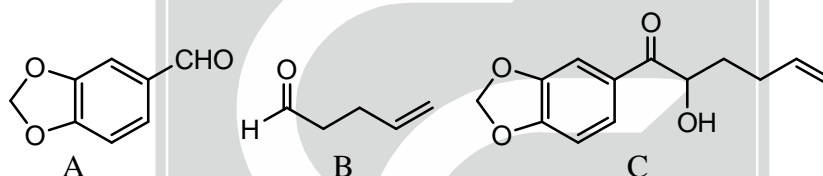17.2. Propose a mechanism for the photochemical reaction given below.
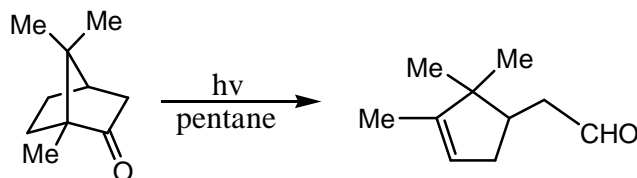
18.1. Draw π orbitals of buta-1, 3-diene and ethylene, and identify their HOMO and LUMO.

18.2. Using "frontier orbital concept", explain why the $\pi^{4s} + \pi^{2s}$ cycloaddition given below is photochemically not allowed?

19.1. Suggest a synthetic route to the hydroxy-ketone C using A and B starting materials.
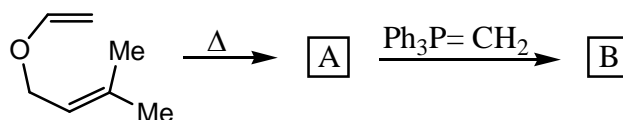

19.2. The reaction of dimethyl fulvene D with PhLi readily gives the anion E. However, the analogous compound F does not react with PhLi to give the corresponding anion G. Explain.
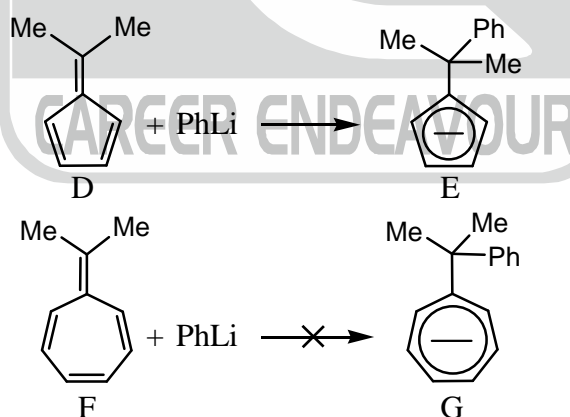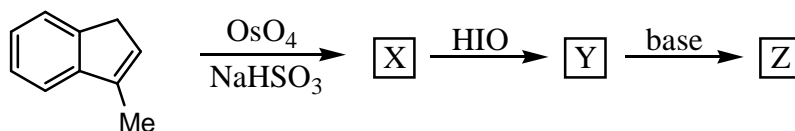

20.1. Outline a synthesis of para-nitropropylbenzene from benzene.

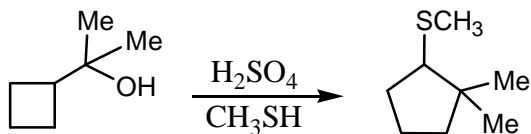20.2. Predict the products in the following reactions.

21.1. Write the structure of the products X, Y and Z in the following sequence of reactions.
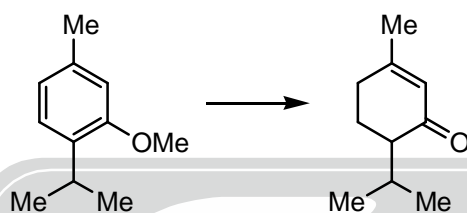

21.2. D-Glucose and D-fructose interconvert into each other in aqueous alkaline solution. Suggest a mechanism for the interconversion.
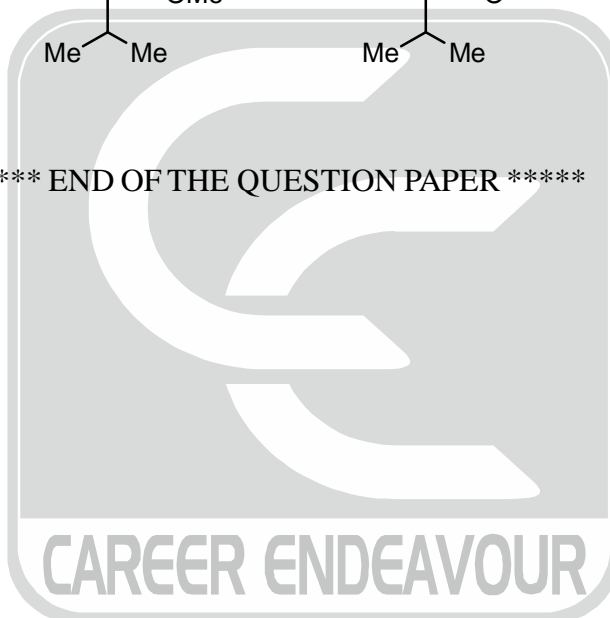
22.1. Propose a mechanism of the following reaction.

22.2. Suggest a route for synthesis of the enone B from A.

***** END OF THE QUESTION PAPER *****

SECTION-A

1. *This question consists of TWENTY FIVE sub-questions (1.1 to 1.25) of ONE mark each. For each of these sub-questions, four possible answers (a, b, c and d) are given, out of which only one is correct.*   **[25×1 = 25]**

1.1. The ground state of aluminium atom is

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

1.2. The point group symmetry of the free nitrate ion is:

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

1.3. The total number of vibrational degrees of freedom of H_2O_2 is

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

1.4. 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

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

     (a) $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl\,(s)$ (b) $Ag(s) + 1/2Cl_2(g) \rightarrow AgCl(s)$

     (c) $AgCl \rightarrow Ag(s) + 1/2Cl_2(g)$ (d) $Ag(s) + AuCl \rightarrow Au(s) + AgCl(s)$

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

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

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

1.7. 0.1 M 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) $Al_2(SO_4)_3$

1.8. 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

1.9. 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

1.10. 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

1.11. The complex which obeys the 18 electron rule is
   (a) $Fe(CO)_4$ (b) $Ni(CO)_3(PPh_3)$ (c) $Cr(CO)_5$ (d) $Cr(C_5H_5)_2$

1.12. 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) $Cu(OH)(CO_3)$ (c) $Cu(HCO_3)_2$ (d) $Cu(OH)_2$

1.13. The complex formed in the brown ring test for nitrates is:

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

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

1.14. 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

1.15. The species which has a square planar structure is

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

1.16. 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) SN_1 mechanism (d) outer sphere electron transfer.

1.17. 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

1.18. 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.

1.19. 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

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

(a) benzyl alcohol and benzoic acid (b) benzyl methyl ether and 2-phenylpropan-2-ol
(c) benzyl alcohol and 2-phenylpropan-2-ol (d) ethyl benzene and benzoic acid

1.21. Benzaldehyde can be prepared by reacting phenylmagnesium bromide with

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

1.22. Proteins are biopolymers. The monomer units present in them are

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

1.23. Among the bromides I-III given below, the order of their reactivity in the S_N^1 reaction is:
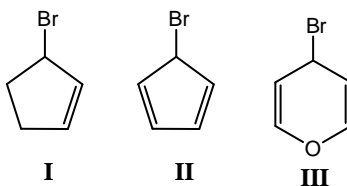
(a) III > II > I (b) II > III > I (c) III > I > II (d) II > I > III

1.24. 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) orth- and para-hydroxyacetophenones

1.25. The major product formed in the reaction of anisole with lithium, 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

2. *This question consists of TWENTY FIVE sub-questions (2.1 to 2.25) of ONE mark each. For each of these sub-questions, four possible answers (a, b, c and d) are given, out of which only one is correct.* **[25×2 = 50]**

2.1. 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

2.2. The spacing between the rotational lines of the is 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}.

2.3. 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^{-1}. The rate coefficient increases approximately by a factor of
(a) 500   (b) 1000   (c) 2000   (d) 50

2.4. 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) 1/2

2.5. The force between two electrons separated by 0.1 nm in vacuum $\left(\varepsilon_0 = 8.854 \times 10^{-12} \ J^{-2} \ C^{-2} \ m^{-1} \right)$ is
(a) 2.31×10^{-8} N   (b) -2.31×10^{-8} N   (c) -1.15×10^{-8} N   (d) 1.155×10^{-8} N

2.6. Assmuing 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}

2.7. 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) $t_{1/2} \propto T^2$

2.8. The ionization constant of formic acid, which ionizes to an extent of 4.2%, in 0.1 M aqueous solution is
(a) 0.92×10^{-2} (b) 1.84×10^{-2} (c) 1.84×10^{-4} (d) 0.92×10^{-4}

2.9. Radiation of 10^{14} Hz falls in the region of
(a) Radiofrequency   (b) Microwave   (c) Visible   (d) X-rays

2.10. 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) $N_2^- > N_2 > O_2^- > O_2$

2.11. 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) $a/2\sqrt{2}$

2.12. The metals involved in nitrogenase are
(a) Fe and Mg   (b) Mo and K   (c) Mo and Fe   (d) Fe and K.

2.13. 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

2.14. 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) $Cr(H_2O)_6^{3+} < Cr(en)_3^{3+} < CrCl_6^{3-} < Cr(CN)_6^{3-}$

2.15. 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

2.16. 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.

2.17. 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) $V^{2+} > Cr^{2+} > Mn^{2+}$

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

(a)   (b)   (c)   (d)
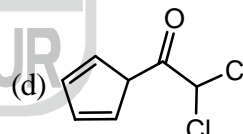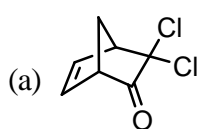
2.19. The configurations at the three chiral centres in the bicyclodecanol given below, are
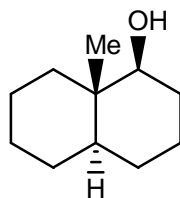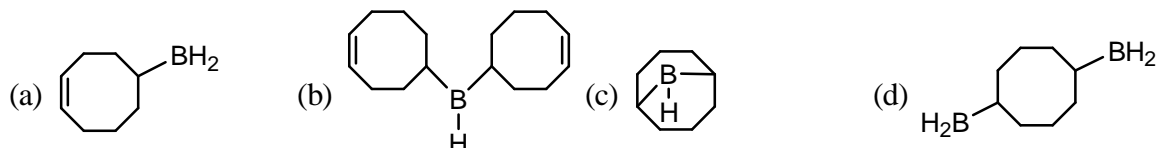
(a) 1S, 2S, 6R   (b) 1S, 2S, 6S   (c) 1R, 2S, 6R   (d) 1R, 2S, 6R

2.20. 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)
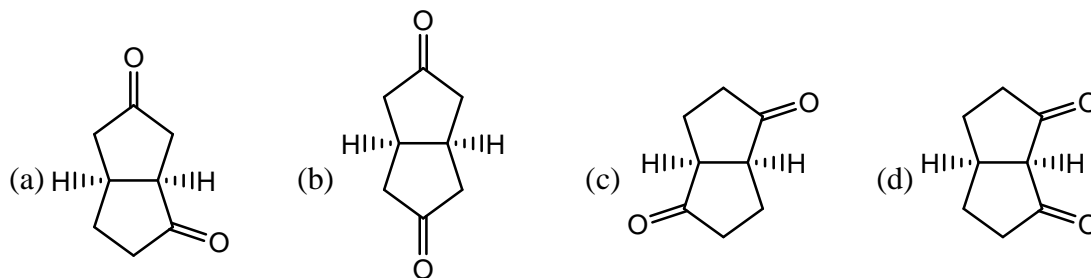
2.21. The major product formed in the reaction of 1, 5-cyclooctadiene with 0.5 equivalent of diborane is

(a)   (b)   (c)   (d)

2.22. The two pericyclic reactions successively involved in the thermal transformation given below are
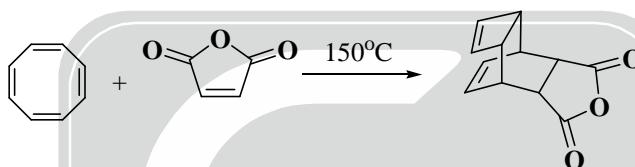
(a) 6π-electrocyclization followed by $[4+2]$ π-cycloaddition
(b) 8π-cycloaddition followed by $[2+2]$ π-electrocyclization
(c) 6π-cycloaddition followed by $[2+2]$ π-electrocyclization
(d) 4π-electrocyclization followed by $[4+2]$ π-cycloaddition.

2.23. 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)
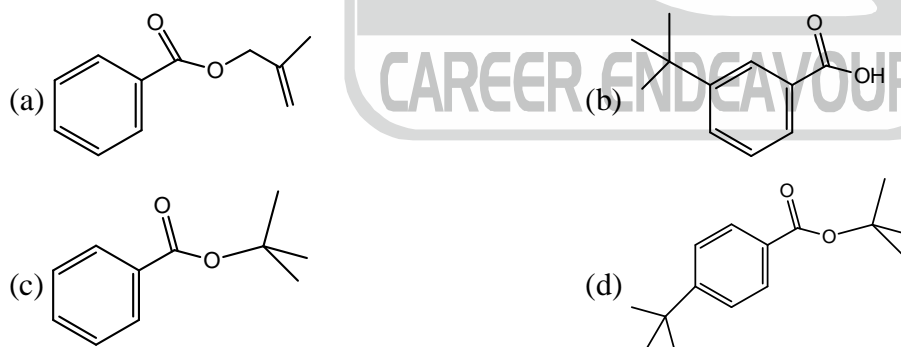
2.24. The major product formed in the reaction of the oxime given below with sulfuric acid is

(a)   (b)   (c)   (d)
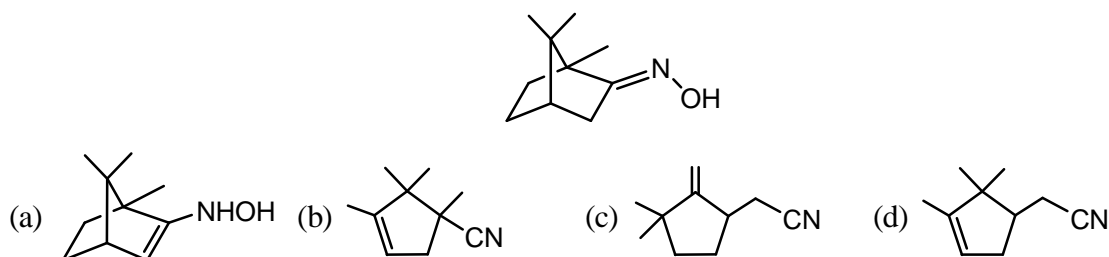
2.25.   The major product formed in the thermal reaction given below, is

$$\xrightarrow{\ 180^{0}C\ } \ ?$$
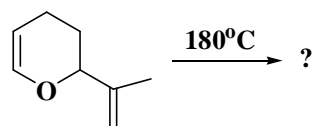
(a) $4(H)-$Furan   (b)   (c)   (d)

SECTION-B

This section consists of TWENTY questions of FIVE marks each. ANY FIFTEEN out of these questions have to answered on the Answer Book provided.   **[75 Marks]**

3.   For the reaction, trans-$PtL_2Cl_2 + Y \rightarrow$ trans-$PtL_2ClY + Cl^-$ the rate constant K varies as follows:

	Y	L	$K\left(10^3\ M^{-1}\ S^{-1}\right)$
(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.

4.1.   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 10 s.

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

4.3.   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

5.   Write down the products formed in each of the following reactions.

5.1. $P_2S_5 + PCl_5 \longrightarrow$

5.2. $S + NH_3$ (liquid) $\rightleftharpoons$

5.3. $NaBH_4 + I_2 \longrightarrow$

5.4. $XeO_3 + OH^- \rightleftharpoons$

5.5. $SiO_2 + HF$ (aq) $\longrightarrow$

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

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

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

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

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

8.1. Give the structures of

(a) H_3CPF_4 and

(b) XeO_2F_2

8.2. 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?

8.3. 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 ?

9.1. 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 and 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.

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

10.1. Calculate the vapour pressure of toluence at 100ºC assuming that Trouton's rule is obeyed. The boiling point of toluene is 110ºC.

10.2. The vapour pressure of ethanol at 20ºC 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 weigth of A.

11.1. 0.1 M $CuSO_4$ solution is electrolyzed employing Cu electrodes using a current of 10 A for 1 h. Calculate the weight of Cu deposited.

11.2. 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?

12.1. 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.

12.2. Give the symmetry operation equivalent to

(i) C_4^6 (ii) S_4^2

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

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

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.

14.1. 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.

14.2. The 1s wavefunction for the hydrogen atom is

$$R_{1s}(r) = (1/\sqrt{\pi})\,(1/a_0)^{3/2}\,\exp(-r/a_0)$$

Calculate the probability that the electron will be found within the first Bohr radius.

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

15.2. The root mean square velocity of O_2 molecules is 575 m s^{-1}. Find out the temperature of O_2 gas.

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

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

17.1. Identify the structure of the major product formed in the following reaction, and give a mechanism of its formation.
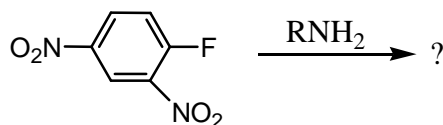
17.2. Give a suitable mechanism for the following transformation.
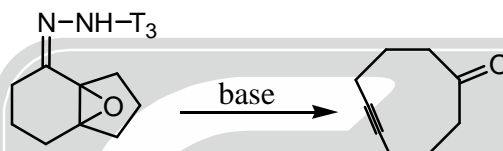
18.1. Identify the products/reagents (A-C) in the following sequence.
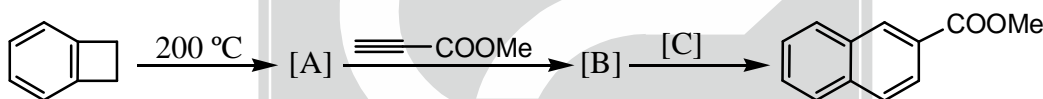
18.2. Write structures of the products formed in the following reaction.
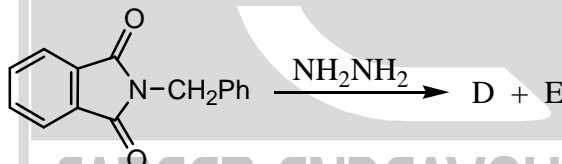
19.1. Write the conformational structures of the two cyclic isomers of glucose which are responsible for the phenomenon of mutarotation.

19.2. The optically active compound given was found to racemise on heating in a microwave oven. Give a suitable explanation.
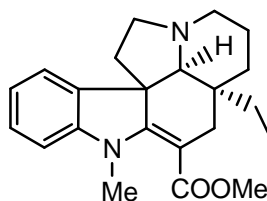
20. Suggest suitable reagents to bring about the following transformations (may require more than one step).

   (i) PhBr $\xrightarrow{?}$ PhD

       PhBr $\xrightarrow{?}$ PhD

   (ii) $\xrightarrow{?}$

   (iii) MeO— $\xrightarrow{?}$ MeO—

   (iv) $\xrightarrow{?}$

   (v) $\xrightarrow{?}$ —OH
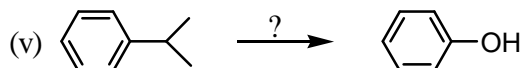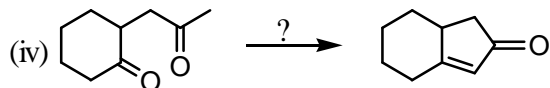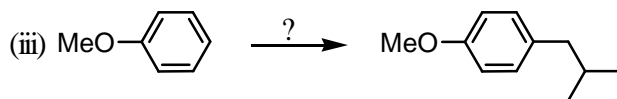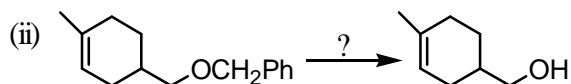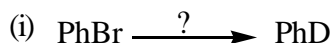
21.1. Among the two hydroxyesters given below, which one will readily lactonise on treatment with a mild base. Write the structure of the product and justify your answer briefly.
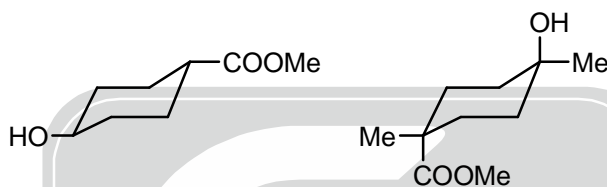
21.2. Identify the reactive intermediate involved in the reaction of furan with a mixture of HNO_3 and H_2SO_4. Write the mechanism and the structure of the final product.

22. 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 δ 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.

***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.30 : Carry ONE mark each.

1. Adiabatic reversible expansion of a monoatomic gas (M) and a diatomic gas (D) at an initial temperature T_i, has been carried out independently from initial volume V_1 to final volume V_2. The final temperature (T_M for monoatomic and T_D for diatomic) attained will be

    (a) $T_M = T_D > T_i$ (b) $T_M < T_D < T_i$ (c) $T_M > T_D > T_i$ (d) $T_D < T_M < T_i$

2. The rate of evaporation of a liquid is always faster at a higher temperature because
    (a) The enthalpy of vaporisation is always endothermic
    (b) The enthalpy of vaporisation is always exothermic
    (c) The enthalpy of vaporisation is zero
    (d) The internal pressure of the liquid is less than that of the gas.

3. The internal pressure of a vander waals gas is:
    (a) Independent of the molar volume   (b) Inversely proportional to the molar volume
    (c) Inversely proportional to square of the molar volume   (d) Directly proportional to the molar volume.

4. In a consecutive first order reaction, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

    (where k_1 and k_2 are the respective rate constants) species B has transient existence. Therefore,

    (a) $k_1 \approx k_2$ (b) $k_1 = 2k_2$ (c) $k_1 \gg k_2$ (d) $k_1 \ll k_2$

5. For a free radical polymerisation reaction, the kinetic chain length 'γ', is defined as the ratio

    (a) $\dfrac{\text{propagation rate}}{\text{initiation rate}}$ (b) $\dfrac{\text{initiation rate}}{\text{propagation rate}}$ (c) $\dfrac{\text{initiation rate}}{\text{termination rate}}$ (d) $\dfrac{\text{propagation rate}}{\text{termination rate}}$

6. The reaction that proceeds autocatalytically is
    (a) an oscillatory reaction   (b) hydrolysis of an ester by a mineral acid
    (c) the synthesis of ammonia (Haber's process) (d) Ziegler-Natta polymerisation

7. An example for an ion-selective electrode is
    (a) quinhydrone electrode   (b) hydrogen electrode
    (c) glass electrode   (d) dropping mercury electrode

8. The following equilibrium is established for an aqueous acetic acid solution
    $$CH_3COOH \rightleftharpoons CH_3COO^- OH^+ \uparrow$$
    Upon addition of 1.0 g of solid sodium chloride to 20 ml of IN solution of acetic acid,
    (a) the pH of the solution does not change   (b) the pH of the solution decreases
    (c) the pH of the solution increases   (d) the pH of the solution is 7

9. According to MO theory, for the atomic species 'C_2'
    (a) bond order is zero and it is paramagnetic   (b) bond order is zero and it is diamagnetic
    (c) bond order is two and it is paramagnetic   (d) bond order is two and it is diamagnetic

10. The sensitivity of a 600 MHz NMR spectrometer is more than that of a 60 MHz spectrometer because
    (a) Population of spin states is directly proportional to the applied magnetic field.
    (b) Population of spin states is inversely proportional to the applied magnetic field
    (c) According to the Boltzmann distribution law, the excess population in the lower spin state increases with increasing applied magnetic field.
    (d) The spectral scan width is more for a 600 MHz spectrum compared to a 60 MHz spectrum.

11. The magnetic moment of an octahedral Co (II) complex is $4.0\ \mu_\beta$. The electronic configuration of the complex is:

    (a) $t_{2g}^5\ e_8^2$ (b) $t_{2g}^6\ e_g^1$ (c) $t_{2g}^3\ e_g^4$ (d) $t_{2g}^4\ e_g^{-3}$

12. The square planar complex, $\left[IrCl(PPh_3)_3\right]$ undergoes oxidative addition of Cl_2 to give two products, which are

    (a) fac–and mer–isomers   (b) cis–and trans–isomers

    (c) linkage isomers   (d) enantiomers

13. The ligand field bands of lanthanide complexes are generally sharper than those of transition metal complexes because

    (a) transitions are allowed for lanthanide complexes

    (b) intensity of the bands are higher for lanthanide complexes

    (c) f–orbitals have higher energy than d–orbitals

    (d) f–orbitals, compared to d–orbitals, interact less effectively with ligands

14. Nature has chosen Zn(II) ion at the active site of many hydrolytic enzymes because

    (a) Zn(II) is poor Lewis acid

    (b) Zn(II) does not have chemically accessible redox states

    (c) Zn (II) forms both four and higher coordination complexes

    (d) Zn (II) forms weak complexes with oxygen donor ligands.

15. $BH_3\bullet CO$ is more stable than $BF_3.CO$ because

    (a) CO is a soft base and BH_3 and BF_3 are soft and hard acids respectively.

    (b) CO is a hard base and BH_3 and BF_3 are hard and soft acids respectively.

    (c) CO is a soft base and BH_3 and BF_3 are hard and soft acids respectively.

    (d) CO is a soft acid and BH_3 and BF_3 are soft and hard bases respectively.

16. Using chlorobenzene as solvent, the reagents needed for an efficient synthesis of borazine are

    (a) NH_4Cl and BCl_3 (b) NH_4Cl, BCl_3 and $NaBH_4$

    (c) NH_4Cl and $NaBH_4$ (d) NH_3 and BCl_3

17. The crystal systems having the highest and the lowest symmetries respectively, are

    (a) cubic and rhombohedral   (b) cubic and triclinic

    (c) rhombohedral and monoclinic   (d) cubic and monoclinic

18. The dark purple colour of $KMnO_4$ is due to

    (a) d-d transition   (b) ligand field transition

    (c) charge transfer transition   (d) $\sigma - \pi^*$ transition

19. The metallic character of beryllium is due to

    (a) partially filled 2s band   (b) completely filled 2s band

    (c) overlap of 2s and 2p bands   (d) empty 2p band

20. The values of CO stretching frequencies of (1) $Ni(CO)_4$, (2) $Ni(CO)_3(PMe_3)$ and (3) $Ni(CO)_2(PMe_3)_2$ follow the trend.

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

21. The products formed in the following reaction are

(a) [structure] + DMSO   (b) [structure] + $CH_3SO_2CH_3$

(c) [structure] + DMSO   (d) [structure] + DMSO
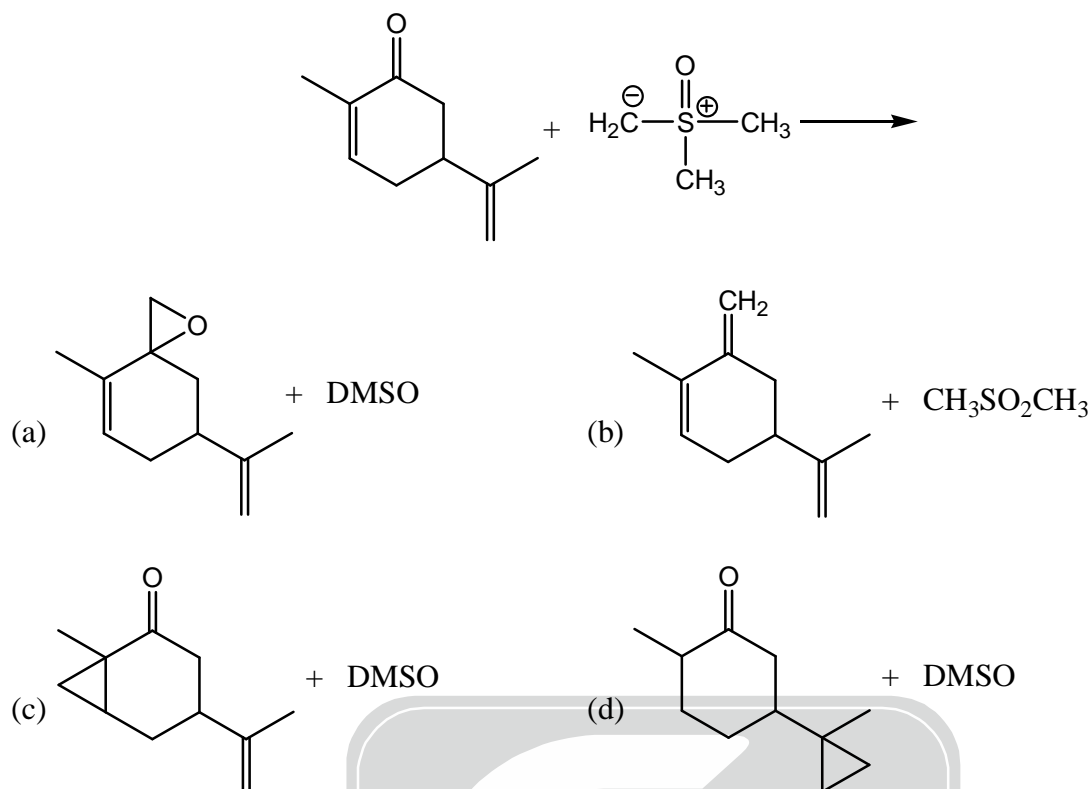
22. The acyl anion equivalents, among the following compounds (P–S), are

(P) [structure]   (Q) [structure]   (R) [structure]   (d) [structure]

(a) P and Q   (b) Q and R   (c) P and S   (d) Q and S

23. ^{1}H–NMR spectrum of a compound with molecular formula $C_4H_9NO_2$ shows δ 5.30 (broad, 1H), 4.10 (q, 2H), 2.80 (d,3H), 1.20 (t, 3H) ppm. The structures of the compound that is consistent with the above data is:

(a) $CH_3NHCOOCH_2CH_3$ (b) $CH_3CH_2NHCOOCH_3$

(c) $CH_3OCH_2CONHCH_3$ (d) $CH_3CH_2OCH_2CONH_2$

24. Among the following compounds, the one that undergoes deprotonation most readily in the presence of a base, to form a carbanion is:

(a) [structure]   (b) MeO [structure] OMe   (c) MeO [structure]   (d) [structure]
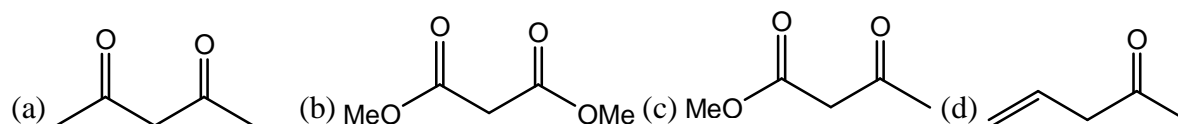
25. The structure of the product formed in the reaction given below is

(a) [structure]   (b) [structure]   (c) [structure]   (d) [structure]
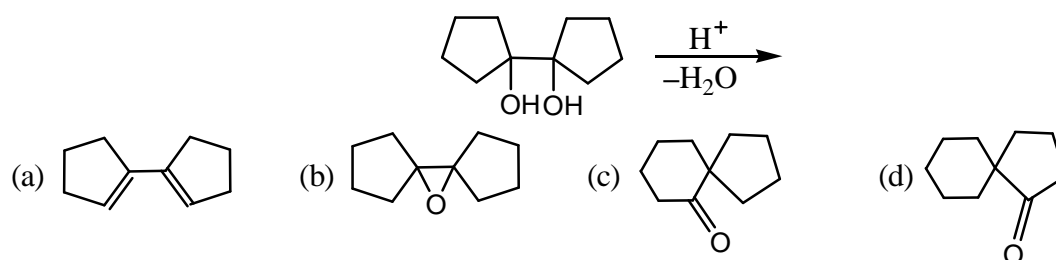
26. Hydroboration of 1-methylcyclopentene using B_2D_6, followed by treatment will alkaline hydrogen peroxide, gives

    (a) [structure: cyclopentane with Me, D (wedge up), OH, H]

    (b) [structure: cyclopentane with Me, D, OH, OH]

    (c) [structure: cyclopentane with Me, D, OH, H]

    (d) [structure: cyclopentane with Me, OH, H, OH]
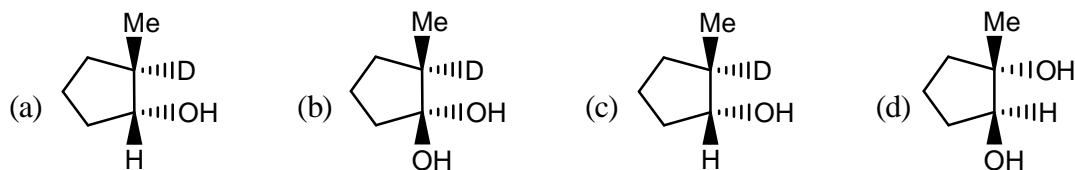
27. The enolate ion that reacts with 3-buten-2-one to form (Y) is

    [structure of bicyclic diketone Y]

    (a) [structure: cyclohexanone with 2-methyl, anion]

    (b) [structure: cyclohexanone with 3-methyl, anion]

    (c) [structure: cyclohexane-1,3-dione with methyl, anion]

    (d) [structure: cyclohexane-1,3-dione with methyl, anion]
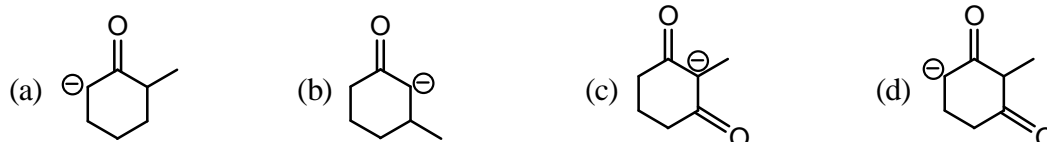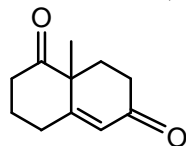
28. Electrocyclization of E, Z, E-octa-2, 4, 6-triene under photochemical condition,
    (a) trans-5, 6-dimethylcyclohexa=1, 3-diene
    (b) cis-5, 6-dimethylcyclohexa-1, 3-diene
    (c) a mixture of trans-and cis-5, 6-dimethylcyclohexa-1, 3-diene
    (d) 1, 2-dimethylcyclohexa-1, 3-diene

29. The absolute configurations of the two chiral centers in the following molecule are

    [Fischer projection:
    1 COOH
    H—2—Br
    H—3—CN
    OH]
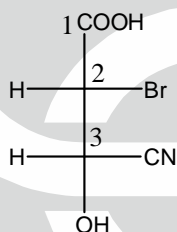
    (a) 2(R), 3(S)   (b) 2(R), 3(R)   (c) 2(S), 3(S)   (d) 2(S), 3(R)

30. A pyridine derivative (P) reacts with (Y). (Y) can be a free radical, cation or anion. The structure of intermediate (Q) formed in the reaction is given below. (P) and (Y) respectively, are

    [structure of Q: 4-substituted pyridine N-oxide with H and Y at position 4]

    (a) [pyridine N-oxide with $\ominus$] + Y•

    (b) [pyridine with :OH⁻] + Y•

    (c) [pyridine N-oxide] + $\overset{\ominus}{Y}$

    (d) [pyridine N-oxide] + $\overset{\oplus}{Y}$
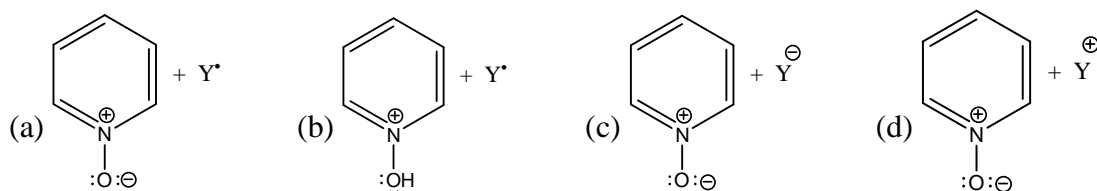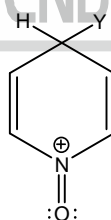
Q.31 – Q.90 : Carry TWO marks each.

Q. 31–36 are "Matching" exercises. choose the correct one from the alternatives A, B, C and D.

31. **Column-I**   **Column-II**

P. $ZnSO_4(aq) + K_4\big[Fe(CN)_6\big][aq] \rightarrow Products$ 1. Enzymatic reaction

Q. $Zn(s) + CuSO_4(aq) \rightarrow Products$ 2. Chain reaction

R. $H_2 + Cl_2 \xrightarrow{\Delta} Products$ 3. Redox reaction
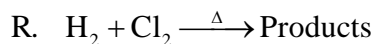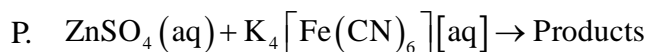
S.   Fischer-Tropsch synthesis of hydrocarbons   4. Precipitation reaction

                                                                      5. Surface reaction

                                                                      6. Hydrolysis reaction

(a) P-2, Q-4, R-5, S-6   (b) P-1, Q-3, R-2, S-4

(c) P-4, Q-3, R-2, S-5   (d) P-1, Q-6, R-2, S-5

32. **Column-I**   **Column-II**

P.   Supporting electrolyte   1. Overpotential

Q. $Zn(Hg)_{Q=1} \mid ZnCl_2(aq) \mid Zn(Hg)_{Q=2}$ 2. Residual current

R.   Inversion temperature   3. Electrolyte concentration cell

S.   Entropy of vapourisation   4. Electrode concentration cell

                                                                      5. Trouton's rule

                                                                      6. Joule-Thomson expansion

(a) P-2, Q-4, R-6, S-5   (b) P-2, Q-4, R-3, S-6

(c) P-1, Q-4, R-6, S-3   (d) P-1, Q-3, R-6, S-6

33. **Column-I**   **Column-II**

P.   Kroenecker delta   1. Electronic transition

Q.   Franck-Condon principle   2. Isothermal process

R.   Kirchoff's equation   3. Orthonormal set

S.   Glass transition temperature   4. Reaction enthalpy

                                                                      5. Turnover number

                                                                      6. Polymer

(a) P-1, Q-3, R-5, S-6   (b) P-3, Q-1, R-4, S-6

(c) P-1, Q-3, R-5, S-2   (d) P-3, Q-1, R-6, S-2

34. Matching exercises. Choose the correct one from the alternatives A, B, C and D.

   Column-I   **Column-II**

   P : Liver alcohol dehydrogenase   1. Cu at the active site

   Q : Cytochrome C oxidase   2. Fe and Cu at the active site

   R : Hemocyanin   3. Zn at the active site

   S : Myoglobin   4. Fe at the active site

                                                 5. Mo at the active site

                                                 6. Cu and Zn at the active site.

(a) P -6, Q-2, R-1, S-4   (b) P-3, Q-2, R-1, S-4

(c) P-3, Q-2, R-4, S-5   (d) P-5, Q-6, R-1, S-2

35. **Column-I**   **Column-II**

(P) $(PPh_3)_3\,RhCl$ (1) Friedel-Crafts catalyst

(Q) $\left[Rh(CO)_2\,I_2\right]$ (2) Hydroformylation of alkenes

(R) $\left[PdCl_4\right]^2$ (3) Hydrogenation catalyst

(S) $\left[HCo(CO)_4\right]$ (4) The Wacker process

                                            (5) Monsanto catalyst for acetic acid

                                            (6) Reppe catalyst

(a) P-3, Q-5, R-4, S-2   (b) P-4, Q-1, R-6, S-2

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

36. **List-I**   **List-II**

P. $\left[Cr(H_2O)_6\right]^{3+}$ 1. C_{3v}

Q. $Fe_2(CO)_9$ 2. D_{3h}

R. Eclipsed ferrocene   3. O_h

                                            4. D_{3d}

                                            5. D_{5h}

                                            6. D_{4d}

(a) $P-3, Q-2, R-5$ (b) $P-2, Q-4, R-1$

(c) $P-6, Q-2, R-5$ (d) $P-3, Q-6, R-4$

37. For the reaction, $Hg_2Cl_2(s)+H_2(g)\rightarrow 2Hg(\ell)+2HCl(aq),$ the correct representation of the cell and the thermodynamic properties ΔG, ΔH and ΔS at 298 K respectively, are (given : $E_{298}=0.2684\ V$ and temperature coefficient $=-3\times10^{-4}\ VK^{-1}$)

(a) $Pt\left|H_2(g,1\,atm)\right|HCl(aq)\left|Hg_2Cl_2(s)\right|Hg(\ell)$

    $\Delta G=-51.8\ kJmol^{-1}, \Delta H=-69\ kJ\ mol^{-1}, \Delta S=-58\ JK^{-1}mol^{-1}$

(b) $Pt\left|H_2(g,1\,atm)\right|HCl(aq)\left|Hg_2Cl_2(s)\right|Hg(\ell)$

    $\Delta G=-25.9\ kJmol^{-1}, \Delta H=-34.5\ kJ\ mol^{-1}, \Delta S=-29\ JK^{-1}mol^{-1}$

(c) $Hg(\ell)\left|Hg_2Cl_2(s)\right|HCl(aq)\left|H_2(g,1\,atm)\right|Pt$

    $\Delta G=-51.8\ kJmol^{-1}, \Delta H=-69\ kJ\ mol^{-1}, \Delta S=58\ JK^{-1}mol^{-1}$

(d) $Hg(\ell)\left|Hg_2Cl_2(s)\right|HCl(aq)\left|H_2(g,1\,atm)\right|Pt$

    $\Delta G=51.8\ kJmol^{-1}, \Delta H=69\ kJ\ mol^{-1}, \Delta S=58\ JK^{-1}mol^{-1}$

38. Among $CH_3Cl, CH_2Cl_2, CHCl_3, CH_3Br$ and CH_3I in the gaseous state, the one having highest molar entropy value at room temperature is

(a) $CHCl_3$ (b) CH_3Cl (c) CH_3Br (d) CH_3I

39. Two solid components form a congruent melting solid in situ. The phase diagram of the system has
   (a) five invariant points, two equilibria involving three phases and two equilibria involving two phases
   (b) three invariant points, two equilibria involving three phases and three equilibria involving two phases
   (c) five invariant points, two equilibria involving three phases and three equilibria involving two phases
   (d) three invariant points, three equilibria involving three phases and two equilibria involving two phases

40. H_2 and Br_2 react to give HBr by the following steps

$$Br_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br + M (fast), \qquad (K = k_1/k_{-1})$$

$$Br + H_2 \xrightarrow{k_2} HBr + H (slow)$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br (fast)$$
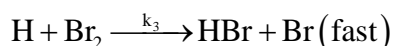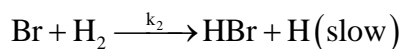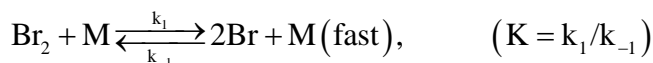
   The probable rate law for the above sequence is:

   (a) $rate = k_2 [H_2][Br_2]^{1/2}$

   (b) $rate = k_2 [H_2][Br_2]$

   (c) $rate = k_2 (K)^{1/2} [H_2][Br_2]^{1/2}$

   (d) $rate = k_2 (K)^{1/2} [H_2][Br]^{1/2}$

Common data for Q. 41 and Q. 42.

For the opposing reaction, $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$

The forward reaction has values $E_a = 100$ kJ mol^{-1} and $A = 1.0 \times 10^{10}$ M^{-1}s^{-1}. The equilibrium concentration of A, B, C and D are 1.0 M, 2.0 M, 5.0 M and 4.0 M respectively, at 700 K.

41. The values of k_1 and k_{-1}, respectively, at this temperature are
   (a) 20 M^{-1}s^{-1} and 2.0 M^{-1}s^{-1}
   (b) 345 M^{-1}s^{-1} and 34.5 M^{-1}s^{-1}
   (c) 34.5 M^{-1}s^{-1} and 3.45 M^{-1}s^{-1}
   (d) 200 M^{-1}s^{-1} and 20 M^{-1}s^{-1}

42. The rate constant (k_1) for the forward reaction at 1000 K is:
   (a) 5.98×10^4 M^{-1} min^{-1}
   (b) 5.98×10^2 M^{-1} s^{-1}
   (c) 1.00×10^3 M^{-1} s^{-1}
   (d) 5.98×10^4 M^{-1} s^{-1}

43. For the reaction $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$. Compute the entropy change (in J/K/mol) for the process and comment on the sign of the property

   Data:

Species	$NH_3(g)$	$N_2(g)$	$H_2(g)$
S^0(J/K/mol)	192.3	191.5	130.6

   (a) $\Delta S^0 = -37.65$ J/K/mol; negative sign indicates that there is a decrease in the gaseous species during the reaction

   (b) $\Delta S^0 = -198.7$ J/K/mol; negative sign indicates that there is a decrease in the gaseous species during the reaction.

   (c) $\Delta S^0 = -31.25$ J/K/mol; negative sign indicates that there is a decrease in the gaseous species during the reaction.

   (d) $\Delta S^0 = +31.25$ J/K/mol; the positive sign indicates that the reaction is spontaneous.

44. The translational partition function of a hydrogen molecule confined in a 100 mL flask at 298 K (Mol. wt. of hydrogen = 2.016) is:
   (a) 2.8×10^{20}
   (b) 2.8×10^{25}
   (c) 2.8×10^{26}
   (d) 2.8×10^{27}.

45. ΔH^0_{298} for the reaction, $C_2H_4O(g) \rightarrow CH_4(g) + CO(g)$,

    is -16.0 kJ. From the given data, evaluate the temperature at which ΔH will be zero.

Substance:	$C_2H_4O(g)$	$CH_4(g)$	$CH_4(g)$
$C_P \, (J/K/mol)$	50	36	30

    (a) 1298 K   (b) 1000 K   (c) 1298 °C   (d) 1100 °Cm

46. At 273 K, N_2 is adsorbed on a mica surface. A plot of $1/V$ vs $1/P$ (V in m^3 and P in torr) gives a straight line with a slope equal to 2.0×10^{-5} torr m^{-3} and an intercept equivalent V_m equal to $4.0 \times 10^{-8} \, m^3$. The adsorption coefficient and the number of molecules of N_2 forming the mono layer, respectively, are

    (a) 1.25×10^{12} torr^{-1} and 1.075×10^{18} (b) 2.5×10^{12} torr^{-1} and 1.075×10^{18}

    (c) 2.5×10^{12} torr^{-1} and 1.75×10^{18} (d) 1.25×10^{10} torr^{-1} and 1.075×10^{18}

47. For the reaction,
    $$2Cl(g) \rightarrow Cl_2(g)$$
    the thermodynamics properties:

    (a) $\Delta G, \Delta H$ and ΔS are positive

    (b) $\Delta G, \Delta H$ and ΔS are negative.

    (c) ΔG and ΔH are negative and ΔS is positive.

    (d) ΔG is negative and ΔH and ΔS are positive.

48. The standard free energies of formation of $H_2S(g)$ and CdS (s) at 100°C are -49.0 kJ/mol and -127.2 kJ/mol, respectively. Use these data to predict whether $H_2(g)$ will reduce CdS (s) to metallic Cd at this temperature

    (a) $\Delta G = -78.2$ kJ/mol and H_2 reduces CdS

    (b) $\Delta G = -39.1$ kJ/mol and H_2 reduces CdS

    (c) $\Delta G = 0$ kJ/mol and the reaction is at equilibrium

    (d) $\Delta G = +78.2$ kJ/mol and the reaction is not feasible

49. From the data of two half-cell reactions:

    $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$ $E^0 = +0.22$ V

    $Ag^+(aq) + e^- \rightarrow Ag(s)$ $E^0 = +0.80$ V

    the solubility product of AgCl at 298 K, is calculated to be

    (a) 1.5×10^{-10} (b) 2.1×10^{-7} (c) 3.0×10^{-3} (d) 1.2×10^{-5}

50. For the energy level $\left(2h^2/ma^2\right)$ the probability for a particle of mass 'm' over the length 'a' of a one-dimensional box is depicted by

(a)

(b)

(c)

(d)
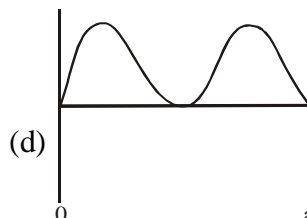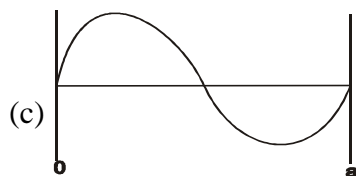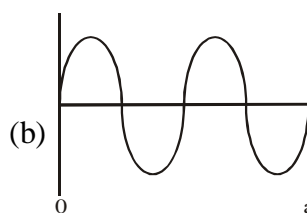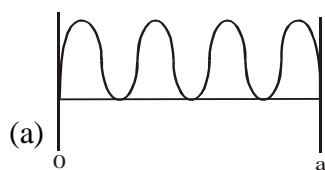
51. Among the complexes (i) $\left(C_6H_6\right)_2 Cr$, (ii) $\left[HMn\left(CO\right)_5\right]$, (iii) $\left[\left(CH_3CO\right)Rh\left(CO\right)I_3\right]^-$ and (iv) $CpFe\left(CO\right)_2\left(CH_3\right)$, the 18-electron rule is not followed in

(a) iii only
(b) ii and iii
(c) i and iv
(d) ii only.

52. The incorrect statement regarding the Fischer-type metal carbene complexes is that
(a) carbene acts as a σ-donor and π-acceptor
(b) all atoms directly connected to carbene C atom are coplanar
(c) the bond between the metal and the carbene C atom has partial double bond character
(d) the carbene C atom is nucleophilic

53. The xenon compounds that are isotructural with IBr_2^- and BrO_3^- respectively are
(a) linear XeF_2 and pyramidal XeO_3
(b) bent XeF_2 and pyramidal XeO_3
(c) bent XeF_2 and planar XeO_3
(d) linear XeF_2 and tetrahedral XeO_3

54. Using chlorobenzene as solvent, the reagents needed for an efficient synthesis of borazine are

(a) NH_4Cl and BCl_3
(b) NH_4Cl, BCl_3 and $NaBH_4$

(c) NH_4Cl and $NaBH_4$
(d) NH_3 and BCl_3

55. The number of manganese ions in tetrahedral and octahedral sites, respectively in Mn_3O_4 are

(a) one Mn^{2+} and two Mn^{3+}
(b) one Mn^{3+} and two Mn^{2+}

(c) two Mn^{3+} and one Mn^{2+}
(d) two Mn^{2+} and one Mn^{3+}

56. Gold crystallizes in face-centered-cubic lattice. The atomic weight and density of gold are 196.97 and 19.4 g/cm³ respectively. The length of the unit cell is

(a) 2.563 Å
(b) 3.230 Å
(c) 4.070 Å
(d) 8.140 Å

57. Solid $Co_2\left(CO\right)_8$ shows infrared CO stretching bands at 1857, 1886, 2001, 2031, 2044, 2059, 2071 and 2112 cm⁻¹. When $Co_2\left(CO\right)_8$ is dissolved in hexane, the carbonyl bands at 1857 and 1886 cm⁻¹ disappear. These changes in the infrared spectrum in hexane are due to.

(a) Loss of terminal CO.

(b) Structural change of $Co_2\left(CO\right)_8$ involving conversion of terminal CO to bridging CO

(c) Dissociation of $Co_2\left(CO\right)_8$ to $CO\left(CO\right)_4$

(d) Structural changes of $Co_2\left(CO\right)_8$, involving conversion of bridging CO to terminal CO.

58. Match the silicate minerals (column I) with their compositions (column II) and order of hardness (column III)

I	**II**	**III**
P. talc	U $KAl_3Si_3O_{10}(OH)_2$	X high
Q. muscovite	V $Mg_3Si_4O_{10}(OH)_2$	Y low
R. margarite	W $CaAl_4Si_2O_{10}(OH)_2$	Z intermediate

    (a) P, V, Y – Q, U, Z – R, W, X   (b) P, U, X – Q, V, Z – R, W, Y
    (c) P, W, X – Q, V, Y – R, U, Z   (d) P, V, Z – Q, U, Y – R, W, X

59. The structure of $P_4N_4Cl_8$ is puckered whereas that of $P_4N_4F_8$ is planar because
    (a) F is more electronegative than Cl
    (b) F is smaller in size than that of Cl
    (c) F is more polarizable than Cl
    (d) Extent of π-electron delocalization is more in $P_4N_4Cl_6$ than in $P_4N_4F_6$.

60. The correct order of addition of NH_3, pyridine (py) and Br^- to $[PtCl_4]^{2-}$ to obtain
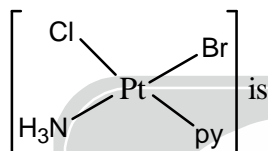
    (a) py, Br^- and NH_3 (b) Br^-, py and NH_3 (c) NH_3py and Br^- (d) NH_3, Br^- and py

61. $[Ru(C_2H_5)Cl(PPh_3)_3]$ is stable only under a pressure of ethene because
    (a) it is a 16-electron complex   (b) it forms an 18-electron adduct with ethene
    (c) one of the decomposition products is ethene   (d) it prevents α–elimination of ethene

62. The ground state term symbols for p^3 and d^3 electronic configuration respectively, are
    (a) ^4S and ^4F (b) ^4D and ^4F (c) ^1D and ^4F (d) ^4S and ^2G

63. The "styx" code for diborane is
    (a) 2020   (b) 2200   (c) 2002   (d) 0220

64. $\left[CoCl(NH_3)_5\right]^{3+} + \left[Cr(H_2O)_6\right]^{2+} \rightarrow \left[Co(H_2O)(NH_3)_5\right]^{2+} + \left[CrCl(H_2O)_5\right]^{3+}$

    The correct statement regarding the above reaction is that
    (a) it follows outer-sphere mechanism
    (b) it follows inner-sphere mechanism with NH_3 acting as the bridging ligand.
    (c) it follows inner-sphere mechanism with Cl^- acting as the bridging ligand
    (d) it is not an electron-transfer reaction.

65. The pecentage transmittance of a transition metal complex at 360 nm and at 25°C is 25% for a 6×10^{-4} mol L^{-1} solution in a 1 cm cell. The molar adsorption coefficient in the unit of L mol^{-1} cm^{-1} is:

    (a) $\sim 1.0 \times 10^{-3}$ (b) $\sim 1.0 \times 10^3$ (c) $\sim 2.0 \times 10^3$ (d) $\sim 1.0 \times 10^4$

66. The bond order of the metal-metal bonds in $[Re_2Cl_8]^{2-}$, $[Re_2Cl_6(P(C_2H_5)_3)_2]$ and $[Re_2Cl_4P(C_2H_5Ph_2)_4]$ respectively are
    (a) 4, 4 and 3   (b) 3, 4 and 4   (c) 4, 2 and 3   (d) 2, 3 and 4

Q. 67–73 Contains a Statement (S) with a Reason (R) and an Assertion (A). for each question, choose the correct answer from the following four choices.

(a) Both R and A are correct   (b) both R and A are wrong

(c) R is correct but A is wrong   (d) R is wrong but A is correct
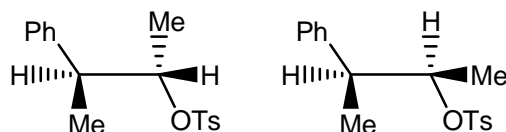
67. **Statement :** solvolysis of tosylates (I) and (II) shown above, in acetic acid yield the corresponding acetates. **Reason :** Due to neighbouring group participation of the bridge phenonium ion, achiral intermediates are formed in both cases of (I) and (II). **Assertion :** Tosylate (I) gives an acetate with retention of configuration and tosylate (II) gives a recemic mixture of acetates.

68. **Statement :** Cyclopentadiene can potentially undergo Diels-Alder reaction $(4\pi + 2\pi)$ and $2\pi + 2\pi$ cycload-dition reactions with ketenes. However, it reacts to give stereospecifically only one product.

    Reason : Due to sp hybridisation of the ketene carbon $2\pi_s + 2\pi_a$ cycloaddition is feasible and thermally this reaction is symmetry allowed.

    Assertion : Ketenes undergo only $2\pi + 2\pi$ cycloaddition reaction with 1, 3-dienes.

69. **Statement :** 1.3-Dichloroallene is optically active and the enantiomers are resolvable. **Reason :** Optical activity is due to the presence of a chiral center in the molecule. **Assertion :** The enantiomers are resolvable because interconversion of enantiomers is possible only if there is a free rotation about C=C bonds, which is absent.

70. **Statement :** At 273 K, the fugacities (in atm) of N_2 are 97.03 and 1839 at the experimental pressures (atm) of 100 and 1000, respectively.

    Reason : At 1000 atm, the system is above the critical temperature and pressure.

    Assertion : The contribution of the repulsive forces is more dominant at 1000 atm.

71. **Statement :** for the equilibrium,

    $$Ag_2CO_3(s) \rightleftarrows Ag_2O(s) + CO_2(g)$$

    A plot of ln K_p vs 1/T gives a linear relationship with a positive slope.

    Reason : The reaction is exothermic.

    Assertion : The free energy change for the reaction is more negative at higher temperatures.

72. **Statement :** The potential for the cell,

    $$Pt \left| H_2 (g, 1atm) \right| HCl(m) \left| AgCl(s) \right| Ag(s)$$
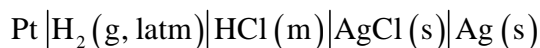
    decreases as the concentration of HCl is increased.

    Reason : The mean ionic activity coefficient decreases with increase in HCl concentration.

    Assertion : In a plot of E vs [HCl], the intercept at the potential axis is equal to the standard reduction potential of the hydrogen electrode.

73. **Statement :** Oxygen is preferred to air for welding metals using acetylene gas.

Reason : With air, metal nitrides are formed resulting in poor welding.

Assertion : With air, inert nitrogen dissipates the heat of combustion and hence, the maximum temperature attained is less than that with oxygen.

74. Among the following, the Newmann projections of meso-2, 3-butanediol are
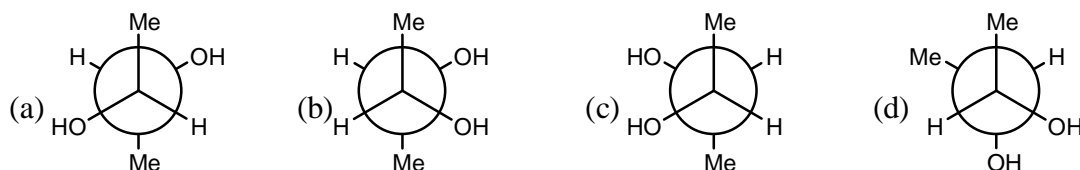
75. The correct description of the following two reactions is that
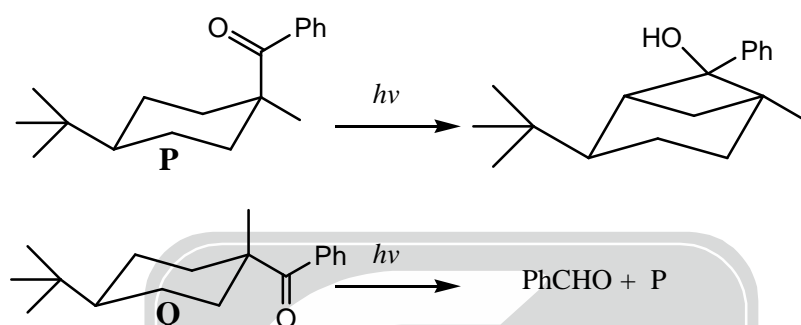
(a) Both P and Q undergo α-cleavage reaction

(b) P undergoes only Norrish type II reaction whereas Q undergoes only Norrish type I reaction.

(c) Q gives P by photochemical chair to chair interconversion of the cyclohexane Ring

(d) Both P and Q undergo Norrish type I reaction, but only Q gives S through this mechanism.

76. A 10.0 g mixture of n-butane and 2-butene was treated with bromine in CCl_4 and it consumed 8.0 g of bromine (Atomic wt. = 80). Another 10.0 g of the same mixture was hydrogenated to get n-butane only. The weight of 2-butene in the original mixture and the gain in the weight of the mixture after hydrogenation, respectively are

(a) 2.8 g and 0.1 g   (b) 5.6 g and 0.4 g   (c) 7.2 g and 0.8 g   (d) 8.0 g and 1.0 g

77. Pyrrole + PhMgBr $\rightarrow$ E + F

E + MeCl $\rightarrow$ G + H

F + MeCl $\rightarrow$ no reaction without a catalyst.
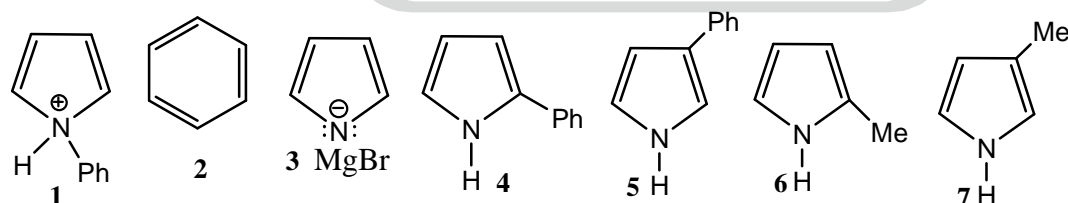
The structure of products E–H, respectively are

(a) 3, 2, 6, 7   (b) 4, 5, 6, 1   (c) 3,4, 5, 2   (d) 3, 2, 4, 5

78. Regarding the saponification of M and N shown below, the correct statement is that
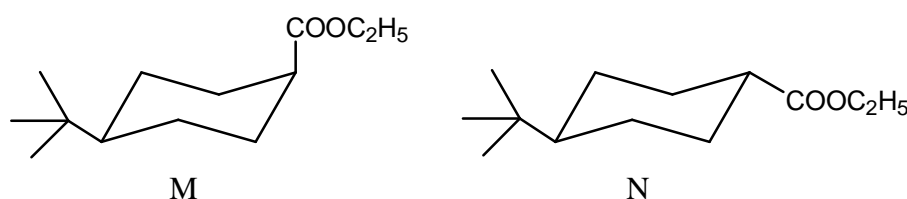
(a) M reacts faster than N because the transition state is less crowded for M than for N.

(b) M reacts slower than N because the transition state is more crowded for M than for N.

(c) N and M react at the same rate because of formation of tetrahedral intermediate in both cases.

(d) N reacts slower than M because of its greater thermodynamics stability.

79. Reactant P labelled with "C (labelled carbon marked with a star) rearranged to product Q on heating
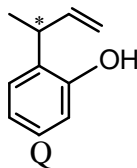
The structure of reactant P is

(a)   (b)   (c)   (d)
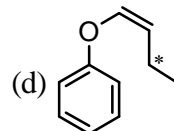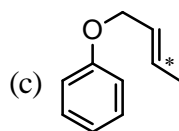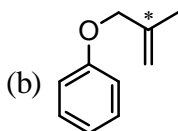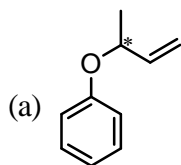
80. $RCH_2COR + R'X \xrightarrow{[(CH_3)_2CH]_2NLi} P + Q$

In the above reaction, X is a halogen and the products P and Q are

(I) $R'N\left[CH(CH_3)_2\right]_2$ (II) $RCH(R')COR$

(III) $\underset{\underset{OR'}{|}}{RHC=C}-R$ (IV) $RH_2C-\underset{\underset{OH}{|}}{\overset{\overset{R}{|}}{C}}-N[CH(CH_3)_2]_2$
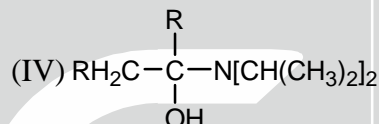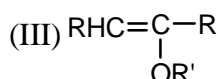
(a) I and II   (b) II and III   (c) III and IV   (d) I and IV

81. Among the halobenzenes, the one that undergoes electrophilic aromatic substitution most readily and the reason for its higher reactivity are

(a) fluorobenzene; the benzenonium ion intermediate is stablished by 2p (F), 2p (C) overlap which is most efficient

(b) chlorobenzene; very high electron affinity of chlorine considerably lowers the energy of activation of the reaction

(c) bromobenzene; high polarising power of the halogen atom helps in effective stabilisation of the benzenonium ion intermediate

(d) iodobenzene; iodine atom has the lowest electronegativity and hence electron density of the phenyl ring is least disturbed

82. Among the carboxylic acids shown below, the ones that exhibit stereoisomerism an also form, on heating, cyclic anhydrides are

(I) $HOOCCH(CH_3)CH_2CH_2COOH$

(II) $HOOCCH(i-C_3H_7)COOH$

(III) $HOOCCH(C_2H_5)CH_2COOH$

(IV) $HOOCC(CH_3)(C_2H_3)COOH$
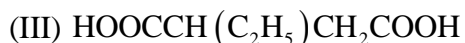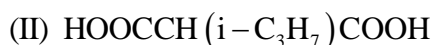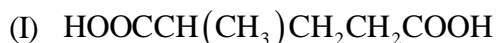
(a) (I) and (II)   (b) (I) and (III)   (c) (II) and (III)   (d) (II) and (IV)

83. The reactants that lead to products (X) and (Y) on ozonolysis are

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

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

84.
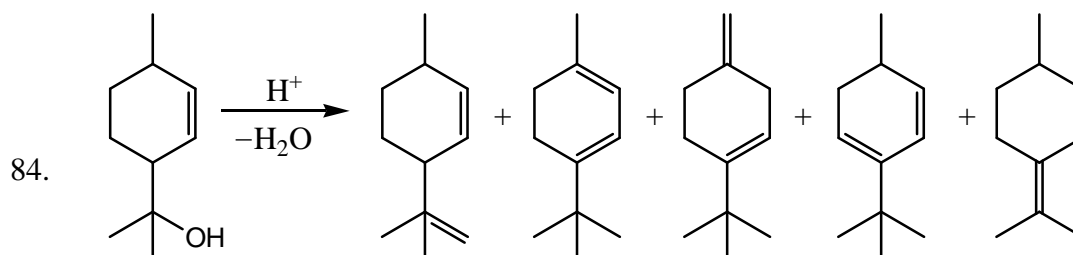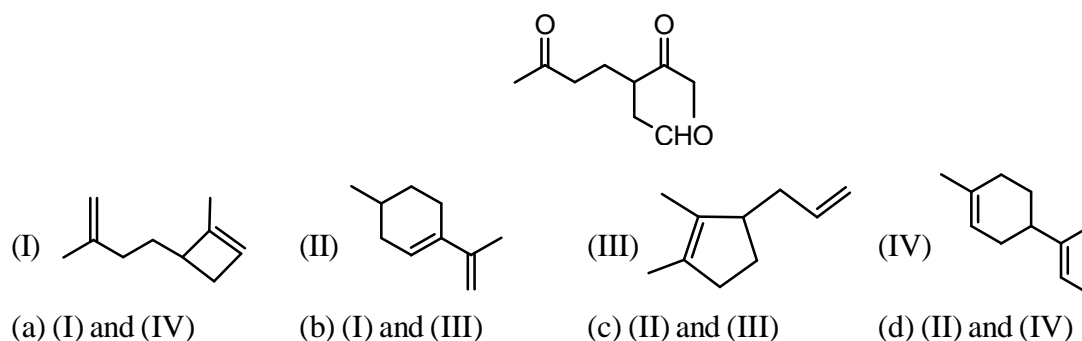
On the basis of Woodward-Fieser rules, the dienes that have λ_{max} values in the range 268-273 nm are

(a) P and Q   (b) P and R   (c) Q and R   (d) Q and S

85.

HOOCCH (Br) Ch (Br) COOH
(X)

HOOCCH (Br) Ch (Br) COOH
(Y)
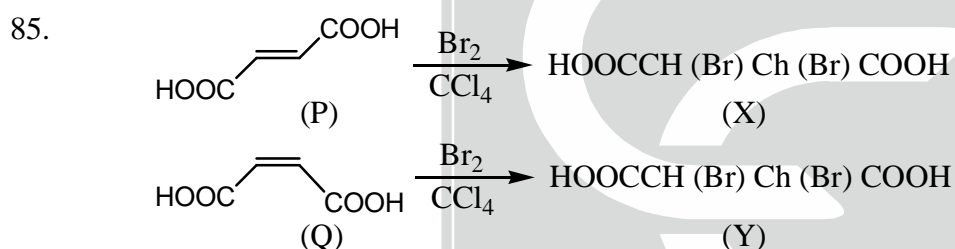
The correct statements with respect to the above pair of reactions are that
(I)   the reactions are stereospecific
(II) (X) is erythro and (Y) is threo isomer
(III) (X) is threo and (Y) is erythro isomer
(IV) each of (P) and (Q) gives a mixture of (X) and (Y)

(a) (I) and (II)   (b) (I) and (III)   (b) (I) and (IV)   (d) (II) and (IV)

86.
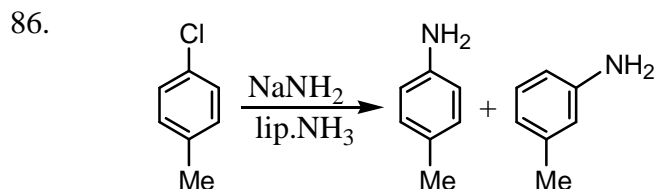
The above reaction is an example of
(a) nucleophilic substitution of addition-elimination mechanism
(b) electrophilic substitution by addition-elimination mechanism
(c) radical substitution reaction
(d) nucleophilic substitution involving benzyne intermediate

87. Diols (I-IV) which react with CrO_3 in aqueous H_2SO_4 and yield products that readii undergo decarboxylation on heating, are

(I)

(II)

(III)

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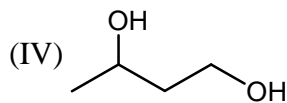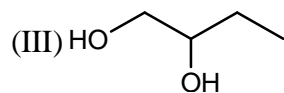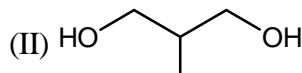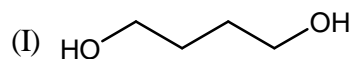
(a) (I) and (II)   (b) (II) and (III)   (c) (II) and (IV)   (d) (I) and (IV)

88. Reactant P gives products Q and/or R.

P   Q   R
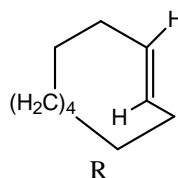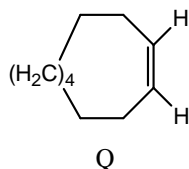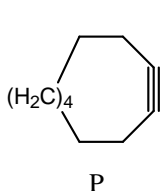
The possible reagents are: (I) 2Na/liq. NH_3 , (II) H_2/Pd/$CaCO_3$ (quinoline), (III) $2H_2$/Pd/C.
The correct statement with respect to the conversion is:
(a) Q is obtained on treatment with reagent (I)   (b) R and Q are obtained on treatment with reagent (III)
(c) R is obtained on treatment with reagent (I)   (d) R is obtained on treatment with reagent (II).

89. The product obtained in the thermal reaction of cyclopentadiene with maleic anhydride is

(a)   (b)   (c)   (d)
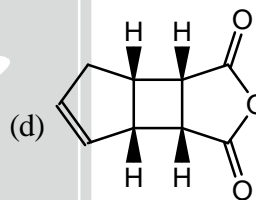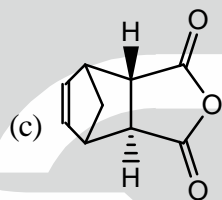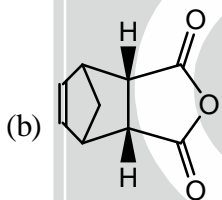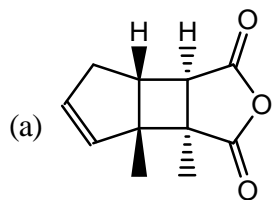
90. Two alkenes, X(91% yield) and Y(9% yield) are formed when the following is heated.

The structures of X and Y, respectively are
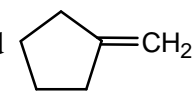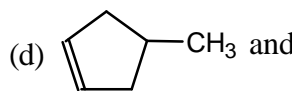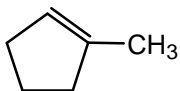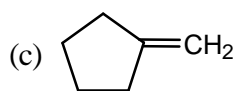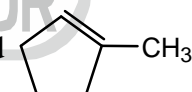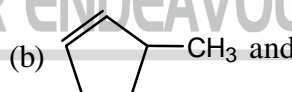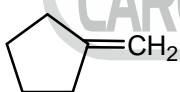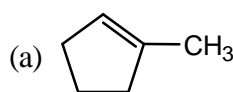
(a)

(b)

(c)

(d)

***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.30 : Carry ONE mark each.

1. In units of $\dfrac{h^2}{8m\ell^2}$, the energy difference between levels corresponding to 3 and 2 node eigenfunctions for a particle of mass m in a one dimensional box of length ℓ is
   (a) 1   (b) 3   (c) 5   (d) 7

2. On the basis o LCAO-MO theory, the magnetic characteristics of N_2 and N_2^+ are
   (a) both diamagnetic   (b) both paramagnetic
   (c) N_2 dimagnetic and N_2^+ paramagnetic   (d) N_2 paramagnetic and N_2^+ diamagnetic

3. The v_{rms} of a gas at 300 K is 30 $R^{\frac{1}{2}}$. The molar mass of the gas, in kg mol^{-1}, is
   (a) 1.0   (b) 1.0×10^{-1} (c) 1.0×10^{-2} (d) 1.0×10^{-3}

4. The coefficient of performance of a perfect refrigerator working reversibly between the temperature T_c and T_h is given by
   (a) $\dfrac{T_c - T_h}{T_c}$ (b) $\dfrac{T_h - T_c}{T_c}$ (c) $\dfrac{T_c}{T_h - T_c}$ (d) $\dfrac{T_h}{T_h - T_c}$

5. At a given temperature and pressure, the phase diagram of a three component system shows a binodal curve. if the two components are chloroform and water, the third component, among the choices given below, is
   (a) benzene   (b) acetic acid   (c) toluene   (d) carbon tetrachloride

6. A certain reaction proceeds in a sequence of three elementary steps with the rate constants k_1, k_2 and k_3. If the observed rate constant (k_{obs}) of the reaction is expressed as $k_{obs} = k_3 (k_1 / k_2)^{\frac{1}{2}}$, the observed activation energy (E_{obs}) of the reaction is
   (a) $\dfrac{1}{2}\left[\dfrac{E_1}{E_2}\right] + E_3$ (b) $\dfrac{E_3 + E_1}{E_2}$ (c) $E_3 \left[\dfrac{E_1}{E_2}\right]^{\frac{1}{2}}$ (d) $E_3 + \dfrac{1}{2}(E_1 - E_2)$

7. Which one of the following is an example of a maximum boiling azeotrope?
   (a) H_2O—HCl   (b) H_2O—C_2H_6OH (c) $CHCl_3$—CH_3OH (d) CCl_4—CH_3OH

8. For the reaction, $A + B \rightleftharpoons X^+ \rightarrow P$, Ea = 20.0 kJ mol^{-1} at 300 K. The enthalpy change for the formation of the activated complex from the reactants in kJ mol^{-1} is
   (a) 12   (b) 15   (c) 23   (d) 25

9. In an osmotic pressure measurement, a plot of height of solution (h) of density (ρ) versus concentration (gL^{-1}) was made at a temperature T. The slope of the plot will be equal to (where g, given in the choices below, is the acceleration of free fall)
   (a) $\dfrac{\rho RT}{gM}$ (b) $\dfrac{gRT}{\rho M}$ (c) $\dfrac{RT}{\rho gM}$ (d) $\dfrac{gRM}{\rho T}$

10. If 0.001 M of a substance quenches the efficiency of fluorescence by 20%, the value of Stem-Volmer constant in M^{-1} is
    (a) 100   (b) 150   (c) 200   (d) 250

11. Which one of the following is NOT a photodetector?
    (a) Bolometer
    (b) Charge-transfer device
    (c) Photomultiplier tube
    (d) Silicon diode

12. The nature of excitation signal used for cyclic voltametry is
    (a) linear scan (b) differential pulse (c) triangular (d) square wave

13. The structure of SF_4 is
    (a) octahedral
    (b) tetrahedral
    (c) trigonal bipyramidal
    (d) square planar

14. The number of metal-metal bonds present in $Ir_4(CO)_{12}$ are
    (a) 4 (b) 5 (c) 6 (d) 8

15. The zero magnetic moment of octahedral K_2NiF_6 is due to
    (a) low spin $d^6 Ni(IV)$ complex
    (b) low spin $d^8 Ni(II)$ complex.
    (c) high spin $d^8 Ni(II)$ complex
    (d) high spin $d^6 Ni(IV)$ complex.

16. The number of hyperfine split lines observed in ESR spectrum of methyl radical is
    (a) 1 (b) 4 (c) 6 (d) 8

17. The absorption of $Co(NH_3)_6^{2+}$ is:
    (a) stronger than that of $\left[Co(NH_3)_5 Cl\right]^{2+}$
    (b) stronger than that of $\left[MnCl_4\right]^{2-}$
    (c) weaker than that of $\left[MnCl_4\right]^{2-}$ but stronger than that of $\left[CO(NH_3)_5 Cl\right]^{2+}$
    (d) weaker than those of both $\left[MnCl_4\right]^{2-}$ and $\left[Co(NH_3)_5 Cl\right]^{2+}$

18. Which one of the following statements about ferrocene is FALSE?
    (a) It obeys the 18-electron rule
    (b) It is diamagnetic
    (c) It is an orange solid
    (d) It resists electrophilic substitution

19. The bond angle of Cl_2O is
    (a) smaller than that of F_3O
    (b) greater than that of H_2O
    (c) smaller than that of H_2O
    (d) same as that of F_2O

20. The half-wave potential for a reversible reduction of a metal ion in polarography is independent of
    (a) Concentration of the supporting electrolyte
    (b) Concentration of the electroactive species.
    (c) Concentration of the complexing agent.
    (d) Temperature of the solution.

21. The major product formed on nitration of N, N-dimethylaniline with conc. $H_2SO_4 HNO_3$ mixture is
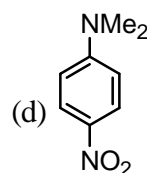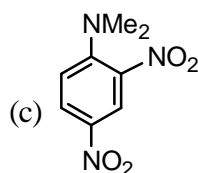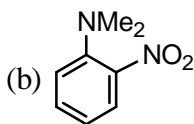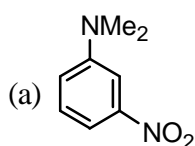
22. Reaction of phenylacetylene with sodamide in liquid ammonia generates

(a)   (b)   (c)   (d)
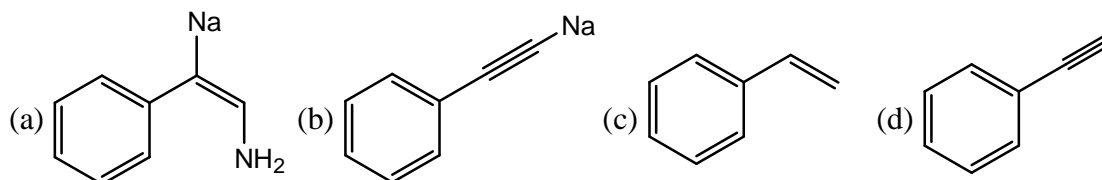
23. Proton decoupled ^{13}C NMR spectrum of a bicyclooctane (C_8H_{14}) exhibits only two signals. The Structure of the compound is:

(a)   (b)   (c)   (d)
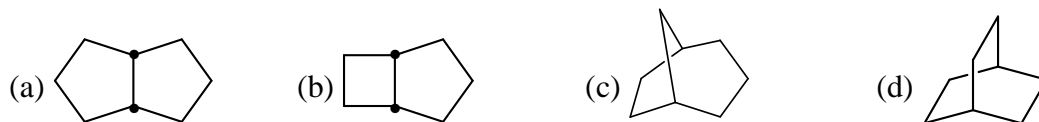
24. Cyclohexyl benzyl ether when reacted with hydrogen in the presence of 10% palladium on charcoal generates a mixture of
    (a) cyclohexanol and benzyl alcohol   (b) cyclohexane and benzyl alcohol
    (c) cyclohexanol and toluene   (d) cyclohexane and toluene

25. In electrophilic aromatic substitution reactions, nitro group is meta-directing, because the nitro group
    (a) increase electron density at meta-position   (b) increase electron density at ortho-and para-positions
    (c) decreases electron density at meta-position   (d) decreases electron density at ortho-and para-positions

26. Among the resonance forms given below, the one which contributes most to the stability of azulene is

(a)   (b)   (c)   (d)
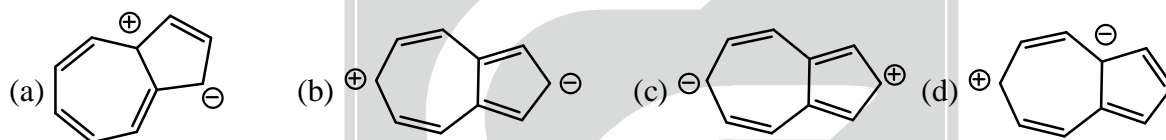
27. The configurations at the two asymmetric centres (C–1 and C–6) in the bicyclo [4.4.0] decane, given below are
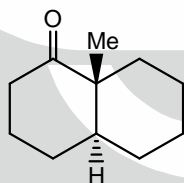
    (a) 1R, 6R   (b) 1R, 6S   (c) 1S, 6S   (d) 1S, 6R

28. The reactive intermediate involved in the conversion of phenol to salicylaldehyde using chloroform and sodium hydroxide is

    (a) $Cl_2C:$ (b) Cl_2CH^+ (c) Cl_2CH^- (d) Cl_2CH^+

29. Conversion of Ph-NH$_2$ into Ph-CN can be accomplished by
    (a) reaction with sodium cyanide in the presence of nickel catalyst
    (b) reaction with chloroform and sodium hydroxide
    (c) diazotisation followed by reaction with CuCN
    (d) reaction with ethyl formate followed by thermolysis

30. The vicinal coupling constant J expected for the protons H_P and H_Q in the compound given below will be in the range
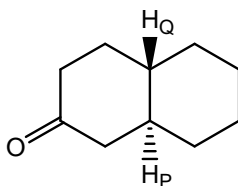
    (a) 0–2 Hz   (b) 4–6 Hz   (c) 8–10 Hz   (d) 12–15 Hz

Q.31 – Q.90 : Carry TWO marks each.

31. For one mole of an ideal gas $\left(\dfrac{\partial P}{\partial T}\right)_V \left(\dfrac{\partial V}{\partial T}\right)_P \left(\dfrac{\partial V}{\partial P}\right)_T =$

    (a) -1 (b) $-\dfrac{R^2}{P^2}$ (c) $+1$ (d) $\dfrac{R^2}{P^2}$

32. Neglecting the mass of hydrogen (1.0 amu) and deuterium (2.0 amu) with respect to that of iodine (127 amu), the ratio between fundamental vibrational frequencies of HI and DI is:

    (a) $\dfrac{1}{2}$ (b) 2   (c) $\dfrac{1}{\sqrt{2}}$ (d) $\sqrt{2}$

33. The population of Jth rotational level N_j is given by $N_j = N_0 (2J+1) e^{\left[j(j+1)B \right]/kT}$. The J value of rotational level with maximum population (J_{max}) is given by

    (a) $\dfrac{(2kT/B)-1}{\sqrt{2}}$ (b) $\dfrac{\sqrt{2kT/B}-1}{2}$ (c) $\dfrac{kT}{B}$ (d) $\dfrac{B}{kT}$

34. The fugacity coefficient ϕ is given by $\ln \phi = \int_0^p \left(\dfrac{z-1}{p} \right) dp$ where z is the compressibility factor, and p the pressure. The fugacity of a gas governed by the gas law $p(V_m - b) = RT$ is

    (a) $p \ln (V_m / RT)$ (b) $pe^{b/RT}$ (c) $pe^{-bp/RT}$ (d) $pe^{bp/RT}$

35. The number and symmetry type of normal modes of vibration of H_2O are
    (a) 3 and $2A_1 + B_2$ (b) 3 and $2A_1 + A_2$
    (c) 3 and $2A_1 + B_1$ (d) 4 and $3A_1 + B_2$

36. The gaseous reaction $2A + B \rightarrow C$, with partial pressures of $p_A = 0.1$ atm; $p_B = 0.001$ atm and $p_C = 1.0$ atm, proceeds to the left at 298 K. The equilibrium constant, K_p for the above reaction is

    (a) 1.0×10^4 (b) 1.0×10^5 (c) 1.0×10^6 (d) 1×10^7

37. The change in entropy when one mole of an ideal gas is compressed to one-fourth of its initial volume and simultaneously heated to twice its initial temperature is

    (a) $(C_v - R) \ln 4$ (b) $(C_v - 2R) \ln 2$ (c) $(C_v - 2R) \ln 4$ (d) $(C_v + 2R) \ln 2$

38. For the reaction, $A(s) \rightleftharpoons B(l) + 2C(g)$, $\Delta G° \text{(in Joules)} = 90800 - 100T$. The partial pressure of $C(g)$ at 600 K in Torr is
    (a) 15   (b) 22   (c) 35   (d) 46

39. Match the following:

    P. $\left(\dfrac{\partial U}{\partial S}\right)_V$ I. A

    Q. $\left(\dfrac{\partial U}{\partial V}\right)_S$ II. $-S$

    R. $\left(\dfrac{\partial G}{\partial P}\right)_T$ III. T

S. $\left(\dfrac{\partial G}{\partial T}\right)_P$ IV. $-P$

V. H

VI. V

(a)   P-III   Q-IV   R-VI   S-II   (b)   P-III   Q-I   R-II   S-V

(c)   P-I   Q-III   R-V   S-II   (d)   P-IV   Q-III   R-VI   S-V

40.   Match the following :

P. $4n + 2$ rule   I.   Woodward-Hoffmann rule

Q. single valued   II.   Bound system

R. $< p_x > = 0$ III.   Hurtree-Fock Theory

S. photochemically allowed   IV.   Huckel theory

                                           V.   Wave function

                                           VI.   unbound system

Codes:

(a) P-I, Q-III, R-IV, S-VI   (b) P-IV, Q-V, R-II, S-VI

(c) P-II, Q-VI, R-III, S-I   (d) P-IV, Q-V, R-II, S-I

41.   The solubility product of silver sulphate at 298 K is 1.0×10^{-5}. If the standard reduction potential of the half-cell $Ag^+ + e \rightarrow Ag$ is 0.80 V, the standard reduction potential of the half-cell $Ag_2SO_4 + 2e \rightarrow 2Ag + SO_4^{2-}$ is:

(a) 0.15 V   (b) 0.22 V   (c) 0.65 V   (d) 0.95 V

42.   The criterion for spontaneous change in terms of the state functions is:

(a) $dU_{S,V} \geq 0$ (b) $dA_{T,V} \geq 0$ (c) $dS_{U,V} \geq 0$ (d) $dG_{T,V} \leq 0$

43.   One mole of an ideal gas $(C_V = 1.5\,R)$ at a temperature 500 K is compressed from 1.0 atm to 2.0 atm by a reversible isothermal path. Subsequently, it is expanded back to 1.0 atm by a reversible adiabatic path. The volume of the final state in litre is:

(a) 15.6   (b) 20.5   (c) 31.1   (d) 41.0

44.   The vapour pressures of the pure components P and Q are 700 Torr and 500 Torr, respectively. When the two phases are in equilibrium at 1.0 atm, the mole fraction of P in the liquid phase is 0.6 and in the vapour phase 0.4. The activity co-efficient of component P in the solution on the basis of Raoult's law is

(a) 0.60   (b) 0.72   (c) 0.92   (d) 1.01

45.   The concentration of oxygen in water in mg L^{-1}. If the Henry's law constant for oxygen at 298 K is 2.80×10^7 Torr, the partial pressure of oxygen in the atmosphere in Torr is,

(a) 28   (b) 32   (c) 50   (d) 15.68

46.   Decomposition of ammonia on tungsten at 850ºC has a rate constant value of 0.10 Torr s^{-1}. If the initial pressure of ammonia is 100 Torr, the pressure of ammonia (in Torr) at t = 200 s is

(a) 10   (b) 20   (c) 50   (d) 80

47.   For the reaction of the type $P \xrightarrow{k_1} Q \xrightarrow{k_2} R$, given that $[P]_0 = 1.0M;\ k_1 = 1 \times 10^{-3}\,s^{-1}$ and $k_2 = 1 \times 10^{-4}\,s^{-1}$, the time at which the concentrations of Q and R are 0.5966 M and 0.0355M, respectively, is

(a) 500s   (b) 750 s   (c) 1000 s   (d) 1500 s

48.   The spinels $CoFe_2O_4$ and $FeFe_2O_4$, respectively, are

(a) inverse and inverse   (b) inverse and normal   (c) normal and normal   (d) normal and inverse

49.   According to Wade's rule, the structures of $B_{10}C_2H_{12}$ and $[B_9C_2H_{11}]^{2-}$, respectively, are

(a) closo and arachno   (b) nido and closo   (c) closo and nido   (d) nido and arachno

50.   The overall charge present on the cyclic silicate anion $[Si_6O_{18}]^{n-}$ is

(a) 6   (b) 12   (c) 18   (d) 24

51.   The ground state term symbols for high spin d^5s^1 and d^5 configurations, respectively, are

(a) ^3S and ^6S (b) ^6P and ^3S (c) ^7S and ^6S (d) ^7P and ^6S

52.   The reagents required for the synthesis of cyclic phosphazene $N_4P_4Cl_8$ are

(a) PCl_5 and NH_3 (b) $POCl_3$ and NH_4Cl
(c) $POCl_3$ and NH_3 (d) PCl_5 and NH_4Cl

53.   The isomerisms that are possible in the Co(III) complexes $\left(Co(NH_3)_3(NO_2)_3\right)$ and $\left[Co(NH_3)_5 NO_2\right]Cl_2$, respectively, are

(a) co-ordination and position   (b) optical and linkage
(c) geometrical and linkage   (d) optical and optical.

54.   The perxenate ion XeO_4^{4-} can be prepared by

(a) direct reaction of Xe with oxygen   (b) reaction of XeF_6 with oxygen
(c) hydrolysis of XeF_6 in acidic medium   (d) hydrolysis of XeF_6 in basic medium.

55.   In tetrahedral geometry, which one of the following sets of electronic configurations will have orbital contribution to the magnetic moment?

(a) d^3, d^4, d^8 and d^9 (b) d^1, d^6, d^7 and d^9
(c) d^3, d^4, d^7 and d^9 (d) d^1, d^3, d^4 and d^9.

56.   The most suitable route to prepare the trans isomer of $\left[PtCl_2(NH_3)(PPh_3)\right]$ is:

(a) $[PtCl_4]^{2-}$ with PPh_3 followed by reaction with NH_3.

(b) $[PtCl_4]^{2-}$ with NH_3 followed by reaction with PPh_3.

(c) $\left[Pt(NH_3)_4\right]^{2+}$ with HCl followed by reaction with PPh_3.

(d) $\left[Pt(NH_3)_4\right]^{2+}$ with PPh_3 followed by reaction with HCl.

57.   A solution containing 5 ppm of $KMnO_4$ (F.W. = 159) has a transmittance of 0.360 measured in a 1 cm cell at 500 nm. The molar absorptivity of $KMnO_4$ in L mol^{-1} cm^{-1} is

(a) 1.1×10^4 (b) 1.4×10^4 (c) 1.9×10^4 (d) 2.7×10^4

58.   Match the following:
P. Coulometry   I. Dropping mercury electrode
Q. Ion selective electrode   II. Current efficiency
R. Polarography   III. Dead stop end point
S. Amperometry   IV. Membrane potential
                                                  V. Conductometer
                                                  VI. Actinometer.

(a) P-II, Q-IV, R-I, S-III   (b) P-I, Q-II, R-III, S-V
(c) P-VI, Q-V, R-III, S-IV   (d) P-III, Q-IV, R-I, S-VI

59. Match the following :
    P: Ferritin   I. electron transport
    Q : Vitamin B_{12} II. Ionophore
    R : Cytochromes   III. Oxygen transport
    S : Valinomycin   IV. Nitrogen fixation
                                  V. Organometallic enzyme
                                  VI. Iron storage.

    (a) P-VI   Q-IV   R-II   S-I
    (b) P-I   Q-III   R-VI   S-IV
    (c) P-III   Q-V   R-IV   S-VI
    (d) P-VI   Q-V   R-I   S-II

60. The number of absorption bands observed $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$, respectively, are
    (a) 1 and 3   (b) 0 and 1   (c) 0 and 3   (d) 3 and 1

61. Regarding the catalytic cycle of hydrogenation of alkenes involving $RhCl(PPh_3)_3$ as the catalyst, the correct statements is:
    (a) Only 18-electron Rh complex is involved.
    (b) 14-, 16- and 18-electron Rh complexes are involved.
    (c) 14- and 16-electron Rh complexes are involved.
    (d) 16- and 18-electron Rh complexes are involved.

62. The infra-red stretching frequency V_{CO} of P–S follows the order

    (P) $Mn(CO)_6^+$ (Q) CO   (R) $H_3B \leftarrow CO$ (S) $\left[V(CO)_6 \right]^-$
    (a) $P > R > S > Q$ (b) $S > P > R > Q$
    (c) $Q > S > P > R$ (d) $R > Q > P > S$

63. The structures of $N(CH_3)_3$ and $N(SiH_3)_3$, respectively, are
    (a) trigonal planar and pyramidal   (b) pyramidal and trigonal planar
    (c) pyramidal and pyramidal   (d) trigonal planar and trigonal planar

64. Which one of the following is NOT correct in chromatography ?

    t_M = Retention time for a species that is not retained by the stationery phase.

    T_R = Retention time for the analyte

    $(t_R)_n$ = Retention time for the component n

    W_n = Width of the peak at its base for the component n

    (a) Resolution $= \dfrac{(t_R)_2 - (t_R)_1}{2(W_1 + W_2)}$ (b) Capacity factor $= \dfrac{t_R - t_M}{t_M}$

    (c) Separation factor $= \dfrac{(t_R)_2 - t_M}{(t_R)_1 - t_M}$ (d) No. of theoretical plates $= 16\left(\dfrac{t_R}{W}\right)^2$

65. Thermal reaction of allyl phenyl ether generates a mixture of ortho-and para-allyl phenols. The para-allyl phenol is formed via
    (a) a[3, 5]-sigmatropic shift
    (b) first ortho-allyl phenol is formed, which then undergoes a [3, 3]-sigmatropic shift
    (c) two consecutive [3, 3]-sigmatropic shifts
    (d) dissociation to generate allyl cation, which then adds at para-position

66. Of the favour vicinal diols shown below, only three are cleaved by HIO_4, the diol which is NOT cleaved HIO_4 is

(a)   (b)   (c)   (d)
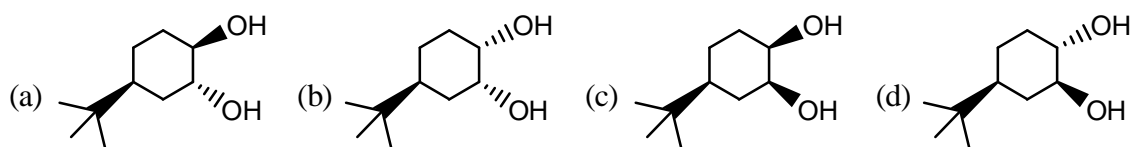
67. With respect to the two reactions shown below, the correct statements about their stereochemical nature is [LDA=LiN(^{i}Pr$_2$)]

(i) $\xrightarrow[\text{2. CH}_3\text{CH}_2\text{CH}_2\text{Br}]{\text{1. LDA}}$ P   (ii) $\xrightarrow[\text{2. CH}_3\text{CH}_2\text{CH}_2\text{Br}]{\text{1. LDA}}$ Q
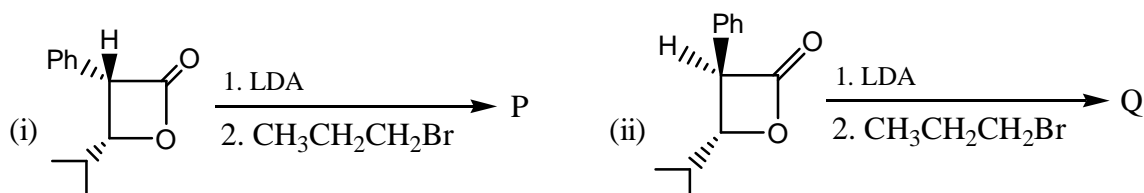
(a) The reactions are stereoselective, because P and Q are the same.
(b) The reactions are non-stereoselective, because P and Q are the same.
(c) The reactions are stereoselective, because P and Q are diastereomers.
(d) The reactions are enantioselective, because P and Q are enantiomers.

68. For the reactions shown below, identify the correct statement with regard to the products formed.

(i) $\xrightarrow{\text{MeOH, H}^+}$ P

(S)-styreneoxide

(ii) $\xrightarrow{\text{NaOMe/MeOH}}$ Q

(S)-styreneoxide

(a) P and Q are identical, both are optically active.
(b) P and Q are positional isomers, P is racemic and Q is optically active.
(c) P and Q are positional isomers, P is optically active and Q is racemic.
(d) P and Q are positional isomers, both are optically active.

69. In the reaction shown below, identify the correct combination of the intermediate P and the product Q.

 $\xrightarrow{\text{excess n-BuLi}}$ (P) $\xrightarrow{\text{Ph—CHO}}$ (Q)

(Ts = 4-methylphenylsulfonyl)

(a)

(P)   and   (Q)

(b)   and

       (P)   (Q)

(c)   and

       (P)   (Q)

(d)   and

       (P)   (Q)
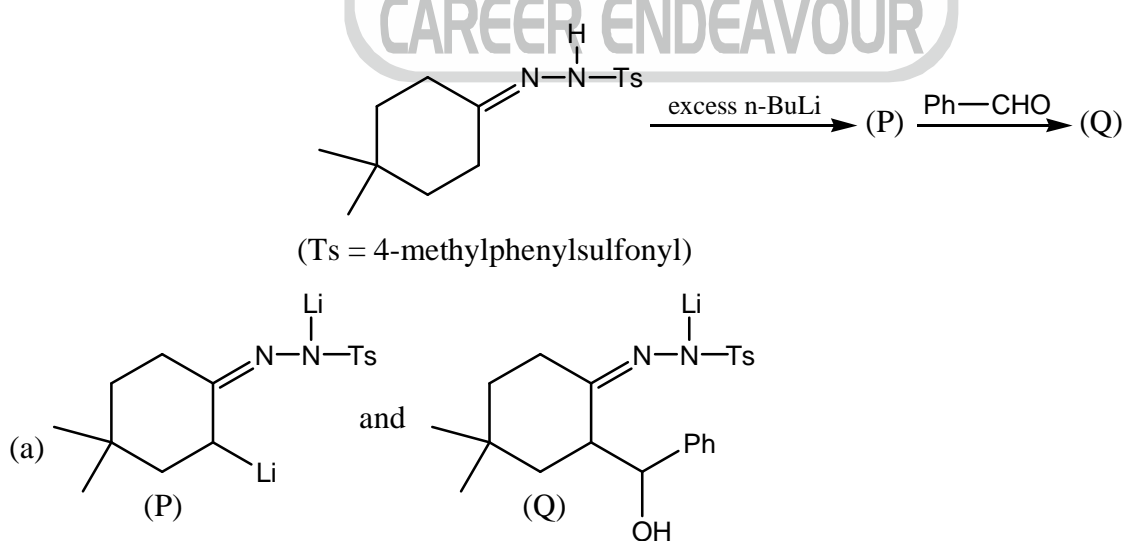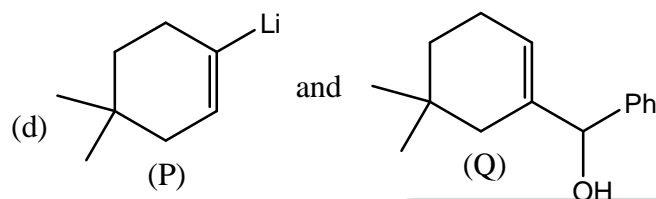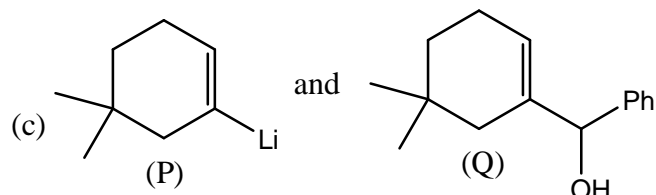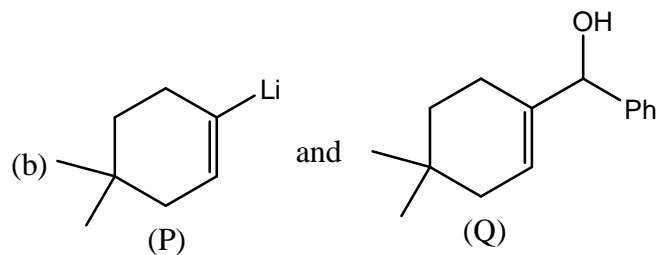
70.   In the two step reaction shown below, identify the correct combination of products P and Q.

(a) P and Q   (b) P and Q   (c) P and Q   (d) P and Q
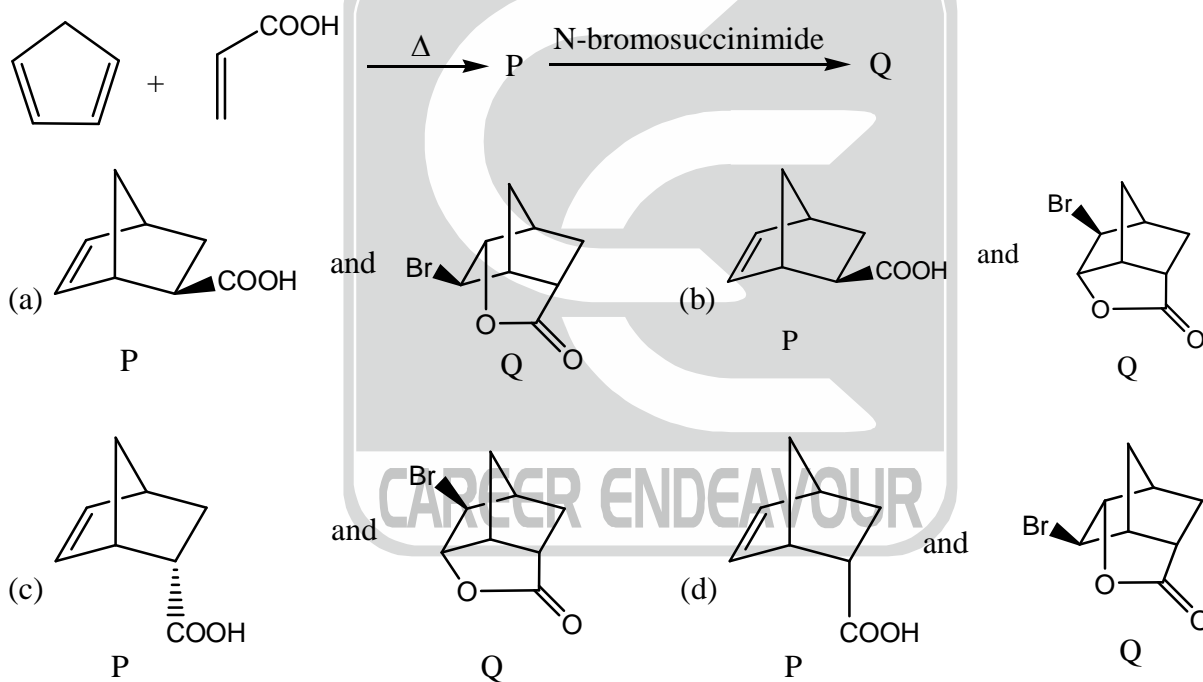
71.   On the basis of Favorskii rearrangement mechanism, the ratio of the products P, Q and R given below, will be, respectively.

(a) 2 : 1 : 1   (b) 1 : 1 : 1   (c) 1 : 0 : 1   (d) 0 : 1 : 1
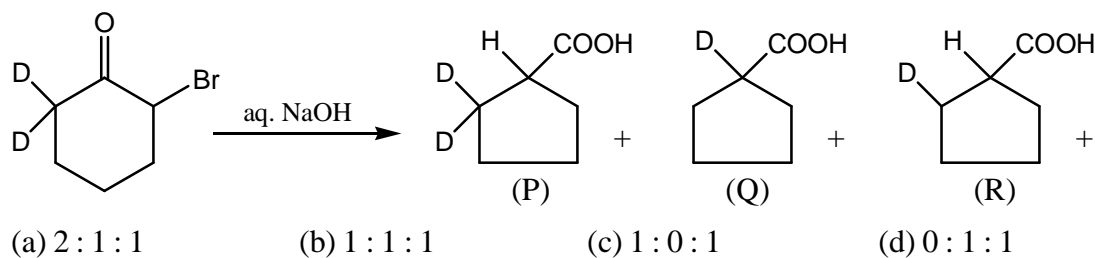
72. An organic compound having molecular formula $C_6H_{11}BrO_2$ exhibits the following peaks in ^1H NMR spectrum. $\delta\ 4.1\,(2H, q, J = 7.5\,Hz),\ 4.0\,(2H, t, J = 7.5\,Hz),\ 1.5 - 2.2\,(4H, m),\ 1.25\,(3H, t, J = 7.5\,Hz)$

The structure of the compound is:

(a)

(b)

(c)

(d)

73. The product P formed in the following three steps reaction is:

$$\xrightarrow[\text{3. } H_3O^+]{\substack{\text{1. LDA; TMSCl} \\ \text{2. } 150°C}} P$$

(a)   (b)   (c)   (d)
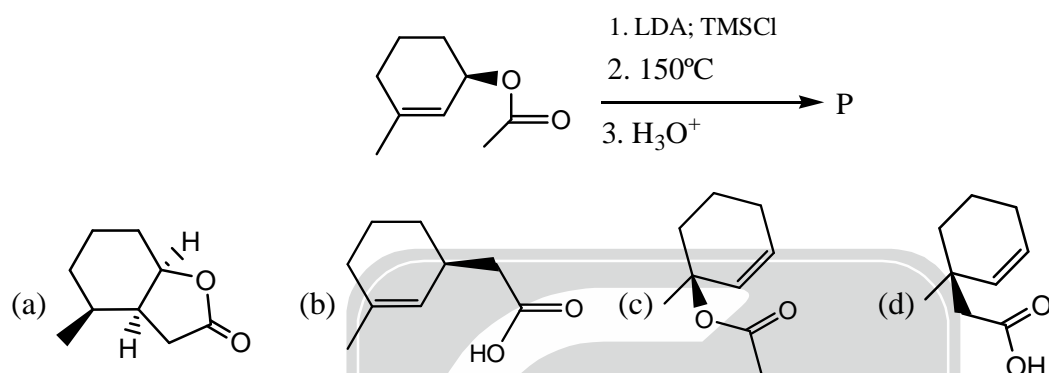
74. Identify the correct choice of reagents, among P, Q and R, for the transformation of norbornene into the epoxides I and II

P = H_2O_2–AcOH   Q = H_2O_2–NaOH   R = HOBr followed by aq. NaOH.

I   II

(a) P gives I and Q gives II   (b) R gives I and P gives II
(c) Q gives I and R gives II   (d) P gives I and R gives II
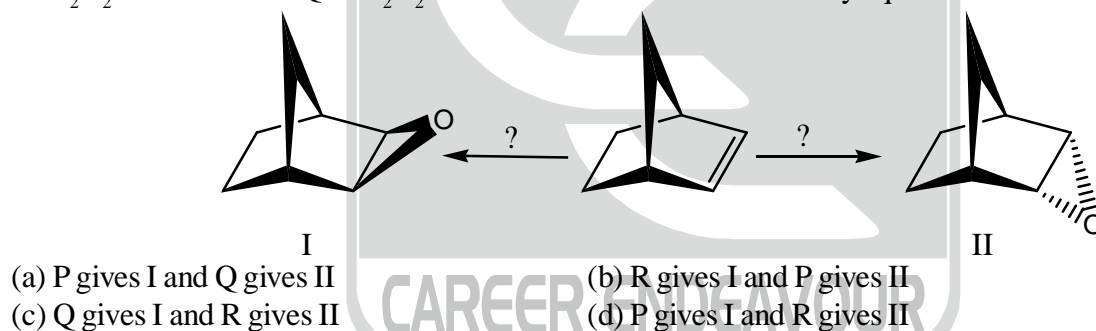
75. Reaction of ethyl acetoacetate with one equivalent of methylmagnesium bromide gives

(a)

(b)

(c)

(d)
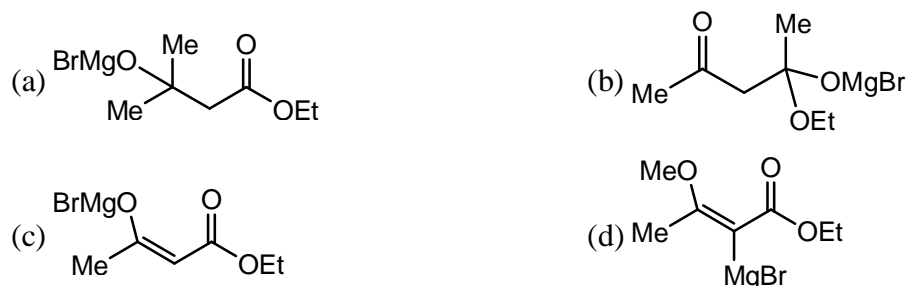
76. For the aldotetroses I-IV, the combination of TRUE statements, among P-T, is:

$$\text{I} \qquad \text{II} \qquad \text{III} \qquad \text{IV}$$
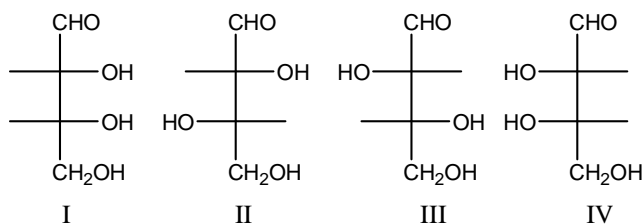
P=I and II are diastereomers and II and III are enantiomers.

Q=I and IV are mesomers and are optically inactive.

R=I and III can be interconverted by a base catalysed isomerisation.

S=only I and IV are HIO_4 cleavable.

T=I and III are D-sugars and II and IV are L-sugars.

(a) Q, R, T   (b) P, R, T   (c) Q, S, T   (d) P, Q, S

77. Match the compounds P-S with their carbonyl stretching frequencies (cm^{-1}) I–VI in IR spectroscopy.

P. acetone   I. 1870

Q. ethyl acetate   II. 1800

R. acetamide   III. 1740

S. acetyl chloride   IV. 1700

                                V. 1660

                                VI. 1600

(a) P-IV, Q-III, R-I, S-VI   (b) P-III, Q-VI, R-V, S-II

(c) P-IV, Q-III, R-V, S-II   (d) P-II, Q-V, R-III, S-VI

78. In the following three step transformation, identify the correct combination of product P, Q and R. [LDA=LiN(^{i}Pr)$_2$].
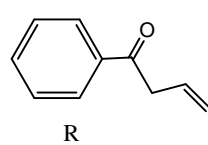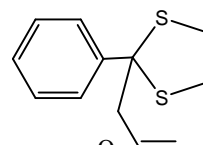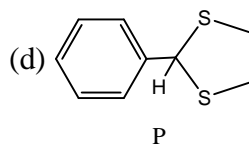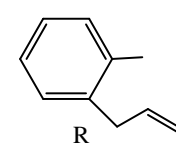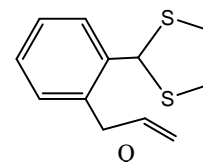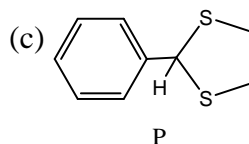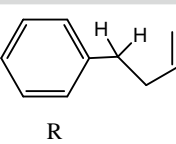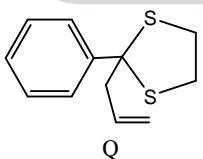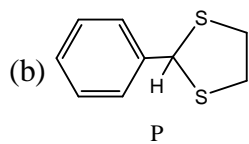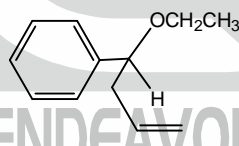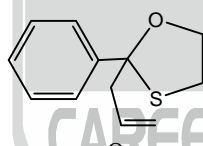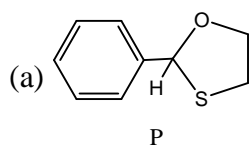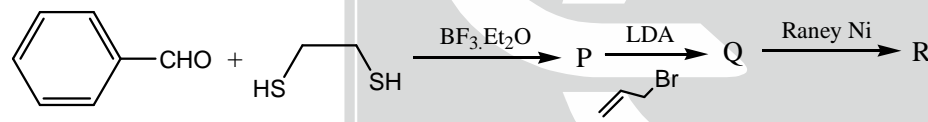
79. The major product P formed in the following photochemical reaction is:
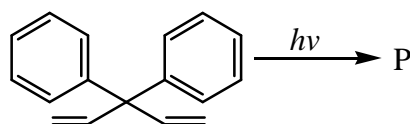
(a)

(b)

(c)

(d)

80. Three molecular ionic states, P-R, are possible for the amino acid histidine. Identify the correct choice of pH values, respectively, for the observation of the ionic states P-R.
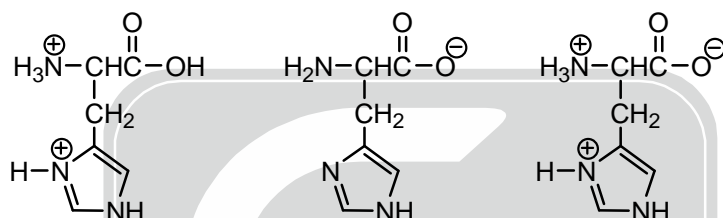
(a) P at pH 1; Q at pH 12 ; R at pH 7   (b) P at pH 7; Q at pH 1; R at pH 12
(c) P at pH 12; Q at pH 7; R at pH 1   (d) P at pH 12; Q at pH 1; R at pH 7

81. In the reaction shown below, identify the correct combination of the intermediate P and the product Q.
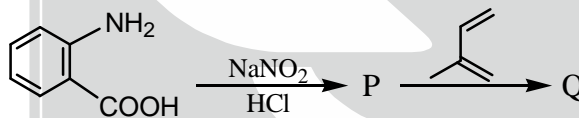
(a) and

(b) and

(c) and

(d) and

82. – 90. contain a Statement with a Reason and an Assertion. for each question, choose the correct answer from the following four choices.
(a) Both Reason and Assertion are correct   (b) Both reason and Assertion are wrong
(c) Reason is correct and Assertion is wrong   (d) Reason is wrong but Assertion is correct

82. **Statement :** solid carbon dioxide is called as dry ice.
Reason : CO_2 sublimes when kept in open atmosphere.
Assertion : Triple point of CO_2 lies above one atmosphere.

83. **Statement :** Entropy of pure, perfectly crystalline substance is zero at absolute zero of temperature.
    Reason : At absolute zero, molecules can have only one orientation.
    Assertion : Statistical definition of entropy is given by the equation, $S = k \ln W$, where W is the probability of orientation

84. **Statement :** Catalytic decomposition of ammonia on platinum takes place at 1000°C.
    Reason : Ammonia is more strongly adsorbed than hydrogen on platinum.

    Assertion : The rate law for the decomposition of ammonia on platinum is given as, $\text{Rate} = k \dfrac{p_{NH_3}}{p_{H_2}}$.

85. **Statement :** $CoCl_4^{2-}$ is a regular tetrahedron but $CuCl_4^{2-}$ is a distorted tetrahedron.

    Reason : Unsymmetrical distribution of electrons in e_g orbital leads to distortion in $CuCl_4^{2-}$.

    Assertion : Cl^- ligands interact differently with orbitals of unequal electron population. This leads to distortion in tetrahedral geometry.

86. **Statement :** Schottky and Frenkel defects are stoichiometric defect occurring in crystal lattices.
    Reason : Schottky defects are due to the absence of one positive and one negative ion and Frenkel defects are due to the presence of one hole and one ion in an interstitial position.
    Assertion : The ratio of number of atoms of one kind to the number of atoms of the other kind does not correspond exactly to the ideal whole number ratio implied by the formula which leads to stoichiometric defects.

87. **Statement :** Ga is below Al in Group IIIA, yet the atomic size of Ga is almost the same as that of Al.
    Reason : Lanthanide contraction
    Assertion : Poor shielding of nuclear charge results in outer electrons being more firmly held by the nucleus.

88. **Statement:** 5-Bromopyrimidine $(C_4H_3BrN_2)$ exhibits two prominent peaks in the mass spectrum at m/z 158 and 160 in the ratio of 1:1.

    Reason: There are two basic centres in the molecule, which are protonated.
    Assertion: There are two isotopes of bromine, ^{79}Br and ^{81}Br, that occur in the ratio of 1:1.
    Choose the correct answer from the following four choices.
    (a) Both Reason and Assertion are correct.   (b) Both Reason and Assertion are wrong
    (c) Reason is correct and Assertion is wrong.   (d) Reason is wrong but Assertion is correct.

89. **Statement :** Pyridine is more basic than pyrrole.
    Reason : The nitrogen in pyrrole carries a proton while the nitrogen in pyridine does not.
    Assertion : Nitrogens in trigonal geometry are generally more basic than the nitrogens in tetrahedral geometry.

90. **Statement :** Replacement of CH_3 with CF_3 decreases the rate decreases the rate of reaction I, but increases the rate of reaction II.
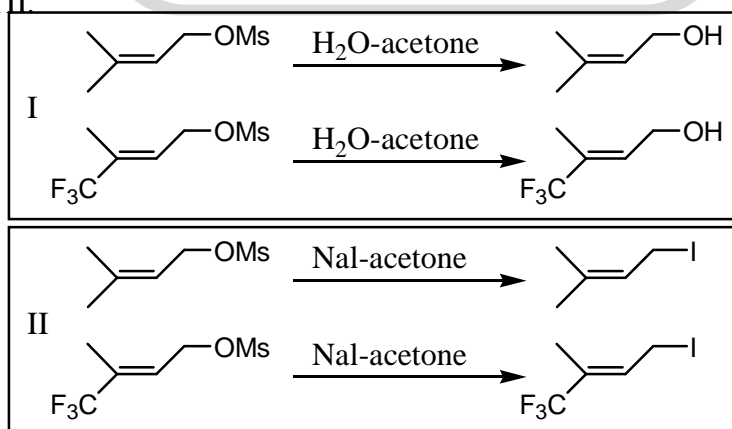
    Reason : Reaction I proceeds through SN_1 mechanism and reaction II proceeds through SN_2 mechanism.
    Assertion : Being an electron withdrawing group, CF_3 destabilizes the transition state in SN_1 reaction, but stabilizes the transition state in SN_2 reaction.

***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.30 : Carry ONE mark each.

1. The complexes $\left[Co(NH_3)_4(H_2O)Cl\right]Br_2$ and $\left[Co(NH_3)_4 Br_2\right]Cl.H_2O$ are examples of
   (a) ionization isomerism
   (b) linkage isomerism
   (c) geometric isomerism
   (d) optical isomerism

2. In the trigonal bipyramidal crystal field, the d orbital with the highest energy is
   (a) d_{xy}
   (b) $d_{x^2-y^2}$
   (c) d_{yz}
   (d) d_z^2

3. The magnetic moment of the complex $K_3\left[CoF_6\right]$ is 5.0 μ_B. The total stabilization energy will be
   (a) $-0.4\,\Delta_0$
   (b) $-0.4\,\Delta_0 + P$
   (c) $-2.4\,\Delta_0 + 3P$
   (d) $-1.8\,\Delta_0 + 3P$

4. The metal present at the active site of the protein carboxypeptidase A is
   (a) Zinc
   (b) molybdenum
   (c) magnesium
   (d) cobalt

5. The neutral complex which follows the 18-electron rule is
   (a) $\left(\eta^5 - C_5H_5\right)Fe(CO)_2$
   (b) $\left(\eta^5 - C_5H_5\right)Mo(CO)_3$
   (c) $\left(\eta^5 - C_5H_5\right)_2 CO$
   (d) $\left(\eta^5 - C_5H_5\right)Re\left(\eta^6 - C_6H_6\right)$

6. The shape of the molecule XeO_2F_2 is
   (a) distorted tetrahedral
   (b) square planar
   (c) trigonal bipyramidal
   (d) tetrahedral

7. Triplet superphosphate is made by treating phosphate rock with
   (a) conc. H_2SO_4
   (b) conc. HNO_3
   (c) conc. HCl
   (d) conc. H_3PO_4

8. The number of hydroxy (OH) groups present in phosphorus acid is
   (a) one
   (b) two
   (c) three
   (d) four

9. Out of the following, the one which is not an excitation source for IR spectrometer is
   (a) Tungsten filament lamp
   (b) Nernst glower
   (c) Deuterium lamp
   (d) Mercury arc

10. One of the following is not related to polarography
   (a) limiting current
   (b) diffusion current constant
   (c) Ilkovic equation
   (d) current efficiency

11. Among the following, the optically inactive compound is:

   (a)

   (b)

   (c)

   (d)
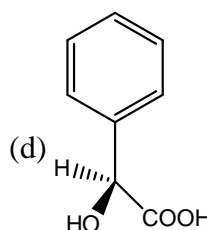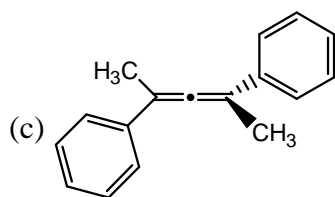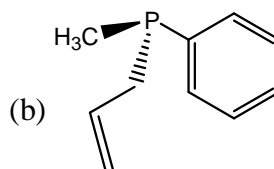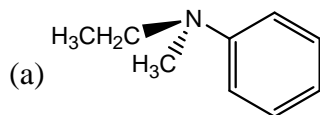
12. Esterification of the acid P with the alcohols Q will give

(S)-P   (±)-Q
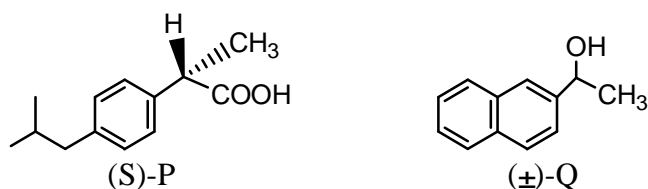
(a) only one enantiomer   (b) a mixture of diastereomers

(c) a mixture of enantiomers   (d) only one diastereomer

13. ^{1}H NMR spectrum of [18]-annulene shows

(a) Only one peak at $\delta\, 7.2\, (18\, H)$

(b) Only one peak at $\delta\, 5.0\, (18\, H)$

(c) Two peaks at $\delta\, 9.0\, (12\, H)$ and $\delta\text{-}3.0\, (6\, H)$

(d) Two peaks at $\delta\, 9.0\, (6\, H)$ and $\delta\text{-}3.0\, (12\, H)$

14. The compound formed on methanolysis of P is
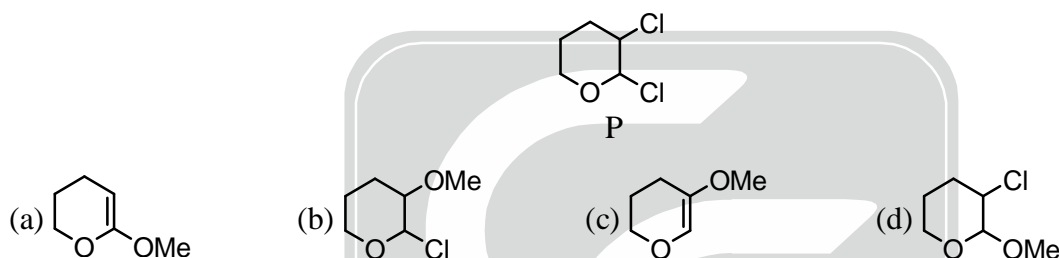
15. The pK_a values for the three ionizable groups X, Y and Z of glutamic acid are 4.3, 9.7 and 2.2 respectively

$$CO_2H - CH_2 - CH - CO_2H$$

X $+NH_3$ Z

Y
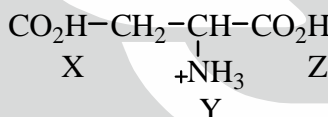
The isoelectric point for the amino acid is

(a) 7.00   (b) 3.25   (c) 4.95   (d) 5.95

16. Bridge-head hydrogen of the conformer of cis-decalin is positioned as

(a) a, a   (b) e, e   (c) a, e   (d) pseudo-a, pseudo-e

[a = axial; e = equatorial]

17. The major product of the acetylation of salicylic acid with Ac_2O/H^+ followed by heating with anhydrous $AlCl_3$ is
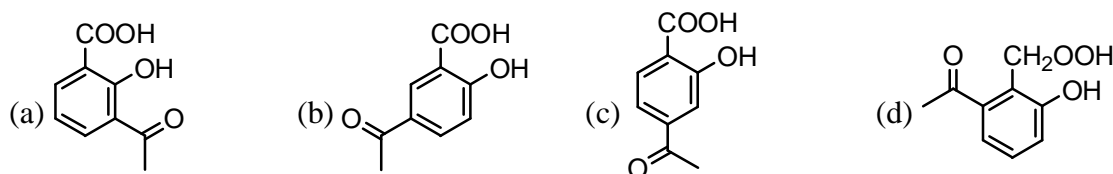
18. Order of reactivity of the following dienes X, Y and Z in Diels-Alder reaction is

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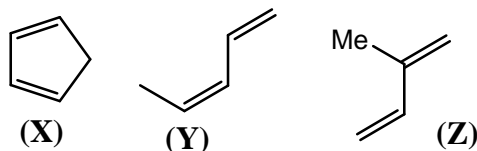
(a) X > Z > Y   (b) Y > X > Z
(c) Y > Z > X   (d) X > Y > Z

19. The major product P of the following reaction is

$$\xrightarrow[\text{t-BuOH}]{\text{Li, Liq. NH}_3} \text{(P)}$$

(a)   (b)   (c)   (d)
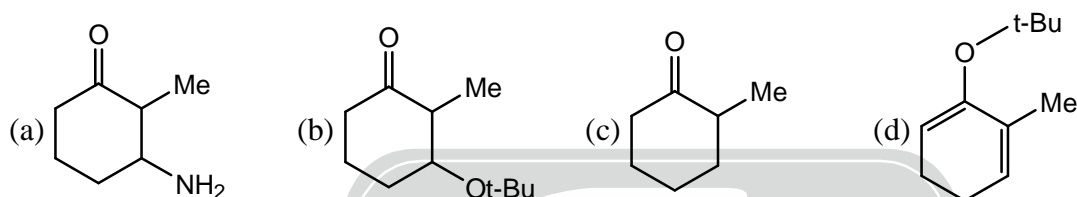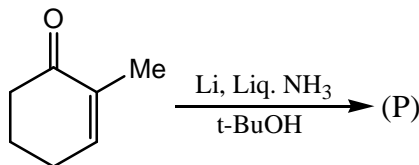
20. Among the following, the most stable isomer for 3-methoxycyclohexanol is:

(a)   (b)   (c)   (d)
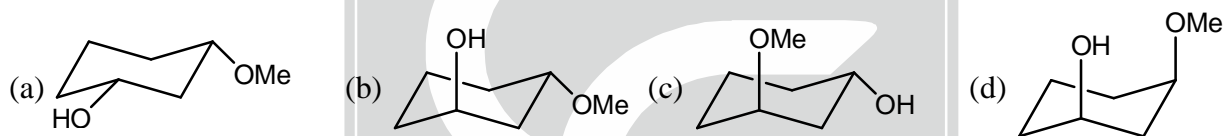
21. A reaction follows second order rate law, $-d[A]/dt = k[A]^2$, if
    (a) a plot of [A] versus t is a straight line   (b) a plot of 1/[A] versus t is a straight line
    (c) a plot of ln[A] versus t is a straight line   (d) a plot of $e^{[A]}$ versus t is a straight line

22. In an adiabatic system, the work done to change its state from A to B is
    (a) dependent on path from A to B
    (b) independent of path from A to B
    (c) path dependence is related to particulars of states A and B
    (d) path dependence is related to both states A and B and choice of path

23. The set of eigenfunctions $\sqrt{\dfrac{2}{a}}\sin\dfrac{n\pi x}{a}\left(0 \le x \le a,\ n = 1, 2, 3...\right)$ is

    (a) orthogonal   (b) normalized
    (c) both orthogonal and normalized   (d) unnormalized

24. The function $e^{ax^2}\ (\alpha > 0)$ is not an acceptable wave function for bound system, because

    (a) it is not continuous   (b) it is multivalued
    (c) it is not normalisable   (d) all of these

25. First order perturbation correction $\Delta\varepsilon_n^{(1)}$ to energy level ε_n of a simple harmonic oscillator due to the

    anharmonicity perturbation γx^3 is given by

    (a) $\Delta\varepsilon_n^{(1)} = \gamma$ (b) $\Delta\varepsilon_n^{(1)} = \gamma^2$ (c) $\Delta\varepsilon_n^{(1)} = \gamma^{-1}$ (d) $\Delta\varepsilon_n^{(1)} = 0$

26. Resonant frequencies for EPR and NMR are respectively in the spectral region
    (a) microwave and far-IR
    (b) far-IR and microwave
    (c) radiofrequency and microwave
    (d) microwave and radiofrequency

27. The 2s orbital of H-atom has radial node at $2a_0$ because ψ_{2s} is proportional to

    (a) $\left(\dfrac{1}{2}+\dfrac{r}{a_0}\right)$ (b) $\left(2+\dfrac{r}{a_0}\right)$ (c) $\left(2-\dfrac{r}{a_0}\right)$ (d) $\left(2-\dfrac{r}{2a_0}\right)$

28. Given that the mean speed of H_2 is 1.78 km s^{-1}, the mean speed of D_2 will be
    (a) 1.26 km s^{-1} (b) 2.52 km s^{-1} (c) 5.04 km s^{-1} (d) 3.17 km s^{-1}.

29. The triple point for water is
    (a) unique
    (b) depends on p but is independent of T
    (c) depends on T but is independent of P
    (d) depends on both P and T

30. Hydrolysis of urea by urease is
    (a) first order at high concentration of urea
    (b) zero order at high concentration of urea
    (c) independent of the concentration of urea
    (d) first order with respect to both urea and urease

Q.31 – Q.85 : Carry TWO marks each.

31. The rate of exchange of cyanide ligands in the complexes (i) $\left[Ni(CN)_4\right]^{2-}$, (ii) $\left[Mn(CN)_6\right]^{3-}$ and (iii)

    $\left[Cr(CN)_6\right]^{3-}$ by ^{14}CN follow the order.
    (a) ii > i > iii   (b) iii > i > ii   (c) i > iii > ii   (d) i > ii > iii

32. Ligand field stabilization energies are smaller for lanthanides compared to transition metals in the same oxidation state because
    (a) size of lanthanide ions are larger
    (b) f orbitals interact less effectively with ligands
    (c) size of lanthanide ions are smaller
    (d) lanthanides favour oxygen donor ligands

33. For the metal-olefin complexes (i) $[PtCl_3(C_2H_4)]^-$ and (ii) $[PtCl_3(C_2F_4)]^-$, the correct statement is that
    (a) carbon-carbon bond length is same both in (i) and (ii)
    (b) carbon-carbon bond length in (i) is smaller compared to that of (ii)
    (c) carbon-carbon bond length in (i) is larger compared to that of (ii0
    (d) a metallacycle is formed in each complex

34. A solution containing 47 ppm of a compound X (FW 225) has a transmittance of 29.7% in a 1.5 cm cell at 400 nm. The molar absorptivity in L mol^{-1} cm^{-1} is

    (a) 1.89×10^3 (b) 1.42×10^3 (c) 1.68×10^3 (d) 1.79×10^3

35. The values of M–C stretching frequencies of (i) $\left[V(CO)_6\right]^-$, (ii) $\left[Cr(CO)_6\right]$ and (iii) $\left[Mn(CO)_6\right]^+$ follow the trend
    (a) (ii) > (i) > (iii)   (b) (ii) > (iii) > (i)   (c) (i) > (ii) > (iii)   (d) (iii) > (ii) > (i)

36. A substance undergoes a two electron reversible reduction at dropping mercury electrode, and gives a diffusion current of $7.5\mu A$. When the potential at the dropping mecury electrode is –0.615 V, the current is

    $1.5 \mu A$. The $E_{1/2}$ (in volt) will be
    (a) –0.683   (b) –0.674   (c) –0.652   (d) –0.633

37. The lanthanide complex (acac = acetylacetonate; phen = 1, 10-phennathroline) that do not have square antiprismatic structure is

(a) $\left[Ce(NO_3)_6 \right]^{2-}$

(b) $\left[La(acac)_3(H_2O)_2 \right]$

(c) $\left[Ce(acac)_4 \right]$

(d) $\left[Eu(acac)_3(Phen) \right]$

38. Among the following, the incorrect statement about SiC is that
(a) it is known as corundum
(b) it is prepared by reducing quartz with a slight excess of coke in an electric furnace at 2000–2500°C
(c) pure SiC is almost colourless or pale yellow
(d) its hardness is slightly less than diamond.

39. The incorrect statement regarding carboranes is that
(a) carbon tends to adopt the position of the lowest coordination number on the polyhedron
(b) CH groups tend to be more positive than BH groups with the same coordination number
(c) carbon tends to keep as close as possible to other carbon atoms
(d) generally, arachno-carboranes are less stable thermally than the corresponding closo-carboranes

40. The incorrect statement for solid sodium chloride is that

(a) both sodium and chloride ions adopt inert gas configuration
(b) the conduction band is full
(c) the condduction band is empty
(d) the valence band is full

Q.41 – Q.48 required matching of items of *Column-I* with the appropriate items in *Column-II*. Choose the correct one from the alternatives (a), (b), (c) and (d)

41. **Column-I**   **Column-II**

(P) Cytochromec   (I) Molybdenum
(Q) Calmodulin   (II) Potassium
(R) Chlorophyll   (III) Magnesium
(Q) Alcohol dehydrogenase   (IV) Zinc
                                                       (V) Iron
                                                       (VI) Calcium

(a) P-V, Q-VI, R-III, Q-V   (b) Q-II, Q-III, Q-IV, Q-VI
(c) R-III, R-IV, R-VI, R-III   (d) S-IV, S-V, S-II, S-IV

42. **Column-1**   **Column-2**

P. Atomic absorption   I. Transition time
Q. Chronopotentiometry   II. Cell constant
R. Spectrophotometry   III. Coulomb
S. Conductometry   IV. Molar absorptivity
                                                       V. Limiting current
                                                       VI. Hollow cathode lamp

Codes:
(a) P-I, Q-III, R-IV, S-V   (b) P-VI, Q-I, R-IV, S-II
(c) P-II, Q-III, R-IV, S-V   (d) P-V, Q-VI, R-II, S-IV

43. Require matching of items of **Column I** with the appropriate items in **Column - II.** Choose the correct one from the alternatives (a), (b), (c) and (d).

Column - I

P: Wilkinson's catalyst

Q: Speiers's catalyst

R: Water gas shift catalyst

S: Zeolite ZSM-5 catalyst

Column - II

I. trans $-IrCl(CO)(PPh_3)_2$

II. Hydrosilylation

III. $RhCl(PPh_3)_3$

IV. Synthetic gasoline

V. hydroformlylation

VI. Zinc-copper oxide.

(a)	(b)	(c)	(d)
P-III	P-I	P-V	P-III
Q-II	Q-V	Q-II	Q-VI
R-VI	R-III	R-VI	R-IV
S-IV	S-IV	S-IV	S-II

44. **Column-1**

P. Ostwald process

Q. Solvay process

R. Mond process

S. Frasch process

Column-2

I. Manufacture of nickel

II. Manufacture of nitric acid

III. Manufacture of Na_2CO_3

IV. Manufacture of silicones

V. Manufacture of caustic soda

VI. Mining of elemental sulfur

Codes:

(a) P-I, Q-III, R-II, S-VI

(b) P-II, Q-III, R-I, S-VI

(c) P-II, Q-I, R-IV, S-V

(d) P-III, Q-II, R-V, S-VI

45. **Column-I (Compounds)**

P. cyclohexanone

Q. cyclopentanone

R. cyclobutanone

S. cyclopropanone

Column-2 (Carbonyl stretching frequency (cm^{-1}))

I. 1910

II. 1715

III. 1813

IV. 1650

V. 1780

VI. 1745

Codes:

(a) P-I, Q-II, R-III, S-IV

(b) P-II, Q-VI, R-V, S-III

(c) P-VI, Q-V, R-IV, S-III

(d) P-I, Q-V, R-IV, S-III

46. **Column-I**

P. Many electron wave function

Q. Low temperature

R. Mean speed

S. Molecular ensemble

Column-2

I. Adiabatic demagnetization

II. Slater determinant

III. Partition function

IV. maxwellian distribution

V. LCAO-MO

VI. Photoejection

Codes:

(a) P-IV, Q-I, R-VI, S-III

(b) P-II, Q-I, R-IV, S-III

(c) P-II, Q-V, R-VI, S-IV

(d) P-VI, Q-IV, R-III, S-II

47. Require matching of items of **column - I** with the approriate items in **column - II.** Choose the correct one from the alternative (a), (b), (c) and (d).

Column - I	**Column - II**
Spectral Technique	**Selection Rule**
P. Rotational transition	**I.** $\Delta v = \pm 1$
Q. Vibrational transition	**II.** $\Delta J = 0$
R. Electronic transition in atoms	**III.** $\Delta J = \pm 1$
S. Molecular ensemble	**IV.** $\Delta l = \pm 1$
	V. $\Delta m_l = \pm 1$
	VI. $\Delta v = 0$
	VII. $\Delta l = 0$

(a) P-I, Q-VI, R-VII, S-V　　　　　(b) P-II, Q-I, R-IV, S-V
(c) P-III, Q-I, R-IV, S-V　　　　　(d) P-I, Q-VI, R-VII, S-V

48.

Column-1 (Molecular species)	**Column-2 (Bond order and magnetic property)**
P.　O_2^-	I.　2.5, paramagnetic
Q.　O_2	II.　2.0, diamagnetic
R.　O_2^+	III.　1.5, diamagnetic
S.　O_2^{2-}	IV.　1.0, diamagnetic
	V.　2.0, paramagnetic
	VI.　1.5, paramagnetic

Codes:
(a) P-III, Q-V, R-IV, S-III　　　　(b) P-II, Q-II, R-IV, S-III
(c) P-III, Q-V, R-IV, S-VI　　　　(d) P-VI, Q-V, R-I, S-IV

49. The major product P formed in the given
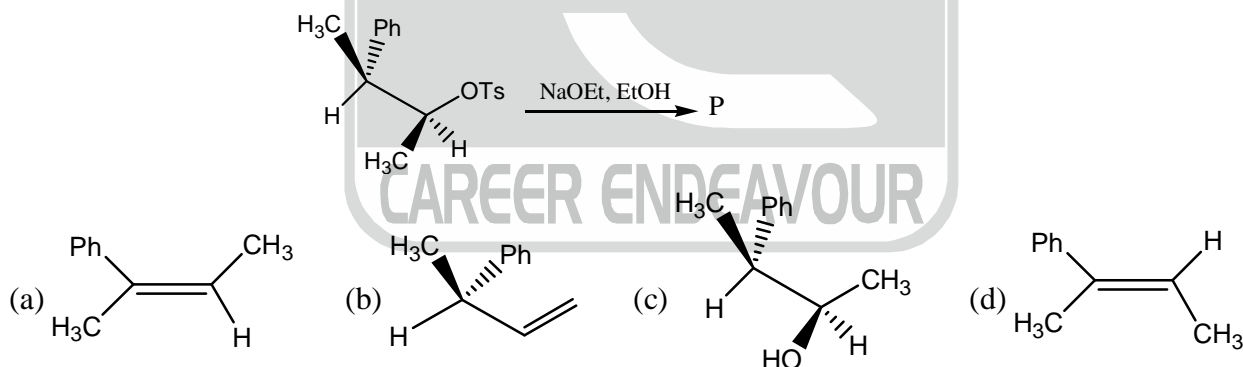
50. The order of reactivity towards acid catalyzed hydrolysis of the following cyclic acetals is:

(a) $Z > Y > X$　　　　(b) $X > Y > Z$　　　　(c) $X > Z > Y$　　　　(d) $Z > X > Y$
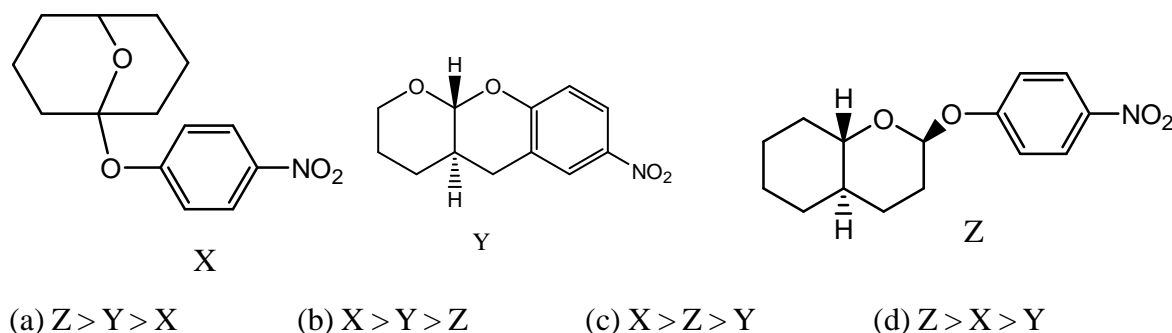
51. The binaphthol (Bnp) is:
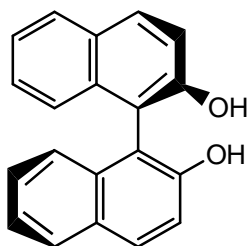
    (a) An optically active compound with (R)-configuration.
    (b) An optically inactive compound.
    (c) A meso compound
    (d) An optically active compound with (S)-configuration.

52. In the given reactions, identify the correct combination of their major products P and Q $[LDA = LiN(i\text{-}Pr)_2]$
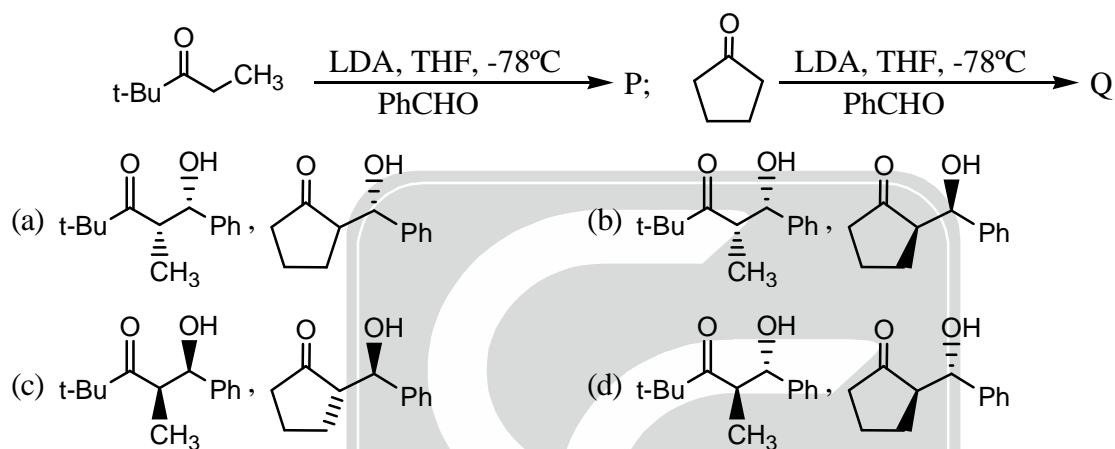
53. The major stereoisomer obtained in the reaction of (S)-2-phenylpropanal with MeMgBr is:
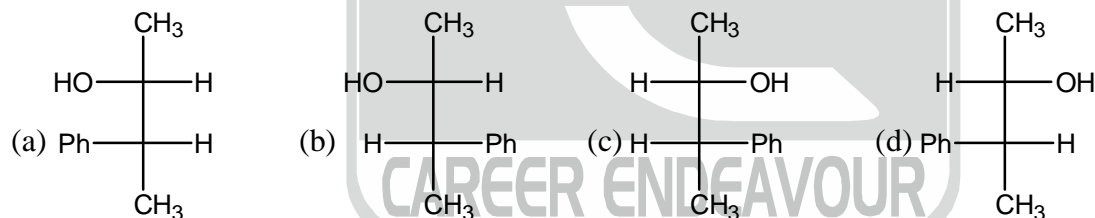
54. The major product P formed in the following reaction is
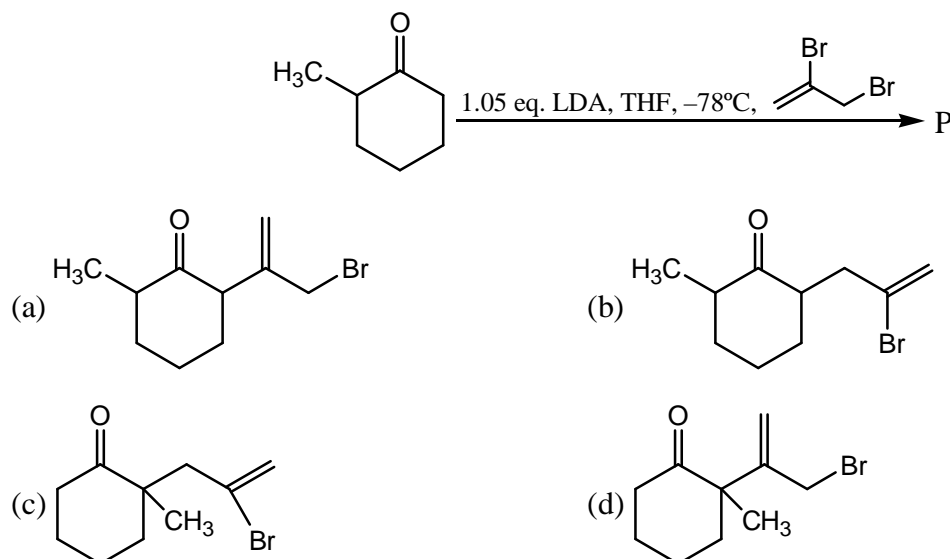
55.   Iodo-lactonization of β, γ – unsaturated carboxylic acid X with I_2 and $NaHCO_3$ gives.

X

(a)   (b)   (c)   (d)
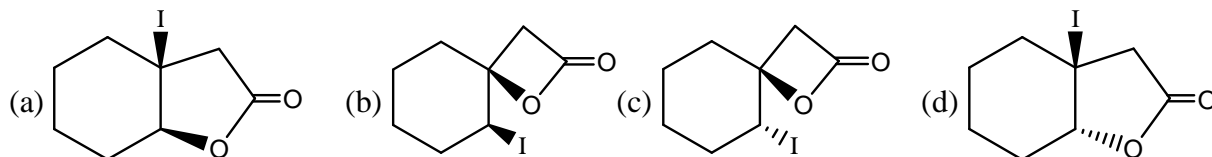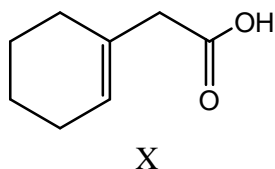
56.   The major stereoisomer P obtained in the following reaction is:

(a)   (b)   (c)   (d)
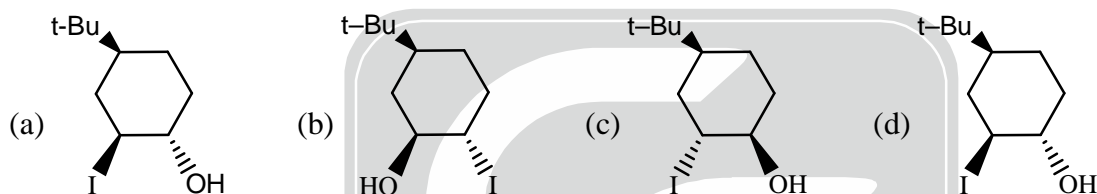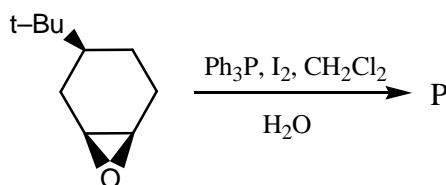
57.   The major product P of the following reaction is:

(a)   (b)   (c)   (d)
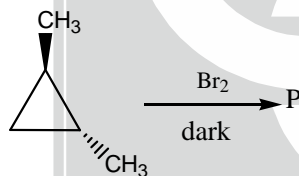
58.   Cis-and trans-2-methyl-5-t-butyl-1, 3-dioxane each can exist as two conformers as shown below
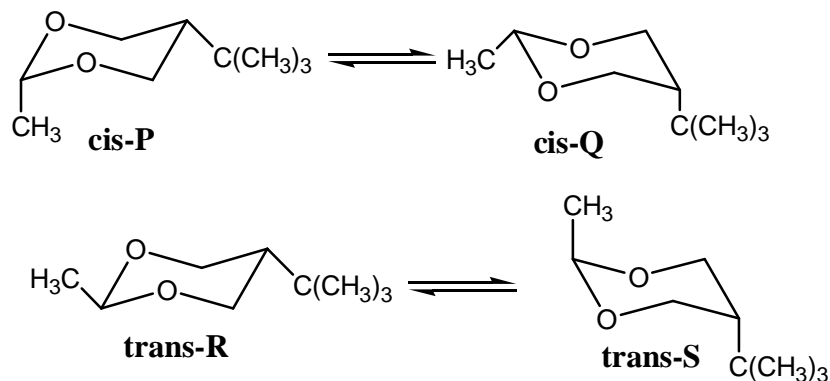
The preferred conformations for the cis- and trans-compounds will be

(a) P, R   (b) Q, S   (c) P, S   (d) Q, R

59. The major product P of the given reaction is
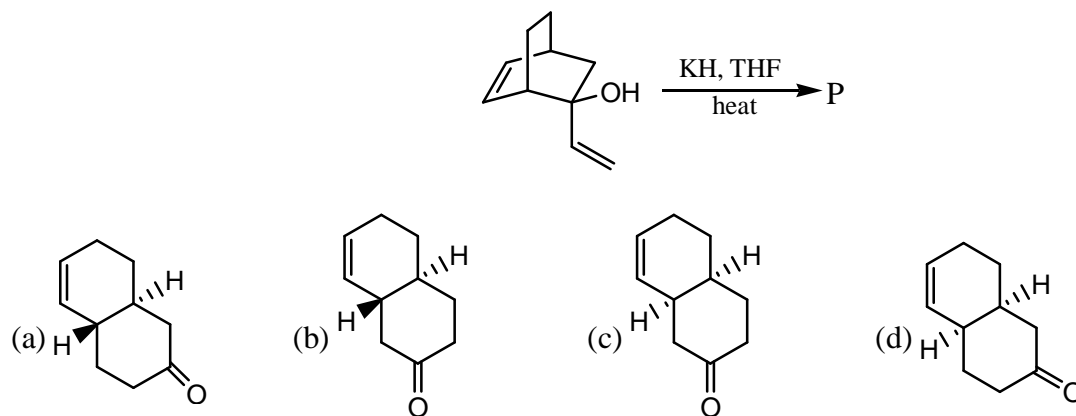
60. The major product P formed in the following photochemical reaction is
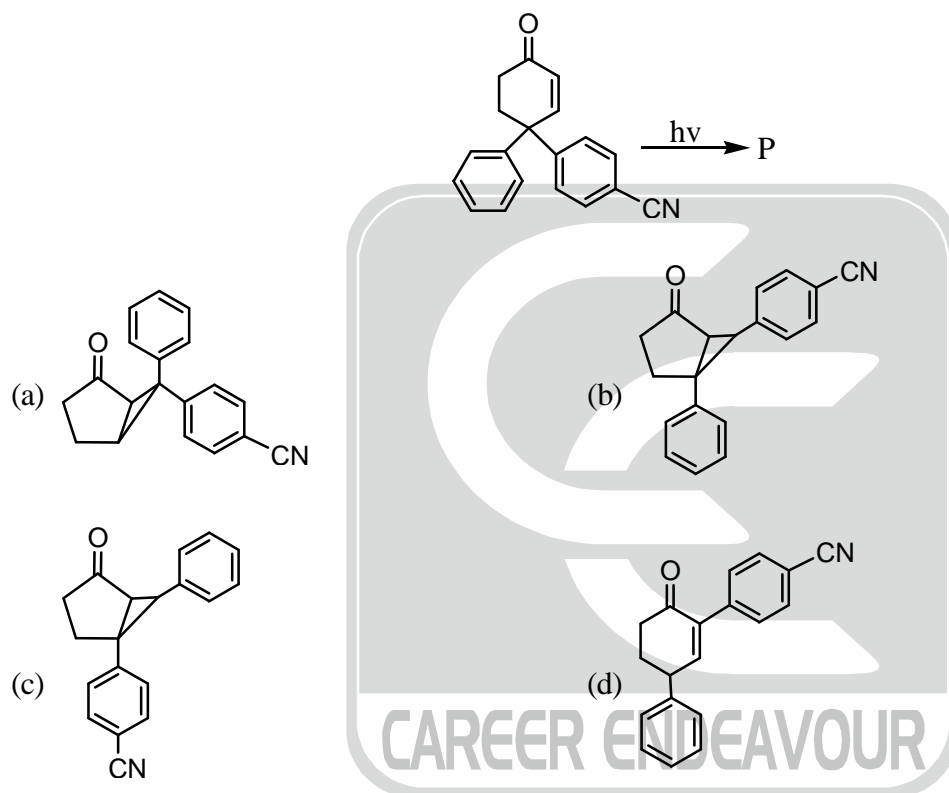
61. An organic compound having molecular formula $C_8H_{12}O_2$ exhibits the following peaks in IR and ^1H NMR spectra.

$IR : 1720 \left(cm^{-1} \right)$

$^1H\ NMR : 6.95\,(1H,\ d,\ J = 8.5\ Hz)\ 5.90\,(1H, d, J = 8.5\ Hz),\ 4.53\,(1H, q, J = 6\ Hz),$

$1.41\,(3H, d, J = 6\ Hz), 1.20\,(3H, s), 1.15\,(3H, s)$
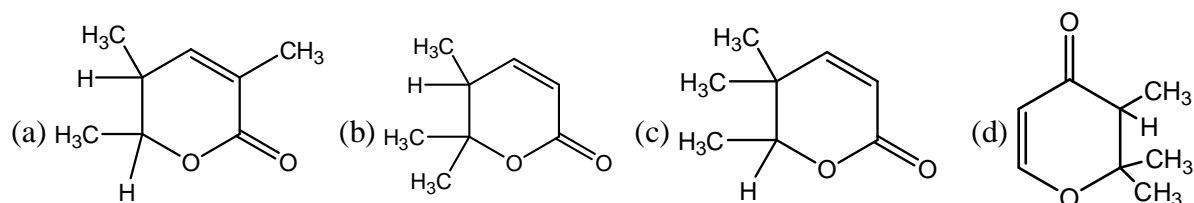
62. The phase diagram of $NaCl-H_2O$ is of simple eutectic type. The utectic composition is 23.3 weight% NaCl and it freezes at –21.1°C. The phases present in a solution containing 10 weight% NaCl at –20°C are
    (a) ice + NaCl solution   (b) ice + solid NaCl
    (c) NaCl + pure water   (d) NaCl + saturated NaCl solution

63. Hydrogen adsorption on a platinum surface is
    (a) Endothermic with positive ΔS and positive ΔG
    (b) Endothermic with positive ΔS and negative ΔG
    (c) Exothermic with negative ΔS and negative ΔG
    (d) Exothermic with positive ΔS and negative ΔG

64. In the reversible chemical reaction taking place under standard condition at 298 K and 1 atm in a Daniel cell,
    $$Zn \left| Zn^{2+}(aq) \right| \left| Cu^{2+}(aq) \right| Cu$$
    the heat change is:
    (a) equal to ΔH^0 (b) equal to $T\Delta S^0$ (c) equal to zero   (d) equal to ΔU^0

65. The orbital $\psi = 1s_{H_A} - 1s_{H_B}$ of water belongs to the irreducible representation
    (a) A_1 (b) B_1 (c) A_2 (d) B_2

66. The vibrational partition function for a molecule with fundamental frequency v is given by
    (a) $\exp\left(-\dfrac{\hbar v}{k_B T}\right)$ (b) $\left[1 - \exp\left(-\dfrac{\hbar v}{k_B T}\right)\right]^{-1}$
    (c) $\exp\left(-\dfrac{\hbar v}{k_B T}\right)\left[1 - \exp-\left(\dfrac{\hbar v}{k_B T}\right)\right]^{-1}$ (d) $\exp\left(-\dfrac{\hbar v}{2k_B T}\right)\left[1 - \exp-\left(\dfrac{\hbar v}{k_B T}\right)\right]^{-1}$

67. The internal pressure, $\pi_T = T\left(\dfrac{\partial P}{\partial T}\right)_V - P$ for one mole a Vander waals gas is
    (a) $\dfrac{a}{V^2}$ (b) $\dfrac{a}{V^2}\left(\dfrac{RT}{V-b}\right)$ (c) Zero   (d) $\dfrac{RT}{V-b}$

68. A gaseous sample on exposure to total radiant energy of 6.626 J at 300 nm results in the photodissociation of 10^{-3} mol of this sample. Assuming the sample absorbs all the light, the quantum yield for this photochemical reaction is:
    (a) 6.023   (b) 0.602   (c) 60.230   (d) 0.060

69. If standard emf of the cell,
    $$Cu \,|\, Cu^{2+}(aq) \,||\, [Cu(NH_3)_4]^{2+}, aq. \, NH_3 \,|\, Cu$$
    is 0.35, then stability constant of the formation cupric amine complex is
    (a) 1.0×10^{27} (b) 8.4×10^5 (c) 7.0×10^{11} (d) 4.3×10^{13}

70. Standard entropy of crystalline carbon monoxide (in J/mol) at 0 K is around
    (a) 0.03   (b) 2.50   (c) Zero   (d) 5.76

71. Matals used in automobile catalytic converters are:
    (a) Pt and Pd   (b) Pt and Rh   (c) Pd and Rh   (d) Rh and Ni

Q. 72 to Q. 77 contain a Statement with a Reason and an Assertion. For each question, choose the correct answer from the following four choices.
(a) Both Reason and Assertion are correct   (b) Both Reason and Assertion are wrong
(c) Reason is correct but Assertion is wrong   (d) Reason is wrong but Assertion is correct

72. Statement: The characteristic spectroscopic feature of the quadruply bonded $\left[Re_2Cl_8\right]^{2-}$ is a strong royal blue colur

Reason: This is due to an absorption band in the visible region due to excitation of an electron from $\sigma^2\pi^4\delta^2$ ground state to $\sigma^2\pi^4\delta^1\delta^{*1}$ excited state

Assertion: This transition is quantum mechanically allowed

73. Statement: For the reaction $L_nMH \rightarrow L_nM^- + H^+$, the important factors are the strength of the M–H bond and the nature of the ligand, L

Reason: The key here is the stability of the complex ion, L_nM^-

Assertion: Weak π-bonding ligands will stabilize L_nM^- and so will disfavour the forward reaction.

74. **Statement:** D-Glucose and D-mannose give the same phenylosazone.   **[GATE 2005]**
Reason: Osazone formation results in a loss of the stereocentre at C_2 but does not affect other stereocenters.
Assertion: D-Glucose and D-mannose are enantiomers.
(a) Both **Reason** and **Assertion** are correct
(b) Both **Reason** and **Assertion** are wrong.
(c) **Reason** is correct but **Assertion** is wrong.
(d) **Reason** is wrong but **Assertion** is correct.

75. **Statement:** Nucleosides are stable in dilute base but undergo hydrolysis in dilute acid.   **[GATE 2005]**

Reason: Nucleosides have an N-glycosidic linkage.
Assertion: N-Glycosidic linkage behaves like an O-glycosidic linkage which is rapidly hydrolyzed by aqueous acid but stable in aqueous base.
(a) Both **Reason** and **Assertion** are correct
(b) Both **Reason** and **Assertion** are wrong.
(c) **Reason** is correct but **Assertion** is wrong.
(d) **Reason** is wrong but **Assertion** is correct.

76. **Statement :** For the reaction of $NO + O_2 \rightarrow 2NO_2$ the rate constant is observed to decrease with temperature.
Reason : As per the proposed mechanism, the first step is the dimerization of nitric oxide which is exothermic.
Assertion : Rate law = $k_2K.[NO]_2[O_2]$
(a) Both Reason and Assertion are correct
(b) Both Reason and Assertion are wrong
(c) Reason is correct but Assertion is wrong
(d) Reason is wrong but Assertion is correct.

77. Statement: Hydrogen gas gets warmer on expanding under isenthalpic condition
Reason: Joule Thomson coefficient for hydrogen is –0.03 K/atm
Assertion: Attractive forces are the dominant intermolecular interactions in hydrogen gas at 273 K.

Common Data for Q. 78, Q.79 and Q.80:
Vapour pressures of water above pure liquid water 24, 529 and 760 torr respectively at 298, 363 and 373 K. Use these data to answer the questions 78, 79 and 80.

78. Change in chemical potential (in kJ/mol) for the equilibrium H_2O (liquid) = H_2O (gas) at 298K is
(a) 8.6   (b) –3.8   (c) 7.87   (d) 3.72

79. Aqueous solution of sodium chloride $(\chi_{NaCl} = 0.015)$ at 298 K is in equilibrium with a water vapour pressure (in torr) of

(a) 23.64   (b) 748.60   (c) 24.36   (d) negligible

80. Average value of enthalpy of vaporisation (in kJ/mol) of water between 363 and 373 K is

(a) 42.50   (b) 40.80   (c) –40.65   (d) –40.80

Linked Answer Q.81(a) and Q.81(b):

81.(a) As per Huckel theory, π-electron energy levels of cyclobutadiene are

(a) $\alpha + 2\beta, \alpha + \beta, \alpha - \beta, \alpha - 2\beta$ (b) $\alpha + 2\beta, \alpha - \beta, \alpha - \beta, \alpha - 2\beta$

(c) $\alpha + 2\beta, \alpha, \alpha, \alpha - 2\beta$ (d) $\alpha + \beta, \alpha - \beta, \alpha - \beta, \alpha - 2\beta$

81.(b) Given that $\beta = -75 \; kJ/mol$, cyclobutadiene is

(a) paramagnetic and its lowest absorption energy is 150 kJ

(b) paramagnetic and its lowest absorption energy is 75 kJ

(c) diamagnetic and its lowest absorption energy is 75 kJ

(d) diamagnetic and its lowest absorption energy is 150 kJ.

Linked Answer Q.82(a) and Q.82(b):

82.(a) For the complex ion $\left[Cu(NH_3)_6 \right]^{2+}$, the coordination geometric will be

(a) octahedral   (b) tetragonally distorted octahedral

(c) trigonal prismatic   (d) trigonal antiprismatic

82.(b) The number of possible d-d transitions will be

(a) one   (b) two   (c) three   (d) four

Linked Answer Q.83(a) and Q.83(b):

83.(a). The following data was obtained with the GLC. Column temperature, 60ºC, inlet pressure, 1270 torr, outlet pressure, 770 torr, flow rate of carrier gas at 25ºC, 18 mL/min and retention time for air, 0.30 min, the pressure drop correction factor will be

(a) 0.648   (b) 0.740   (c) 0.770   (d) 0.715

83.(b). Corrected retention volume for air (mL) will be

(a) 4.02   (b) 4.72   (c) 4.46   (d) 4.25

Linked Answer Q.84(a) and Q.84(b):

84.(a). The major product P of the following reaction is:

(c)

(d)
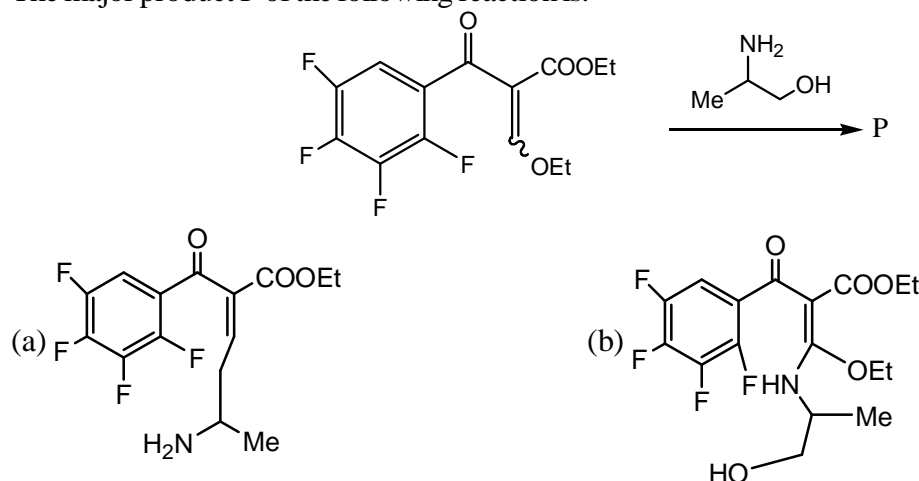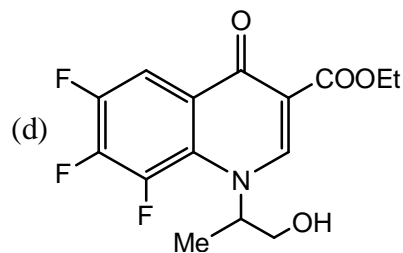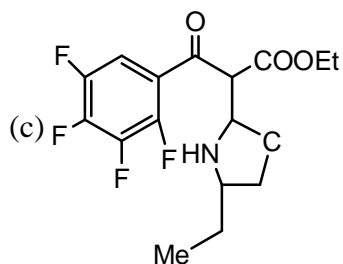
84.(b). Major compound Q obtained on reaction of P with NaH in DMF is:

(a)

(b)

(c)

(d)
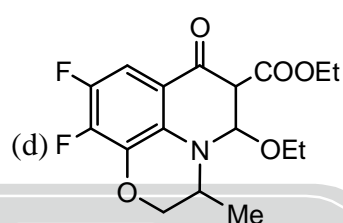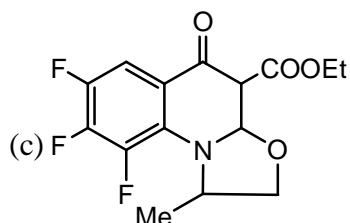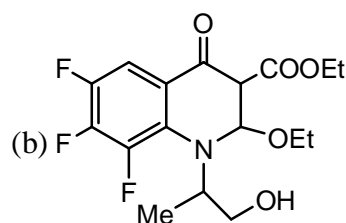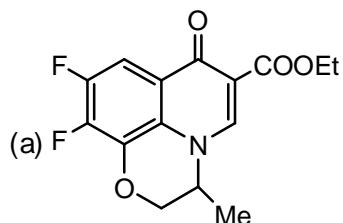
Linked Answer Q.85(a) and Q.85(b):

85. (a) In the follwoing sequence of reactions, the major product Q is:

(a)

(b)

(c)

(d)
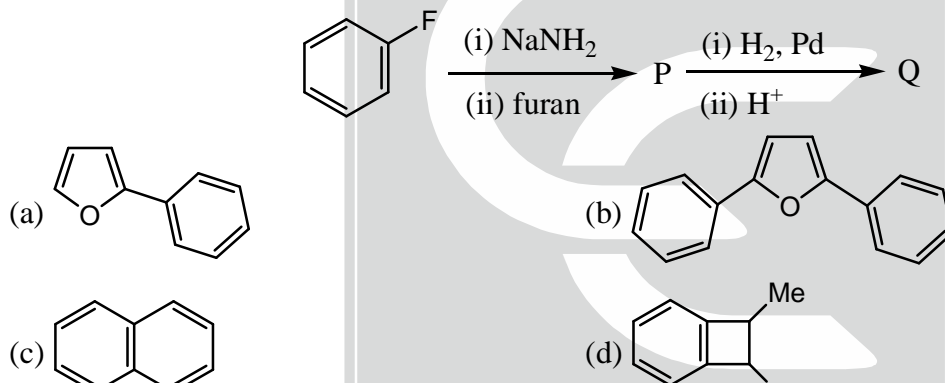
85.(b) The major product on sulphonation of Q with H_2SO_4 at 160ºC is:

(a)

(b)

(c)

(d)
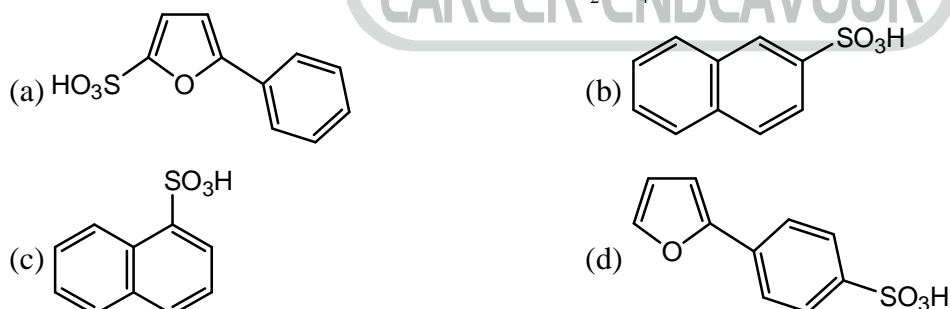
***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.20 : Carry ONE mark each.

1. A molecule has a 2-fold axis and a mirror plane perpendicular to that. The point group must have a

   (a) C_2 axis   (b) Centre of inversion   (c) σ_h plane   (d) σ_v plane

2. In the Huckel model for benzene, the π electronic transitions from the occupied to the unoccupied molecular orbitals do **NOT** occur at

   (a) 4β (b) 3β (c) 2β (d) 1β

3. The plot that describes a Carnot cycle is:
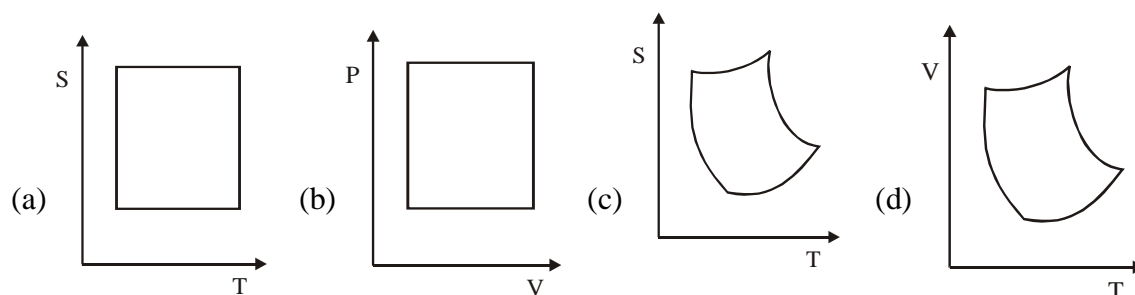
4. As the temperature tends to infinity, the partition function for a two-level system is

   (a) 0   (b) 1   (c) 2   (d) infinity

5. As per the kinetic theory of ideal gases, which of the following statements is NOT correct?
   (a) gas particles have mass but no volume
   (b) particles are in a Brownian motion between collisions.
   (c) during the collision, the system does not lose energy
   (d) particles exert same force per unit area on all sides of the container.

6. Which of the following statements in NOT correct regarding fugacity of a Van der Waals gas?
   (a) fugacity increases with increase in b
   (b) fugacity decreases with increase in a
   (c) fugacity is equal to zero if compressibility is zero
   (d) fugacity is equal to one if compressibility is one

7. The homogeneous catalyst that is used in the hydroformylation or hydrocarbonylation is based on
   (a) Co   (b) Cr   (c) Ti   (d) V

8. The pair of ions that most commonly forms complexes with coordination number 2 is
   (a) Cd (II) and Hg(II)   (b) Cu (II) and Hg (I)   (c) Cd (II) and Hg(I)   (d) Cu (I) and Hg(II)

9. The experimental magnetic moment of $K_3\left[Fe(CN)_6\right]$ is 2.3 μ_B and is attributable to the

   (a) spin - only value of a low - spin Fe   (b) spin-only value of a high-spin Fe.
   (c) low-spin Fe with orbital contribution   (d) high-spin Fe with orbital contribution.

10. Iron-sulphur clusters in biological systems are involved in
    (a) proton transfer   (b) atom transfer   (c) group transfer   (d) electron transfer

11. $Mg_6Si_4O_{10}(OH)_8$ is commercially known as
    (a) asbestos   (b) water-glass   (c) soda-glass   (d) zeolite

12. The series with the correct order of decreasing ionic size is

    (a) $K^+ > Ca^{2+} > S^{2-} > Cl^-$ (b) $S^2 > Cl^- > K^+ > Ca^{2+}$

    (c) $K^+ > Cl^- > Ca^{2+} > S^{2-}$ (d) $Cl^- > K^+ > S^{2-} > Ca^{2+}$

13. The most stable conformation of the following compound is:

(a) (b) (c) (d)
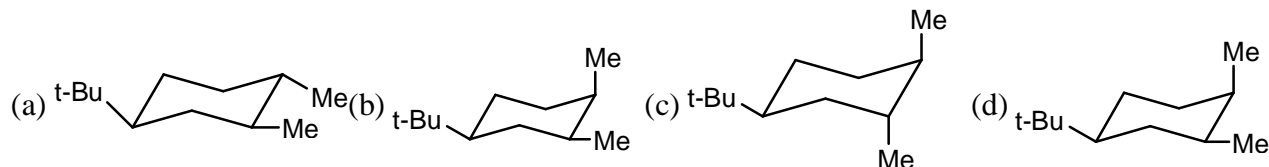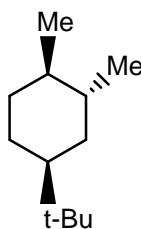
14. The correct order of the basicity of the following compound is
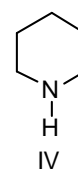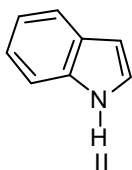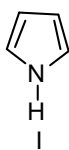
(a) $IV > III > II > I$ (b) $III > IV > I > II$

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

15. Match the following compounds with their respective classes.
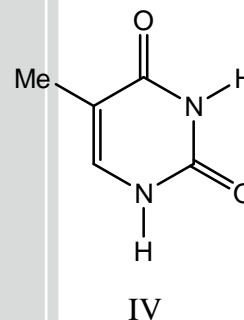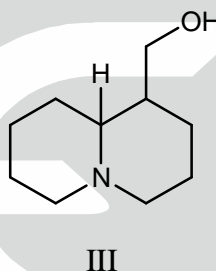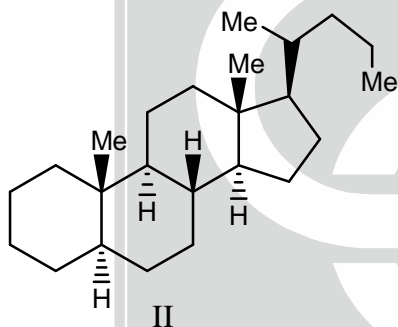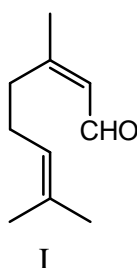
(a) I:Steroid; II: terpenoid; III: alkaloid; IV DNA base
(b) I:terpenoid; II; steroid; III: alkaloid; IV: DNA base
(c) I:terpenoid; II:steroid; III: DNA base; IV: alkaloid.
(d) I:steroid; II: terpenoid; III: DNA base; IV: alkaloid.

16. Which of the following absorptions is shown by 1, 3-butadiene in its UV absorption spectrum recorded in n-hexane $\left(\varepsilon_{max} \text{ is the molar absorptivity} \right)$?

(a) $\lambda_{max} \, 217 nm \left(\varepsilon_{max} = 21,000 \right)$ (b) $\lambda_{max} \, 214 \, nm \left(\varepsilon_{max} = 210 \right)$

(c) $\lambda_{max} \, 253 \, nm \left(\varepsilon_{max} = 50,000 \right)$ (d) $\lambda_{max} \, 250 \, nm \left(\varepsilon_{max} = 500 \right)$

17. Which of the following compounds is expected to show a sharp singlet for one of its protons at $\delta \geq 8 \, ppm$ in ${}^1H$ NMR spectrum, given that this signal remains unaffected on shaking the solution thoroughly with D_2O?

(a) CH_3CO_2H (b) $CH_3CONHC_6H_5$ (c) $n - C_6H_{13}C \equiv CH$ (d) $n - C_6H_{13}CHO$

18. The most appropriate starting materials for one step synthesis of the compound (I) are

(a)   (b)

(c)   (d)
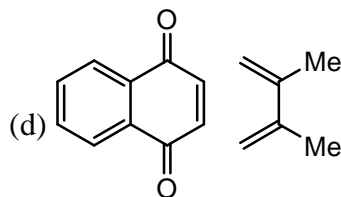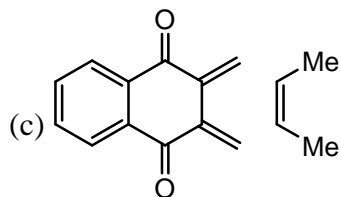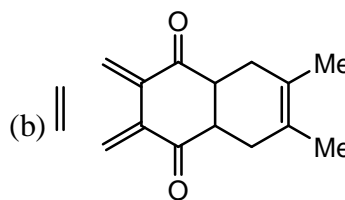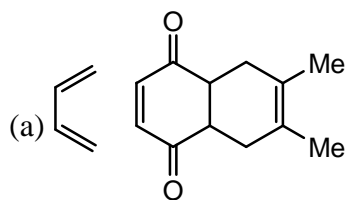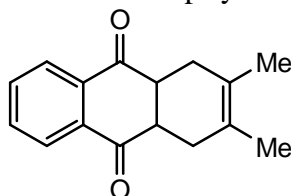
19. Identify the major product P in the following reaction.

(a)   (b)   (c)   (d)
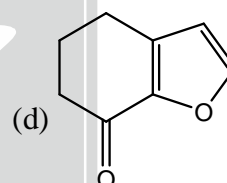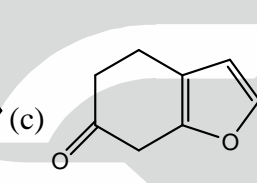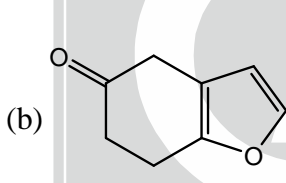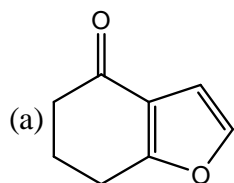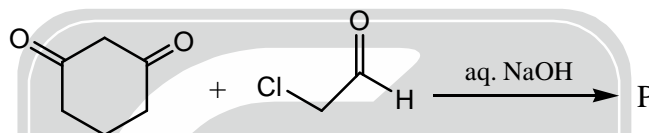
20. Which of the statement is CORRECT about the mechanism of the following reaction?
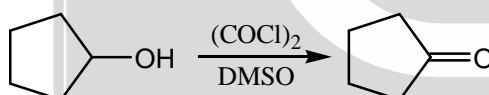
(a) DMSO reacts with alcohol initially to give , which reacts with $(COCl)_2$.

(b) $(COCl)_2$ reacts with the alcohol initially to give Cl, which reacts with DMSO

(c) DMSO reacts with $(COCl)_2$ initially to give , which reacts with the alcohol.

(d) $(COCl)_2$ reacts with DMSO initially to give which reacts with the alcohol.

Q.21– Q.85 : Carry TWO marks each.

21. To demonstrate the variational principle, a trial function $\Psi = C_1 \dfrac{\psi_{2s} + \psi_{3s}}{\sqrt{2}} + C_2 \dfrac{\psi_{2s} - \psi_{3s}}{\sqrt{2}}$

    where C_1 and C_2 are the variational parameters and ψ_{2s} and ψ_{3s} are the 2s, and 3s orbitals of the hydrogen atom, is constructed. The corresponding secular determinant for the hydrogen atom (in eV) is

    (a) $\begin{vmatrix} 3.4(1+4/9)\,2-E & 3.4(1-4/9)/2 \\ 3.4(1-4/9)/2 & 3.4(1+4/9)2-E \end{vmatrix}$

    (b) $\begin{vmatrix} 3.4(1+4/9)\,2-E & 3.4(1-4/9)/2 \\ 3.4(1-4/9)/2 & 3.4(1-4/9)2-E \end{vmatrix}$

    (c) $\begin{vmatrix} 3.4(1+4/9)\,2-E & 3.4(1+4/9)/2 \\ 3.4(1-4/9)/2 & 3.4(1-4/9)2-E \end{vmatrix}$

    (d) $\begin{vmatrix} 3.4(1+4/9)2-E & 0 \\ 0 & 3.4(1+4/9)2-E \end{vmatrix}$

22. The $A_1 \rightarrow A_2$ transition for a molecule having C_{3v} symmetry is
    (a) due to dipole pointing in x direction   (b) due to dipole pointing in y direction
    (c) due to dipole pointing in z direction   (d) not allowed

23. Which of the following pairs of operators commute?

    (a) x and $\dfrac{d}{dx}$ (b) $\dfrac{d}{dx}$ and $\dfrac{d^2}{dx^2} + 2\dfrac{d}{dx}$ (c) $x^2 \dfrac{d}{dx}$ and $\dfrac{d^2}{dx^2}$ (d) x^2 and $\dfrac{d}{dx}$

24. The zero-point energy of the vibration of $^{35}Cl_2$ mimicking a harmonic oscillator with a force cosntant k = 2293.8 Nm^{-1} is

    (a) $10.5 \times 10^{-21} J$ (b) $14.8 \times 10^{-21} J$ (c) $20 \times 10^{-21} J$ (d) $29.6 \times 10^{-21} J$

25. The moleculer active in rotational microwave, infrared absorption as well as rotational Raman spectra is:
    (a) CO_2 (b) SF_6 (c) HCl   (d) H_2.

26. One mole each of H_2CO_3, $NaHCO_3$ and Na_2CO_3 are added to water to prepare one litre solution. The pH of the solution is
    (a) 6.37   (b) 8.31   (c) 10.25   (d) 7

27. Given the standard potential for the following half-cell reaction at 298 K
    $$Cu^+ (aq) + e^- \rightarrow Cu(s) \qquad E_0 == 0.52\ V$$
    $$Cu^{2+}(aq) + e^- \rightarrow Cu^+ (aq) \qquad E_0 = 0.16\ V$$
    Calculate the $\Delta G^0 (kJ)$ for the reaction, $2Cu^+ (aq) \rightarrow Cu(s) + Cu^{2+}$
    (a) –34.740   (b) –65.720   (c) –69.480   (d) –131.440
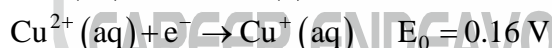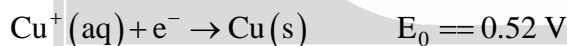
28. One mole each of acetic acid and sodium acetate are dissolved in 1 kg of water. Boiling point of the resulting solution is
    (a) 100.51 ℃   (b) 101.02 ℃   (c) 101.53 ℃   (d) 102.04 ℃

29. ΔS^0_{univ} for the following reaction, at 298 K is:
    $$N_2 + 3H_2 \longrightarrow 2NH_3 \qquad \Delta S^0_{sys} = -197\ JK^{-1}, \qquad \Delta H^0_{sys} = -91.8\ kJ$$
    (a) –197 J K^{-1} (b) 0 J K^{-1} (c) –308 J K^{-1} (d) 111 J K^{-1}
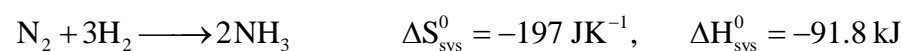
30. Consider an exothermic reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I$ as the temperature increases

    (a) k_1, k_{-1}, and k_1/k_{-1} increases   (b) k_1 increases, k_{-1} decreases, and k_1/k_{-1} increases.
    (c) k_1, k_{-1} increases and k_1/k_{-1} decreases   (d) k_1 and k_{-1} decrease, and k_1/k_{-1} increases.

31. A radical contains $^{14}N(I=1)$ with hyperfine constant 1.61 mT and two equivalent protons $(I=1/2)$ with hyperfine constant 0.35 mT. The ESR spectrum will exhibit.
(a) 3 lines   (b) 6 lines   (c) 7 lines   (d) 9 lines.

32. The set of ions expected to show Janh-Teller distortion in their complexes is
(a) Ti (III), Cu(II), High-spin Fe (III)
(b) Cu (I), Ni(II), High-spin Fe(III)
(c) Cu (II), Low-spin Fe(III), Ti(III)
(d) Low-spin Fe (III), Mn(II), Cu(I)

33. The series with correct order of increasing Δ_0 in their complexes is:
(a) $I^- < PR_3 < CH_3^- < CO$
(b) $PR_3 < CH_3^- < I^- < CO$
(c) $CH_3^- < PR_3 < I^- < CO$
(d) $I^- < CH_3^- < PR_3 < CO$

34. Coordinated water molecules of a Cd(II) complex can be successively replaced by Br^- finally to result in $[CdBr_4]^{2-}$. In this process, the fourth equilibrium constant is observed to be higher than the third one, because
(a) equilibrium constant for the last step is always the highest.
(b) three molecules of H_2O are released during the fourth step.
(c) the aquo-Cd(II) species is octahedral.
(d) an anion (Br^-) replaces a neutral (H_2O) molecule from the coordination sphere.

35. The CORRECT statement regarding the thermodynamic stability and kinetic reactivity of metal ion complexes is that
(a) more stable complexes are less reactive.
(b) there exists a dependence on the bulkiness of the ligand.
(c) there exists no direct relation between these two phenomenon.
(d) there exists a dependence on the size of the metal ion.

36. The CORRECT order of the rate of exchange of water molecules between the coordination sphere and the bulk is:
(a) $Cr^{3+} < Al^{3+} < Cr^{2+} < Ni^{2+}$
(b) $Cr^{3+} < Al^{3+} < Ni^{2+} < Cr^{2+}$
(c) $Cr^{3+} < Ni^{2+} < Cr^{2+} < Al^{3+}$
(d) $Cr^{3+} < Cr^{2+} < Al^{3+} < Ni^{2+}$

37. The amino acid side chain high affinity for Ca^{2+} and Cu^{2+} in metallo-proteins is:
(a) carboxylate in both the cases.
(b) imidazole in both the cases.
(c) caboxylate for Ca^{2+} and imidazole for Cu^{2+}.
(d) imidazole for Ca^{2+} and carboxylate for Cu^{2+}.

38. The CORRECT order of the soft character (as per HSAB principle) of the central metal ion is

(a) $[CrO_4]^{2-} < [CrCl_4]^- < [Cr(bipy)_3] < [Cr(CO)_5]^{2-}$

(b) $[CrCl_4]^- < [Cr(bipy)_3] < [CrO_4]^{2-} < [Cr(CO)_5]^{2-}$

(c) $[CrO_4]^{2-} < [Cr(bipy)_3] < [Cr(CO)_5]^{2-} < [CrCl_4]^-$

(d) $[CrCl_4]^- < [CrO_4]^{2-} < [Cr(CO)_5]^{2-} < [Cr(bipy)_3]$

39. The crystal structure of Pb_3O_4 contains
(a) octahedral and tetrahedral units
(b) only octahedral units
(c) octahedral and pyramidal units
(d) octahedral and square-planar units

40. The symmetry elements that are present in BF_3 are

(a) $C_3, \sigma_v, \sigma_h, 3C_2$ (b) $C_3, 3C_2, S_2, \sigma_v$ (c) $C_3, 3C_2, \sigma_h, S_2$ (d) $C_3, \sigma_h, \sigma_v, i$

41. $[Co(CO)_4]$ is isolobal with

(a) CH_4 (b) CH_3 (c) CH_2 (d) CH

42. The CORRECT order of the CO stretching vibrational frequency is

(a) $\left[Ti(CO)_6\right]^{2-} > \left[V(CO)_6\right]^- > CO > \left[Cr(CO)_6\right]$

(b) $\left[Cr(CO)_6\right] > CO > \left[V(CO)_6\right]^- > \left[Ti(CO)_6\right]^{2-}$

(c) $CO > \left[V(CO)_6\right]^- > \left[Ti(CO)_6\right]^{2-} > \left[Cr(CO)_6\right]$

(d) $CO > \left[Cr(CO)_6\right] > \left[V(CO)_6\right]^- > \left[Ti(CO)_6\right]^{2-}$

43. When a reduced cytochrome transfers an electron from its Fe(II) to the bound O_2,

(a) The bond order of O_2 is reduced by one and v_{O_2} decreases.

(b) A metal bound superoxide is formed and v_{O_2} decreases.

(c) A metal bound superoxide is formed and v_{O_2} increases

(d) The bond order of O_2 is reduced by one and v_{O_2} increases.

44. The atomic radius (in cm) of an element with a body centered cubic unit cell of volume $75.8 \text{ cm}^3 \text{ mol}^{-1}$,

molecular weight 137.3 and density 3.62 g cm^{-3} is

(a) 1.5×10^{-8} (b) 1.6×10^{-8} (c) 2.0×10^{-8} (d) 2.2×10^{-8}

45. If the dipole moment of HCl is 1.08 D and the bond distance is 1.27 Å, then partial charge on hydrogen and chlorine, respectively, are
(a) $+1.0$ and -1.0 (b) $+0.85$ and -0.85
(c) $+0.356$ and -0.356 (d) $+0.178$ and -0.178

46. One gram of ^{90}Sr gets converted to 0.953 g after 2 years. The half life of ^{90}Sr, and the amount of ^{90}Sr

remaining after 5 years are
(a) 1.44 years and 0.916 g   (b) 57.6 years and 0.75 g
(c) 28.8 years and 0.887 g   (d) 100 years and 0.982 g

47. The metal ion that is expected to shift the C_1-methylene group in heptanol from 2 to 10 ppm in ^1H NMR is
(a) Eu (III)   (b) Tl (III)   (c) Al (III)   (d) Sc (III)

48. When Al_4C_3 and Mg_2C_3 reacts with H_2O, then major products formed respectively, are
(a) ethyne and ethane   (b) methane and propyne
(c) propane and propene   (d) methane and propene

49. The arrangement of sulphur in zinc blende and wurtzite structures, respectively, are
(a) hexagonal close packing and cubic close packing
(b) cubic close packing and hexagonal close packing
(c) simple cubic packing in both the structures
(d) hexagonal close packing in both the structures

50. The reaction between Pr_6O_{11} and dilute HCl leads to the formation of
(a) a coloured solution
(b) only a black precipitate PrO_2
(c) a black precipitate of PrO_2 and soluble $PrCl_3$
(d) only soluble $PrCl_3$

51. $[XeO_6]^{4-}$ is octahedral whereas XeF_6 is a disordered one, because
    (a) fluorine is more electronegative than oxygen
    (b) Xe has a lone-pair in XeF_6
    (c) XeF_6 is neutral whereas $[XeO_6]^{4-}$ is anionic.
    (d) Xe-F bond has more ionic character

52. In biological systems, the metal ion involved in the dioxygen transport besides Fe is
    (a) Co   (b) Zn   (c) Mg   (d) Cu

53. $[Ru(2,2'-bipyuridyl)_3]^{2+}$, when it absorbs at 452 nm, is a very good oxidizing as well as reducing agent due to the formation of
    (a) $[Ru^I(2,2'-bipyridyl)_3]^+$
    (b) $[Ru^I(2,2'-bipyridyl)_2(2,2'\ bipyridyl^+)]^{2+}$
    (c) $[Ru^{III}(2,2'-bipyridyl)_3)]^{3+}$
    (d) $[Ru^{III}(2,2'-bipyridyl)_2(2,2'-bipyridyl)]^{2+}$

54. In the proton decoupled ^{13}C and ^{31}P NMR spectra of $(CH_3)_3 P = 0$, the number of lines observed, respectively, are
    (a) two and one   (b) one and two   (c) three and one   (d) two and two.

55. Among, RO^-, $AsMe_3$, ROR', CN^-, RCO_2^-, SCN^-, the set of ligands with good π-acceptor nature are
    (a) RO^-, RCO_2^-, SCN^-
    (b) RO^-, RCO_2^-, $AsMe_3$
    (c) $AsMe_3$, CN^-, SCN^-
    (d) RO^-, ROR', RCO_2^-

56. Identify the correct stereochemical relationship amongst the hydrogen atoms H_a, H_b and H_c in the following molecule:
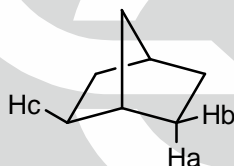
    (a) H_a and H_b: enantiotopic
    (b) H_a and H_b: diastereotopic
    (c) H_a and H_c: enantiotopic
    (d) H_b and H_c: diastereotopic.

57. The configurations of the reactant and the product in the following reaction, respectively, are
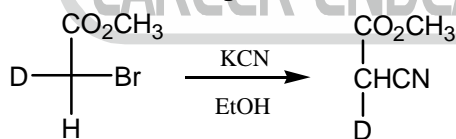
    (a) R, R   (b) R, S   (c) S, R   (d) S, S

58. Match the reactions of some p-substituted benzene derivatives (a)–(d) given in **List I** with the Hammett's p-values (i) - (iv) in **List II** and identify the correct match.
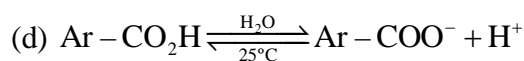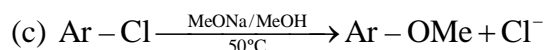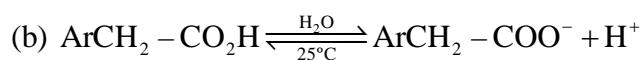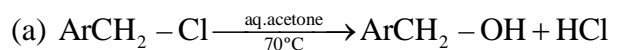
List - I	List - II
(a) $ArCH_2 - Cl \xrightarrow[70°C]{aq.acetone} ArCH_2 - OH + HCl$	(i) $+8.50$
(b) $ArCH_2 - CO_2H \xrightleftharpoons[25°C]{H_2O} ArCH_2 - COO^- + H^+$	(ii) $+1$
(c) $Ar - Cl \xrightarrow[50°C]{MeONa/MeOH} Ar - OMe + Cl^-$	(iii) $+0.49$
(d) $Ar - CO_2H \xrightleftharpoons[25°C]{H_2O} Ar - COO^- + H^+$	(iv) -1.88

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

59. On heating with dilute sulfuric acid, napththalene-1 sulfonic acid gives predominantly
    (a) natphthalene   (b) napththalene-2-sulfonic acid
    (c) 1-naphthol   (d) 2-naphthol

60. Predict the major product P in the following reaction
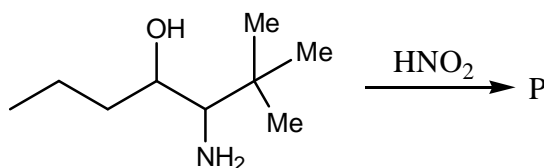
61. Select the correct classification in the following reaction from option I to IV gives below.
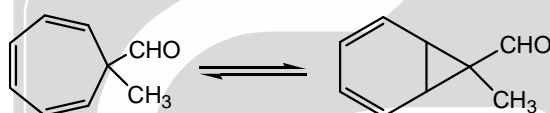
    (I) Conrotatory electrocyclic reaction   (II) Disrotatory electrocyclic reaction

    (III) Valence isomerization   (IV) $\left[_x 4_s + _\pi 2_a \right]$ cycloaddition reaction

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

62. Identify the major product P in the following reaction.
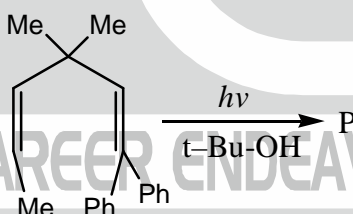
63. Identify the major product P and Q in the following reactions from the list of compounds I to IV.

I   II   III   IV
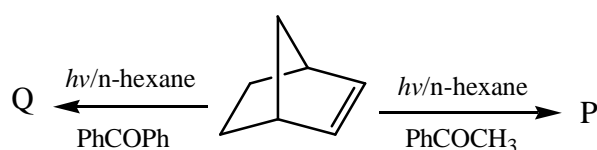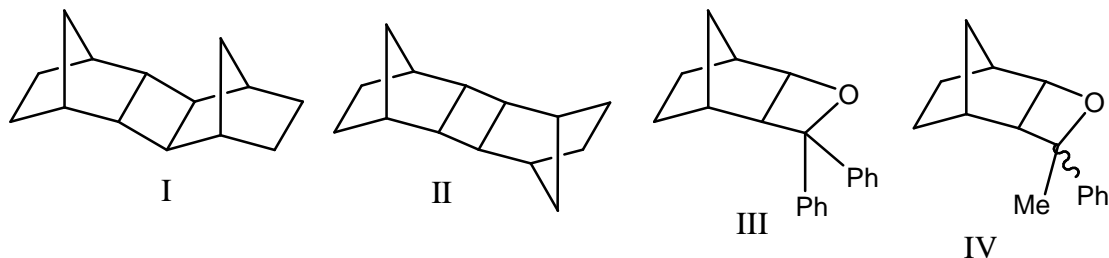
(a) P:I and Q:II   (b) P:II and Q:III   (c) P:IV and Q:II   (d) P:IV and Q: III

64. Identify the major product P in the following reaction:

(a)

(b)

(c)

(d)
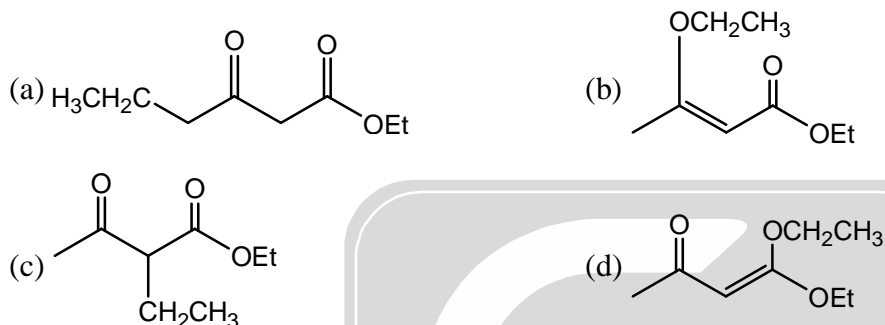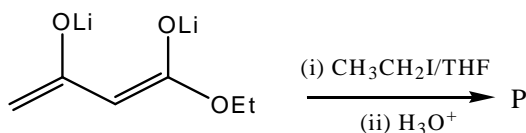
65. Identify the **Correct** set of stereochemical relationships amongst the following monosaccharides I-IV

I   **II**   **III**   **IV**
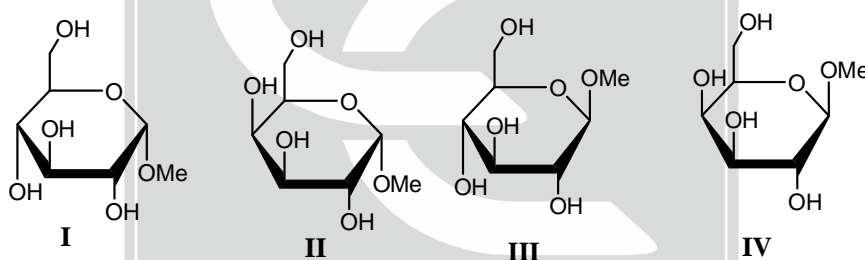
(a) I and II are anomers; III and IV are epimers
(b) I and III are epimers; II and IV are anomers
(c) I and II are epimers; III and IV are anomers
(d) I and III are anomers; I and II are epimers.

66. Select the correct pair of statements:
(I) Complementary strands run antiparallel in a double stranded DNA.
(II) The triplet codons, represented by the genetic code, are expressed by ribonucleic acids.
(III) t-RNA carries the genetic information to the site of DNA replication.
(IV) A nucleoside contains a ribose or deoxyribose and phosphate constituents only.
(a) I and II   (b) II and III   (c) III and IV   (d) I and IV.

67. Match the compounds in **List - I** with the stretching frequencies (cm^{-1}) of the principal functional groups given in **List-II.**

List - I

(1)

(2)

(3)

(4)
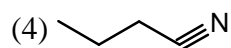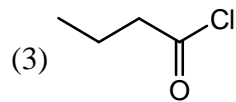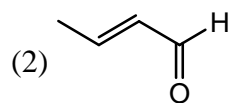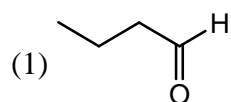
List - II

(i) 2240

(ii) 1795

(iii) 1750

(iv) 1725

(v) 1695

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

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

68. Pick the major product P in the following reaction

[CbzCl is PhCH$_2$OCOCl]

(i) CbzCl, NaOH

(ii)

KHCO$_3$, acetone, 40ºC

(a)

(b)

(c)

(d)
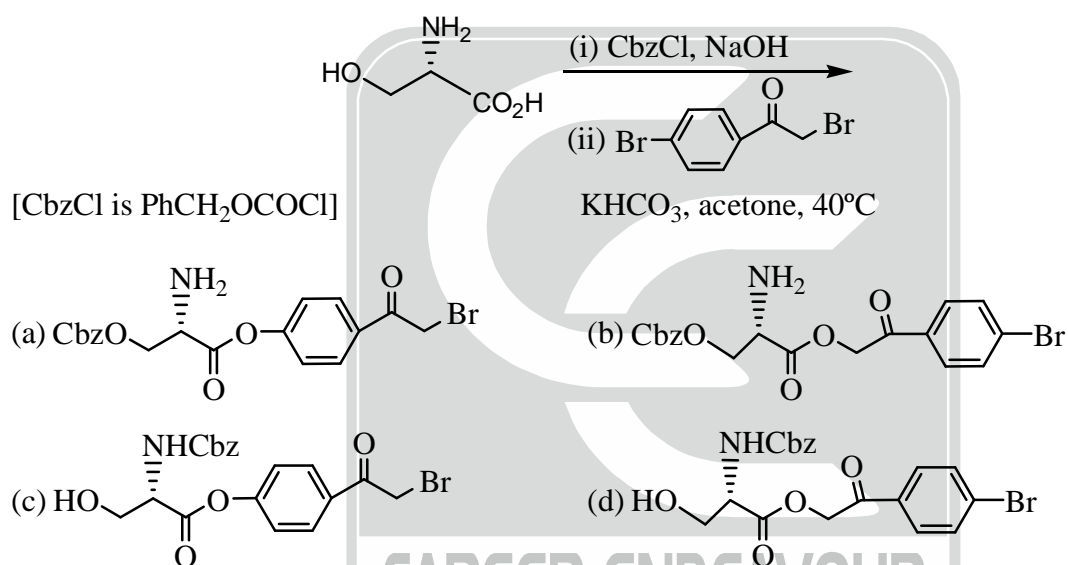
69. Identify the major product P in the following reaction:

$$\xrightarrow[\text{TiCl}_4]{\text{CH}_3\text{COCl}} \text{P}$$

(a)

(b)

(c)

(d)
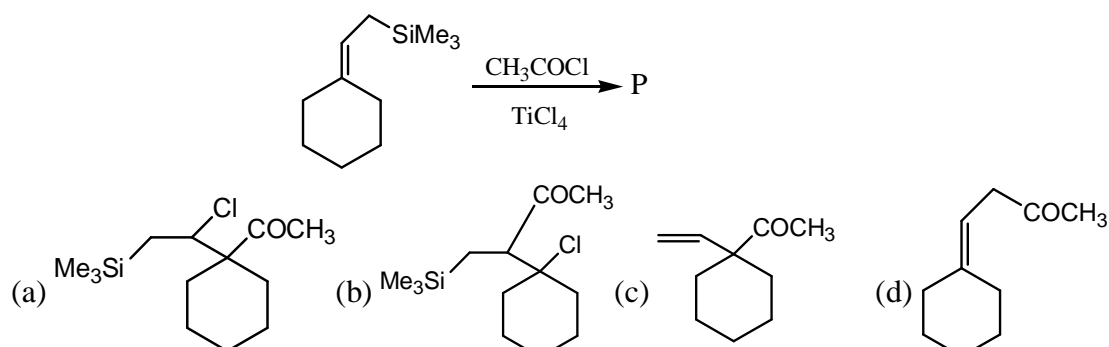
70. Identify the major P in the following two-step reaction:

$$\text{(i) Cl}_3\text{CCOCl}$$
$$\text{Et}_2\text{O, rt}$$
$$\xrightarrow{\hspace{3cm}} \text{P}$$
$$\text{(ii) 90\% HNO}_3$$
$$-50\ ^{\circ}\text{C}$$

(a) O_2N—[pyrrole ring]—$\underset{O}{\overset{}{C}}$—$CCl_3$

(b) O_2N—[pyrrole ring]—$\underset{O}{\overset{}{C}}$—$CCl_3$

(c) O_2N—[pyrrole ring]—$\underset{}{\overset{O}{C}}$—$CCl_3$

(d) O_2N—[pyrrole ring]—$\underset{}{\overset{O}{C}}$—$CCl_3$
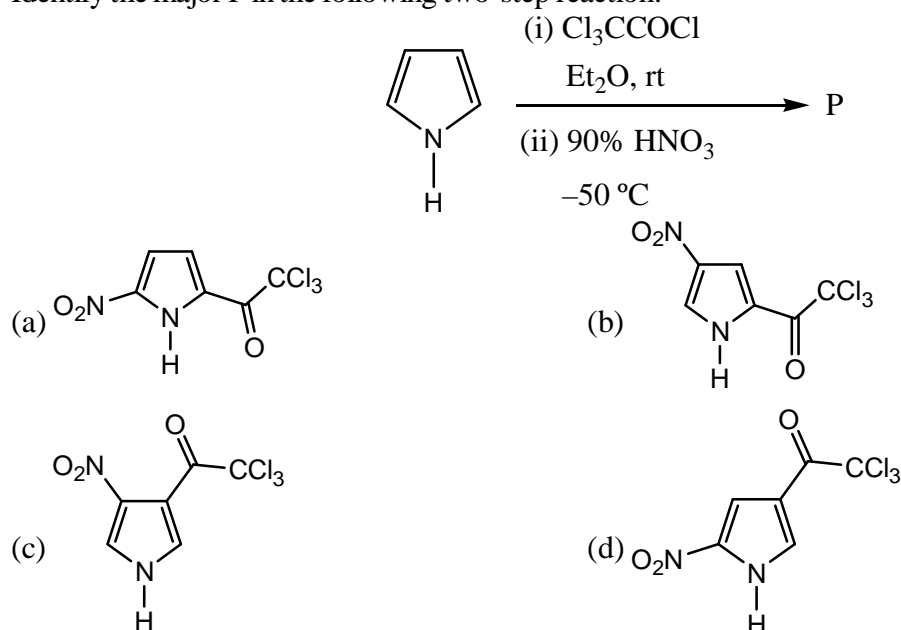
Common Data for Q.71, Q.72 and Q.73:

Methyl ethyl ether (A) and diborane (B) form a compound, which melts congruently at 133 K. The system exhibits two eutectics, one at 25 mole percent B and 123 K and a second at 90 mole percent B and 104 K. The melting points of pure A and b are 131 K and 110 K, respectively.

71. The phases at 55 mole percent B and 108 K are,
    (a) solid AB and a solid B phase
    (b) solid AB and a liquid phase
    (c) solid B and a liquid phase
    (d) solid A and a liquid phase

72. What happens if a small amount of solid B is added to the above mixture while keeping the temperature constant?
    (a) added B forms compound AB
    (b) added B precipitates out
    (c) overall liquid phase percentage increases with respect to the overall solid phase
    (d) complete solidification takes place

73. The mixture at 25 mole percent B and at 124 K is cooled slowly to 114 K. The resulting phases are
    (a) solid AB and solid A
    (b) solid AB and liquid
    (c) solid AB and solid B
    (d) liquid and solid A

Common Data for Q. 74 and Q. 75.

Consider the following P-V diagram for an ideal gas that follows the diagonal path from A to B.

[P-V diagram: axes P(atm) vertical, V(L) horizontal. Point B at (0.5, 20), D at (10, 20), C at (0.5, 1), A at (10, 1). T = 300 K. Diagonal from A to B.]
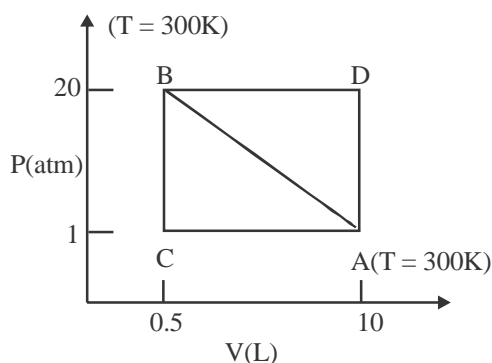
74. The work done (in atm-L) on the gas in the process is
    (a) 9.5   (b) 99.75   (c) 190   (d) 10 ln (20)

75. For the above process,

(a) $\Delta H = W$ (b) $\Delta H = Q$ (c) $\Delta H = \Delta G$ (d) $\Delta H = \Delta E$

Linked Answer Q. 76 and Q.77.

76. The first excited state wavefunction for a particle in a box that spans from $-a$ to $+a$ is

(a) $\sqrt{\dfrac{1}{a}} \cos\left(\dfrac{\pi x}{a}\right)$ (b) $\sqrt{\dfrac{1}{a}} \sin\left(\dfrac{\pi x}{a}\right)$ (c) $\sqrt{\dfrac{2}{a}} \cos\left(\dfrac{2\pi x}{a}\right)$ (d) $\sqrt{\dfrac{2}{a}} \sin\left(\dfrac{2\pi x}{a}\right)$

77. A perturbation $V = \delta\left(x - a/2\right)$ is introduced in the box. The first order energy correction to the first excited state is

(a) 0   (b) $2/a$ (c) $1/a$ (d) $1/2a$

Linked Answer Q. 78 and Q.79.

78. A reaction proceeds through the formation of an intermediate B in an unimolecular reaction

$$A \xrightarrow{k_a} B \xrightarrow{k_b} C$$
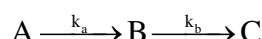
The integrated rate law for this reaction is

(a) $\left[A\right] = \left[A\right]_0 e^{-k_a t}$ (b) $\left[A\right] = \left[A\right]_0 \left(e^{-k_a t} - e^{-k_b t}\right)$

(c) $\left[A\right] = \dfrac{\left[A\right]_0}{2}\left(1 + \dfrac{k_a e^{-k_b t} - k_b e^{-k_a t}}{k_a - k_b}\right)$ (d) $\left[A\right] = \left[A\right]_0 \left(1 + e^{-k_a t} - e^{-k_b t}\right)$

79. If $k_a \gg k_b$, then concentration vs. time plot for the above reaction is:
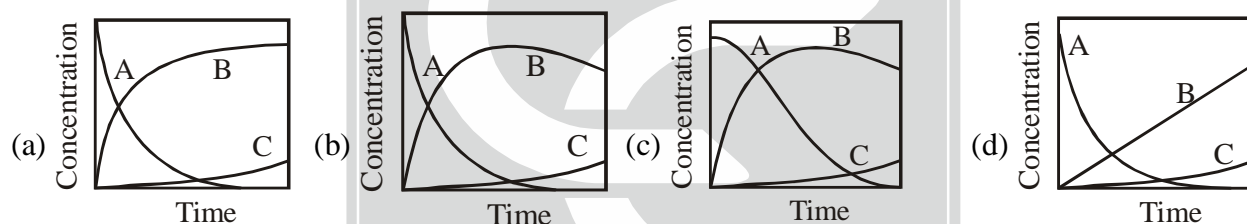
Linked Answer Q.80 and Q.81:

80. Identify the major product P in the following reaction
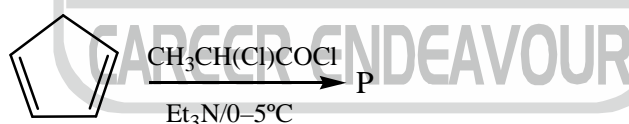
81. Product P of the above reaction transforms to a product Q on treatment with n-Bu$_3$SnH in the presence of AIBN in benzene solution. Identify Q.

Linked Answer Q.82 and Q.83:

82.   In the following wittig reaction, the structure of the major product P and the intermediate [X], respectively, are

$$ArCHO \quad + \quad Ph_3P = CH–CH_2CH_3 \xrightarrow[\substack{\text{Free of} \\ \text{inorganic salts}}]{\text{Benzene}} [X] \longrightarrow P$$

(a)

(b)

(c)

(d)
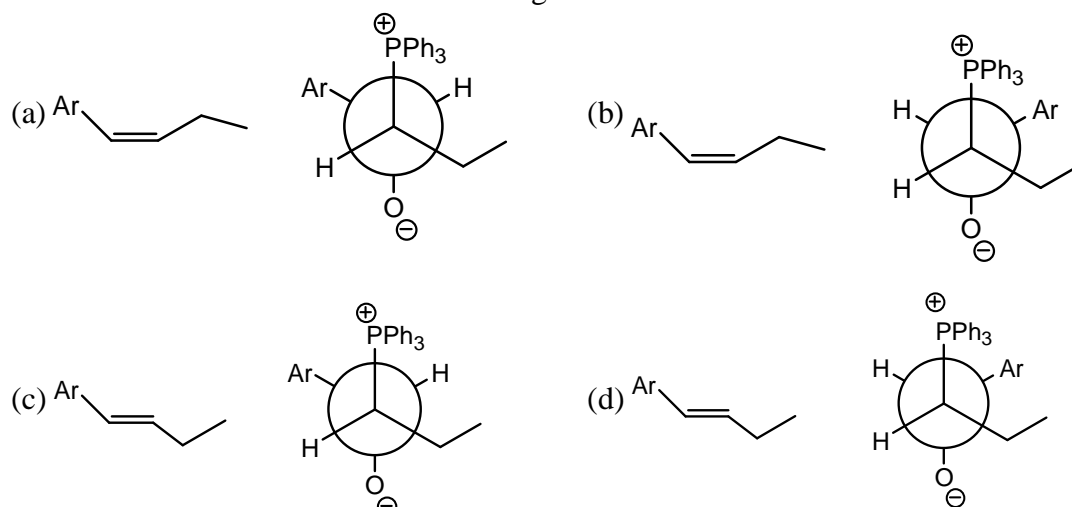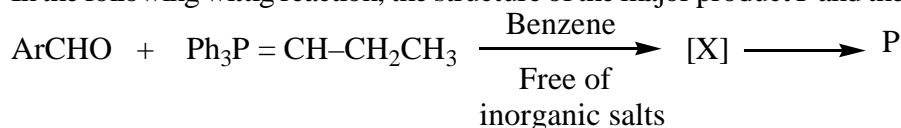
83.   Which of the following sets of characteristic NMR signals will be compatible with the structure of P in the above reaction ?

(a) $\delta 7.18$ (d, J = 6 Hz, 2H), 7.01 (d, J = 6 Hz, 2H), 6.41 (d, J = 18 Hz, 1H)

(b) $\delta 7.11$ (d, J = 6 Hz, 1H), 7.10 (s, 1H), 7.09 (t, J = 5 Hz, 1H)
     6.94 (d, J = 5 Hz, 1H), 6.41 (d, J = 17 Hz, 1H)

(c) $\delta 7.18$ (d, J = 6 Hz, 2H), 7.01 (d, J = 6 Hz, 2H), 6.35 (d, J = 9 Hz, 1H)

(d) $\delta 7.11$ (d, J = 6 Hz, 1H), 7.10 (s, 1H), 7.09 (t, J = 5 Hz, 1H),
     6.94 (d, J = 5 Hz, 1H), 6.35 (d, J = 10 Hz, 1H)

Linked Answer Type Q.84 and Q.85

84.   The products P and Q in the following sequence of reactions, respectively, are

(a)

(b)

(c)

(d)
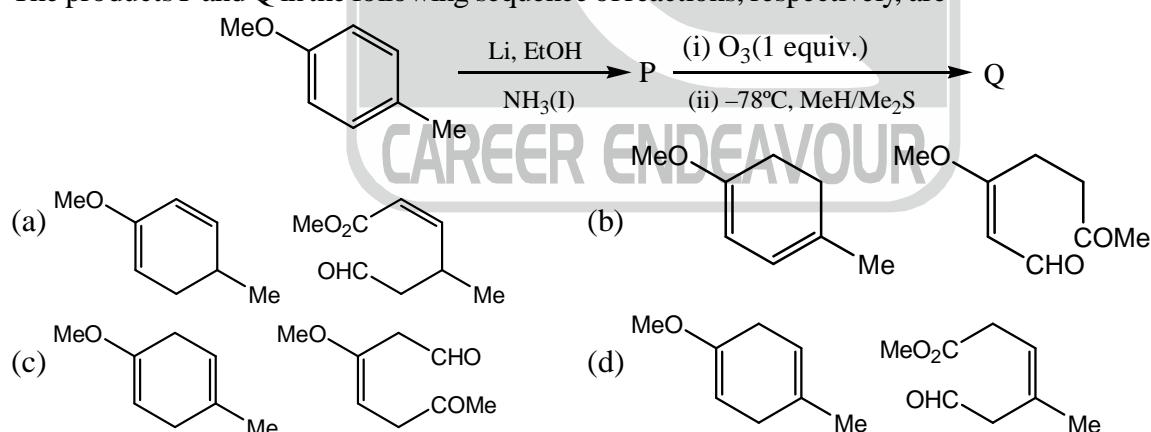
85.   The reagent for selective reduction of the aldehyde group in Q obtained in the above reaction is

(a) H_2, $(Ph_3P)_3RhCl$

(b) $\left((H_3C)_2 CHCH_2 \right)_2 AlH$

(c) $Na \left(CH_3COO \right)_3 BH$

(d) $LiAlH_4$

***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.20 : Carry ONE mark each.

1.　The rate of sulphonation of benzene can be significantly enhanced by the use of

　(a) a mixture of HNO_3 and H_2SO_4　　　　(b) conc. H_2SO_4

　(c) a solution of SO_3 in H_2SO_4　　　　(d) SO_3

2.　The reaction,
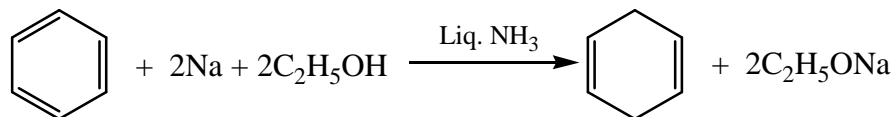
　is an example of a

　(a) Birch reduction　　　　　　　　　　(b) Clemmenson reduction
　(c) Wolff-Kishner reduction　　　　　　(d) hydride reduction

3.　The major product (X) of the monobromination reaction is
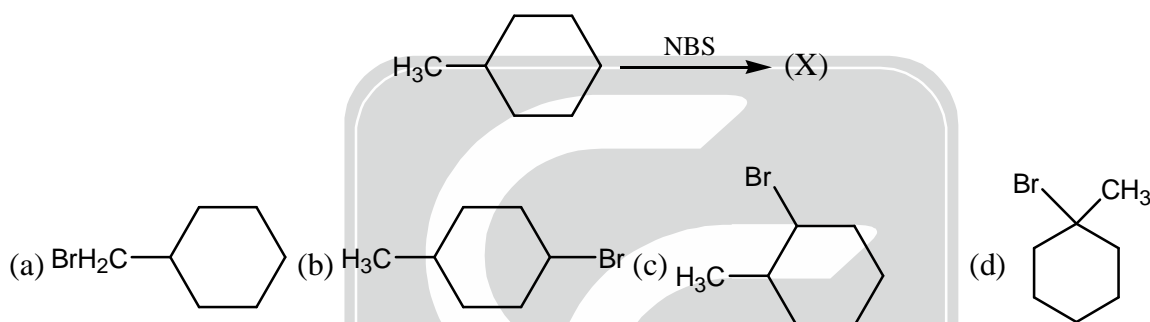
4.　Benzene can not be iodinated with I_2 directly. However, in presence of oxidants such as HNO_3, iodination
　is possible. The electrophile formed in this case is

　(a) $\left[I^+ \right]$　　　　　(b) I^*　　　　　(c) $\left[\overset{\delta}{\underset{*}{I}} ......\overset{+\delta}{OH_2} \right]^+$　　　(d) $\left[\overset{+\delta}{I} ......\overset{-\delta}{OH_2} \right]^+$

5.　Classify the following species as electrophiles (E) and nucleophiles (N) in routine organic synthesis

　　　SO_3　　Cl^+　　CH_3NH_2　　H_3O^+　　BH_3　　CN^-

　(a) $E = SO_3, Cl^+, BH_3$　　　　；　$N = CH_3NH_2, H_3O^+, CN^-$

　(b) $E = Cl^+, H_3O^+$　　　　　　；　$N = SO_3, CH_3NH_2, BH_3, CN^-$

　(c) $E = Cl^+, H_3O^+, BH_3$　　　；　$N = SO_3, CH_3NH_2, H_3O^+, CN^-$

　(d) $E = SO_3, Cl^+, H_3O^+, BH_3$；　$N = CH_3NH_2, CN^-$

6.　The major product obtained upon treatment of compound X with H_2SO_4 at 80ºC is:
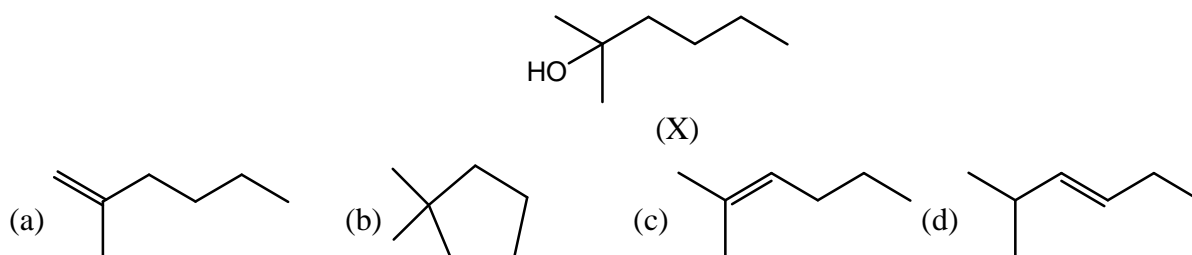
7. $BaTi[Si_3O_9]$ is a class of
   (a) ortho silicate   (b) cyclic silicate   (c) chain silicate   (d) sheet silicate

8. The ground state term fro V^{3+} ion is
   (a) ^3F (b) ^2F (c) ^3P (d) ^2D

9. In photosynthesis, the predominant metal present in the reaction centre of photosystem II is
   (a) Zn   (b) Cu   (c) Mn   (d) Fe

10. The octahedral complex/complex ion which shows both facial and meridonial isomers is
    (a) Triglycinatocobalt (III)   (b) Tris(etihylenediamine) cobalt(III)
    (c) Dichlorodiglycinatocobalt(III)   (d) Trioxalactocobaltate (III)

11. Zn in carbonic anhydrase is co-ordinated by three histidine and one water molecule. The reaction of CO_2 with this enzyme is an example of

    (a) electrophilic addition   (b) electron transfer
    (c) nucleophilic addition   (d) electrophilic substitution

12. The difference in the measured and calculated magnetic moment (based on spin-orbit coupling) is observed for

    (a) Pm^{3+} (b) Eu^{3+} (c) Dy^{3+} (d) Lu^{3+}

13. For a redox reaction, $Cd^{2+} + 2e^- \rightleftharpoons Cd$, the $(E_p)_{anodic}$ observed in cyclic voltametry at hanging mercury drop electrode is –650 mV vs. SCE. The expected value for $(E_p)_{cathodic}$ is
    (a) –708 mV   (b) –679 mV   (c) –650 mV   (d) –621 mV

14. The dimension of Planck constant is (M, L and T denote mass, length and time respectively)
    (a) ML^3T^{-2} (b) ML^2T^{-1} (c) $M^2L^{-1}T^{-1}$ (d) $M^{-1}L^2T^{-2}$

15. For a homonuclear diatomic molecule, the bonding molecular orbital is
    (a) σ_u of lowest energy   (b) σ_u of second lowest energy
    (c) π_g of lowest energy   (d) π_u of lowest energy

16. The selection rules for the appearance, of P branch in the rotational-vibrational absorption spectra of a diatomic molecule within rigid rotor-harmonic oscillator model are
    (a) $\Delta v = \pm 1$ and $\Delta J = \pm 1$ (b) $\Delta v = +1$ and $\Delta J = +1$
    (c) $\Delta v = +1$ and $\Delta J = -1$ (d) $\Delta v = -1$ and $\Delta J = -1$

17. The S_2 operation on a molecule with the axis of rotation as the z axis, moves a nucleus at (x, y, z) to
    (a) $(-x, -y, x)$ (b) $(x, -y, -z)$ (c) $(-x, y, -z)$ (d) $(-x, -y, -z)$

18. The expression which represents the chemical potential of the ith species(μ_i) in a mixture $(i \neq j)$ is:

    (a) $(\partial E / \partial n_i)_{s,v,nj}$ (b) $(\partial H / \partial n_i)_{s,v,nj}$ (c) $(\partial A / \partial n_i)_{s,v,nj}$ (d) $(\partial G / \partial n_i)_{s,v,nj}$

19. Which of the following statements is NOT correct for a catalyst?
    (a) It increases the rate of a reaction
    (b) It is not consumed in the course of a reaction
    (c) It provides an alternate pathway for the reaction
    (d) It increases the activation energy of the reaction

20. The value of the rate constant for the gas phase reaction $2NO_2 + F_2 \rightarrow 2NO_2F$ is $38 \, dm^3 \, mol^{-1} \, s^{-1}$ at 300K. The order of the reaction is
   (a) 0　　　　　(b) 1　　　　　(c) 2　　　　　(d) 3

Q.21 – Q.75 : Carry TWO marks each.

21. Boric acid in aqueous solution in presence of glycerol behaves as a strong acid due to the formation of
   (a) an anionioc metal-chelate　　　　　(b) borate anion
   (c) glycerate ion　　　　　(d) a charge transfer complex

22. Match the compounds in List I with the corresponding structue / property given in List II

   List - I

   A. $(Ph_3P)_3 \, RhCl$

   B. LiC_6

   C. PtF_6

   D. Ni_3S_4

   List - II

   (i) Spinel

   (ii) Intercalation

   (iii) Oxidising agent

   (iv) Catalyst for alkene hydrogenation

   (a) A-iii, B-i, C-ii, D-iv　　　　　(b) A-iv, B-ii, C-iii, D-i
   (c) A-iii, B-ii, C-i, D-iv　　　　　(d) A-iv, B-iii, C-ii, D-i

23. $W(CO)_6$ reacts with MeLi to give an intermediate which upon treatment with CH_2N_2 gives a compound X. X is represented as

   (a) WMe_6

   (b) $(CO)_5 \, W-Me$

   (c) $(CO)_5 \, W=C(Me)OMe$

   (d) $(CO)_5 \, W\equiv CMe$

24. Considering the quadrupolar nature of M-M bond in $[Re_2 Cl_8]^{2-}$, the M-M bond order in $[Re_2 Cl_4 (PMe_2Ph)_4]^+$ and $[Re_2 Cl_4 (PMe_2Ph)_4]$ respectively are
   (a) 3.0 and 3.0　　　　(b) 3.0 and 3.5　　　　(c) 3.5 and 3.5　　　　(d) 3.5 and 3.0

25. A student recorded a polarogram of 2.0 mM Cd^{2+} solution and forgot to add KCl solution. What type of error do you expect in his results?
   (a) Only migration current will be observed
   (b) Only diffusion current will be observed
   (c) both migration current as well as diffusion current will be observed
   (d) Both catalytic current as well as diffusion current will be observed

26. The separation of trivalent lanthanide ions, Lu^{3+}, Yb^{3+}, Dy^{3+}, Eu^{3+} can be effectively done by a cation exchange resion using ammonia o-hydroxy isobutyrate as the eluent. The order n which the ions will be separated is
   (a) Lu^{3+}, Yb^{3+}, Dy^{3+}, Eu^{3+}　　　　　(b) Eu^{3+}, Dy^{3+}, Yb^{3+}, Lu^{3+}
   (c) Dy^{3+}, Yb^{3+}, Eu^{3+}, Lu^{3+}　　　　　(d) Yb^{3+}, Dy^{3+}, Lu^{3+}, Eu^{3+}

27. Arrange the following metal complexes in order of their increasing hydration energy.

   $\underset{P}{[Mn(H_2O)_6]^{2+}}$　　　$\underset{Q}{[V(H_2O)_6]^{2+}}$　　　$\underset{R}{[Ni(H_2O)_6]^{2+}}$　　　$\underset{S}{[Ti(H_2O)_6]^{2+}}$

   (a) $P < S < Q < R$　　　(b) $P < Q < R < S$　　　(c) $Q < P < R < S$　　　(d) $S < R < Q < P$

28. In the complex, $\left[Ni_2 \left(\eta^5 - Cp \right)_2 (CO)_2 \right]$, the IR stretching frequency appears at 1857 cm^{-1} (strong) and 1897 cm^{-1} (weak). The valence electron count and the nature of the M-CO bond respectively are
    (a) 16 e$^-$, bridging   (b) 17 e$^-$, bridging   (c) 18 e$^-$, terminal   (d) 18 e$^-$, briding.

29. The correct classification of $\left[B_5 H_5 \right]^{2-}$, $B_5 H_9$ and $B_5 H_{11}$ respectively is
    (a) closo, arachno, nido   (b) arachno, closo, nido
    (c) closo, nido, arachno   (d) nido, arachno, closo

30. The compounds X and y in the following reaction are
    $$P_4 S_{10} \xrightarrow{\text{EtOH}} (X) \xrightarrow{Cl_2} (Y) \xrightarrow{p-O_2NC_6H_4ONa} \text{Parathion}$$
    (a) $X = \left(Et \right)_2 P(S)SH$; $Y = \left(Et \right)_2 P(S)Cl$ (b) $X = (EtO)_2 P(S)SH$; $Y = (EtO)_2 P(S)Cl$
    (c) $X = (EtO)_2 PSH$; $Y = (EtO)_2 PCl$ (d) $X = (Et)_3 PO$; $Y = (Et)_3 PCl$
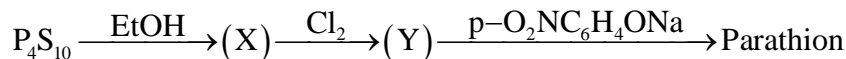
31. Consider the reactions
    1. $\left[Cr(H_2O)_6 \right]^{2+} + \left[CoCl(NH_3)_5 \right]^{2+} \rightarrow \left[Co(NH_3)_5 (H_2O) \right]^{2+} + \left[CrCl(H_2O)_5 \right]^{2+}$
    2. $\left[Fe(CN)_6 \right]^{4-} + \left[Mo(CN)_8 \right]^{3-} \rightarrow \left[Fe(CN)_6 \right]^{3-+} + \left[Mo(CN)_8 \right]^{4-}$
    Which one of the following is the correct statement?
    (i) Both involve an inner sphere mechanism.
    (ii) Both involve an outer sphere mechanism
    (iii) Reaction 1 follows inner sphere and reaction 2 follows outer sphere mechanism
    (iv) Reaction 1 follows outer sphere and reaction 2 follows inner sphere mechanism.
    (a) i   (b) ii   (c) iv   (d) iii
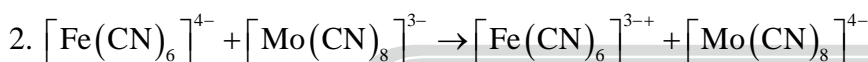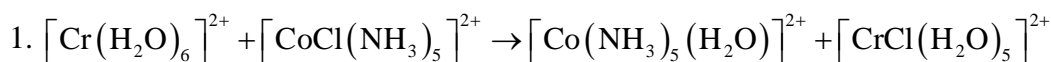
32. The pair of compounds having the same hybridization for the central atom is
    (a) XeF_4 and $\left[SiF_6 \right]^{2-}$ (b) $\left[NiCl_4 \right]^{2-}$ and $\left[PtCl_4 \right]^{2-}$
    (c) $Ni(CO)_4$ and XeO_2F_2 (d) $\left[Co(NH_3)_6 \right]^{3+}$ and $\left[Co(H_2O)_6 \right]^{3+}$

33. In the reaction shown below, X and Y respectively are
    $$Mn_2 (CO)_{10} \xrightarrow{Na} (X) \xrightarrow{CH_3COCl} (Y)$$
    (a) $\left[Mn(CO)_4 \right]^{2-}$, $\left[CH_3C(O)Mn(CO)_5 \right]^-$ (b) $\left[Mn(CO)_4 \right]^{2-}$, $CH_3C(O)Mn(CO)_5$
   (c) $\left[Mn(CO)_5 \right]^-$, $\left[ClMn(CO)_5 \right]$ (b) $\left[Mn(CO)_4 \right]^{2-}$, $\left[ClMn(CO)_5 \right]^-$
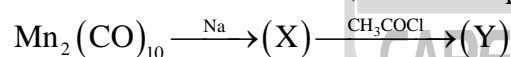
34. The Lewis acid character of BF_3, BCl_3 and BBr_3 follows the order
    (a) $BF_3 < BBr_3 < BCl_3$ (b) $BCl_3 < BBr_3 < BF_3$
    (c) $BF_3 < BCl_3 < BBr_3$ (d) $BBr_3 < BCl_3 < BF_3$

35. The compound which shows $L \leftarrow M$ charge transfer is
    (a) $Ni(CO)_4$ (b) $K_2Cr_2O_7$ (c) HgO (d) $\left[Ni(H_2O)_6 \right]^{2+}$

36. The reaction of $\left[PtCl_4 \right]^{2-}$ with NH_3 gives rise to
    (a) $\left[PtCl_4 (NH_3)_2 \right]^{2-}$ (b) $trans - \left[PtCl_2 (NH_3)_2 \right]$
    (c) $\left[PtCl_2 (NH_3)_4 \right]$ (d) $cis - \left[PtCl_2 (NH_3)_2 \right]$

37. Zeise's salt is represented as

    (a) H_2PtCl_6 (b) $[PtCl_4]^{2-}$ (c) $[ZnCl_4]^{2-}$ (d) $\left[PtCl_3\left(\eta^2-C_2H_4\right)\right]^-$

38. The catalyst used in the conversion of ethylene to acetaldehyde using Wacker process is

    (a) $HCo(CO)_4$ (b) $[PdCl_4]^{2-}$ (c) V_2O_5 (d) $TiCl_4$ in the presence of $Al(C_2H_5)_3$

39. The temperature of 54 g of water is raised from 15ºC to 75ºC at constant pressure. The change in the enthalpy of the system (given that $C_{p.m}$ of water $=75\ JK^{-1}mol^{-1}$) is:

    (a) 4.5 kJ   (b) 13.5 kJ   (c) 9.0 kJ   (d) 18.0 kJ

40. The specific volume of liquid water is 1.001 mL g^{-1} and that of ice is 1.0907 mL g^{-1} at ºC. If the heat of fusion of ice at this temperature is 333.88 J g^{-1}, the rate of change of melting point of ice with pressure in deg atm^{-1} will be

    (a) –0.0075   (b) 0.0075   (c) 0.075   (d) –0.075

41. Given that $E_0\left(Fe^{3+},Fe\right)=-0.04\ V$ and $E_0\left(Fe^{2+},Fe\right)=-0.44\ V$, the value of $E_0\left(Fe^{3+},Fe^{2+}\right)$ is:

    (a) 0.76 V   (b) –0.40 V   (c) –0.76 V   (d) 0.40 V

42. For the reaction $P+Q+R \longrightarrow S$, experimental data for the measured initial rates is given below.

Expt.	Initial conc. P (M)	Initial conc. Q (M)	Initial conc. R (M)	Initial rate (Ms^{-1})
1	0.2	0.5	0.4	8.0×10^{-5}
2	0.4	0.5	0.4	3.2×10^{-4}
3	0.4	2.0	0.4	1.28×10^{-3}
4	0.1	0.25	1.6	4.0×10^{-5}

   The order of the reaction with respect to P, Q and R respectively is:

    (a) 2 2, 1   (b) 2, 1, 2   (c) 2, 1, 1   (d) 1, 1, 2

43. Sucrose is converted to a mixture of glucose and fructose in a pseudo first order process under alkaline conditions. The reaction has a half life of 28.4 min. The time required for the reduction of a 8.0mM sample of sucrose to 1.0 mM is

    (a) 56.8 min   (b) 170.4 min   (c) 85.2 min   (d) 227.2 min

44. The reaction, $2NO(g)+O_2(g)\rightarrow 2NO_2(g)$

    proceeds via the following steps

$$NO+NO \xrightarrow{\ k_a\ } N_2O_2$$
$$N_2O_2 \xrightarrow{\ k_{a'}\ } NO+NO$$
$$N_2O_2+O_2 \xrightarrow{\ k_b\ } NO_2+NO_2$$
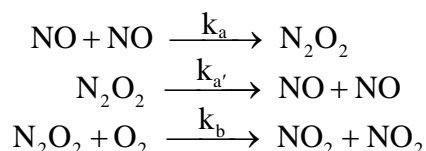
    The rate of this reaction is equal to

    (a) $2k_b[NO][O_2]$ (b) $(2k_ak_b[NO]^2[O_2])/(k_a+k_b[O_2])$

    (c) $2k_b[NO]^2[O_2]$ (d) $k_a[NO]^2[O_2]$

45. 40 millimoles of NaOH are added to 100 mL of a 1.2 M HA and Y M NaA buffer resulting in a solution of pH 5.30. Assuming that the volume of the buffer remains unchanged, the pH of the buffer ($K_{HA} = 1.00 \times 10^{-5}$) is

(a) 5.30   (b) 5.00   (c) 0.30   (d) 10.30

46. The entropy of mixing of 10 moles of helium and 10 moles of oxygen at constant temperature and pressure, assuming both to be ideal gas, is:

(a) 115.3 JK^{-1} (b) 5.8 JK^{-1} (c) 382.9 JK^{-1} (d) 230.6 JK^{-1}

47. The ionisation potential of hydrogen atom is 13.6 eV. The first ionistaion potential of a sodium atom, assuming that the energy of its outer electron can be represented by a H-atom like model with an effective nuclear charge of 1.84, is

(a) 46.0 eV   (b) 11.5 eV   (c) 5.1 eV   (d) 2.9 eV

48. The quantum state of a particle moving in a circular path in a plane is given by

$$\psi_m(\phi) = \left(1/\sqrt{2\pi}\right)e^{im\phi}, \; m = 0, \pm 1, \pm 2, \dots$$

When a perturbation $H_1 = P\cos\phi$ is applied (P is a constant), what will be the first order correction to the energy of the mth state

(a) 0   (b) $P/(2\pi)$ (c) $P/(4\pi)$ (d) $Pm^2/\left(4\pi^2\right)$

49. The correct statement(s) among the following is/are
(i) The vibrational energy levels of a real diatomic molecule are equally spaced.
(ii) At 500K, the reaction $A \to B$ is spontaneous when $\Delta H = 18.83 \text{ kJ mol}^{-1}$ and $\Delta S = 41.84 \text{ J K}^{-1}\text{mol}^{-1}$.
(iii) The process of fluorescence involves transition from a singlet electronc state to another singlet electronic state by absorption of light.
(iv) When a constant P is added to each of the possible energies of a system, its entropy remains unchanged.
(a) Only i   (b) Only ii   (c) Both i and iii   (d) Both ii and iv

50. Assuming H_2 and HD molecules having equal lengths, the ratio of the rotational partition functions of these molecules, at temperature above 100K is
(a) 3/8   (b) 3/4   (c) 1/2   (d) 2/3

51. N non-interacting molecules are distributed among three non-degenerate energy levels

$\varepsilon_0 = 0$, $\varepsilon_1 = 1.38 \times 10^{-21} \text{J}$ and $\varepsilon_2 = 2.76 \times 10^{-21} \text{J}$, at 100K. If the average total energy of the system at this temperature is $1.38 \times 10^{-18} \text{J}$, the number of molecules in the system is:
(a) 1000   (b) 1503   (c) 2354   (d) 2987

53. The rate constants of two reactions at temperature T are $k_1(T)$ and $k_2(T)$ and the corresponding activation energies are E_1 and E_2 with $E_2 > E_1$. When temperature is raised from T_1 and T_2, which one of the following relations is correct?

(a) $\dfrac{k_1(T_2)}{k_1(T_1)} = \dfrac{k_2(T_2)}{k_2(T_1)}$ (b) $\dfrac{k_1(T_2)}{k_1(T_1)} > \dfrac{k_2(T_2)}{k_2(T_1)}$ (c) $\dfrac{k_1(T_2)}{k_1(T_1)} \geq \dfrac{k_2(T_2)}{k_2(T_1)}$ (d) $\dfrac{k_1(T_2)}{k_1(T_1)} < \dfrac{k_2(T_2)}{k_2(T_1)}$

54. The number of degrees of freedom for a system consisting of NaCl(s), Na^+(aq) and Cl^-(aq) at equilibrium is

(a) 2   (b) 3   (c) 4   (d) 5

55. Match the structures in **List - I** with their correct names in **List - II.**

List - I   **List - II**
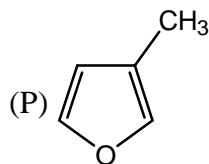
(P)   (i) 3-methyl furan
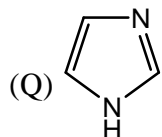
(Q)   (ii) Imidazole
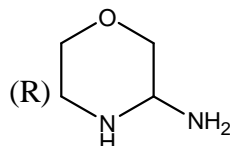
(R)   (iii) 5-hydroxybenzothiazole
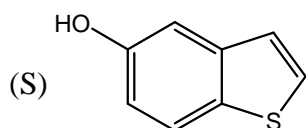
(S)   (iv) 2-amino piperidine.
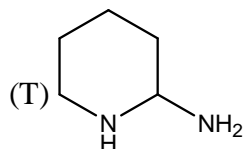
(T)   (v) 2-amino morpholine

(a) P-i, Q-ii, R-v, S-iii, T-iv   (b) P-ii, Q-iii, R-iv, S-v, T-i

(c) P-iii, Q-iv, R-v, S-i, T-ii   (d) P-iv, Q-v, R-i, S-ii, T-iii

56. The result of the reduction of either (R) or (S) 2-methylcyclohexanone, in separate reactions, using $LiAlH_4$ is that the reduction of

(a) The R enantiomer is stereoselective   (b) The R enantiomer is stereospecific.

(c) The S enantiomer is stereospecific   (d) Both the R and S enantiomers is stereoselective.

57. The increasing order of basicity among the following is

(X)   (Y)   (Z)
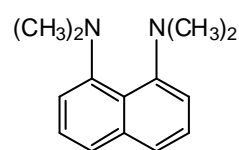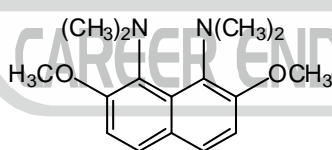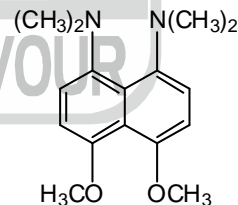
(a) $Y < X < Z$ (b) $Y < Z < X$ (c) $X < Z < Y$ (d) $X < Y < Z$

58. In the reaction,
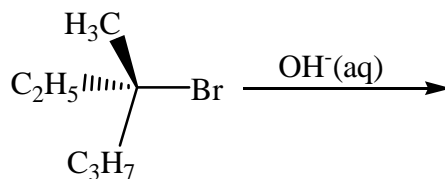
if the concentration of both the reactants is doubled, then the rate of the reaction will

(a) remain unchanged   (b) quadruple

(c) reduce to one fourth   (d) double

59. Match the structures in **List - I** with the coupling constant $\left[^1\text{H J(Hz)} \right]$ given in **List - II**

List - I   **List - II**

(1) [structure: Br, Cl on one side, H, H — cis/trans alkene]

(i) ~ 1 Hz

(2) [structure: Br, H; H, Cl alkene]

(ii) ~ 10 Hz

(3) [structure: Br, H; Cl, H alkene]
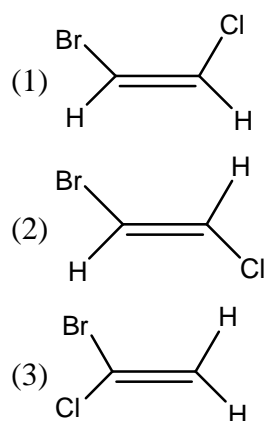
(iii) ~ 15 Hz

(a) 1-(i), 2- (ii), 3-(iii)   (b) 1-(ii), 2-(iii), 3-(i)
(c) 1-(iii), 2-(ii), 3-(i)   (d) 1-(iii), 2-(i), 3-(ii)

60. Phenol on reaction with formaldehyde and dimethyl amine mainly gives

(a) [structure: phenol with OH and ortho $CH_2N(CH_3)_2$]

(b) [structure: phenol with OH and para $CH_2N(CH_3)_2$]

(c) [structure: benzene with CHO and ortho $CH_2N(CH_3)_2$]

(d) [structure: benzene with CHO and para $CH_2N(CH_3)_2$]
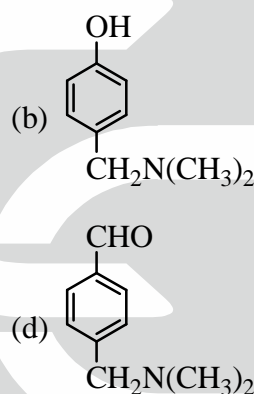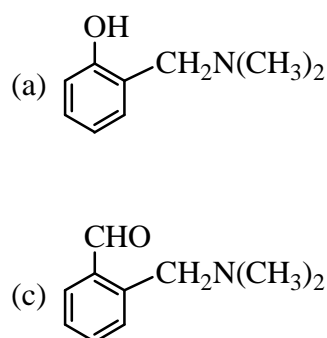
61. The mono protonation of adenine (X) in acidic solution

[structure of adenine (X) with numbered positions 1 (NH_2), 2 (N), 3 (N-H), 4 (N), 5 (N)]
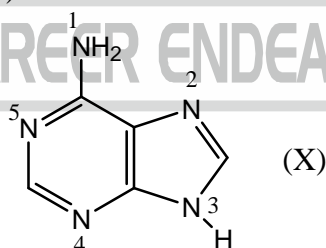
mainly occurs at
(a) position 1   (b) position 2   (c) position 3   (d) either position 4 or 5.

62. In the following reaction,

[reaction scheme: CH_2N_2 (diazomethane, H-C(=N$_2$)-H) $\xrightarrow[\text{benzophenone}]{hv}$ (X) $\xrightarrow{\text{cis-2-butene}}$ (Y)]
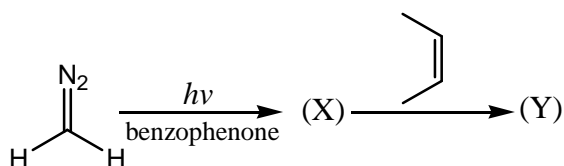
(X) and (Y) respectively are

(a) ^{1}:CH_2 and cis 1, 2-dimethylcyclopropane

(b) ^{3}:CH_2 and cis 1, 2-dimethylcyclopropane

(c) ^{1}:CH_2 and a mixture of cis/trans 1, 2-dimethylcyclopropane

(d) ^{3}:CH_2 and a mixture of cis/trans 1, 2-dimethylcyclopropane

63. The major products obtained upon treating a mixture of
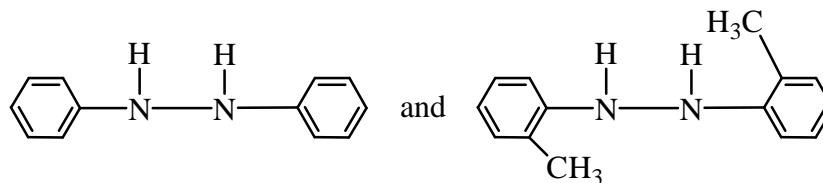
with a strongly acidic solution of H_2SO_4 is

(a)

(b)

(c)

(d)
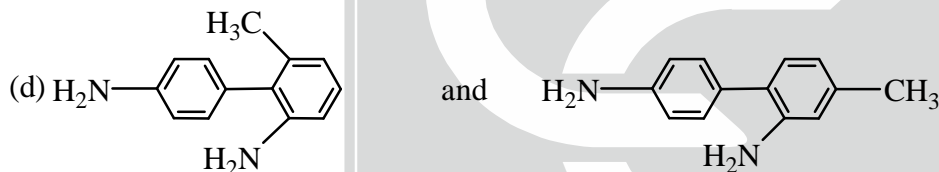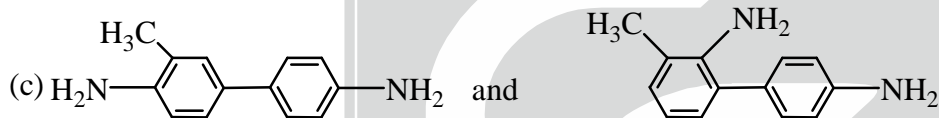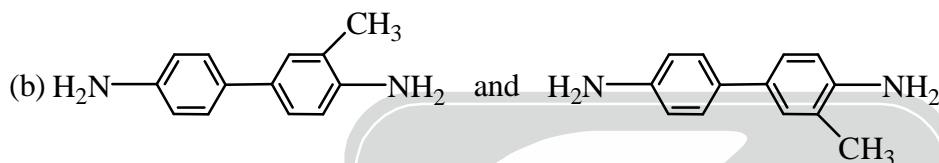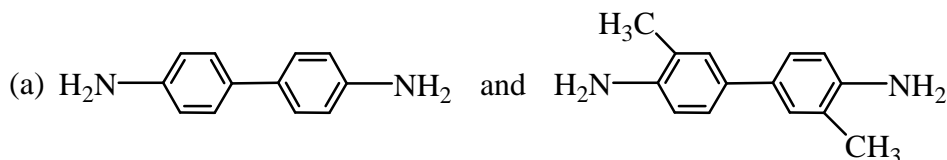
64. Match the observed pricipal absorptions in the visible spectrum shown in **List - I** with the bond shows this absorption in **List - II.**

List - I	List - II
(1) $\sigma \to \sigma^*$	(i) C–C
(2) $n \to \sigma^*$	(ii) C–O
(3) n, π^*	(iii) C=O
(3) π, π^*	(iv) C = C

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

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

65. Among the isomers $C_{10}H_{14}$ shown,
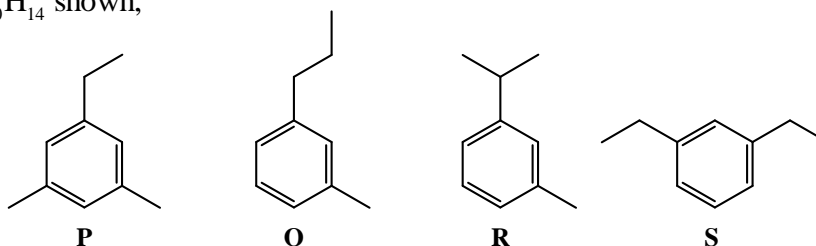
the isomer that can be identified uniquely by mass spectrometry alone is:

(a) P   (b) Q   (c) R   (d) S

66. The direction of rotation of the following thermal electrocyclic ring closures.
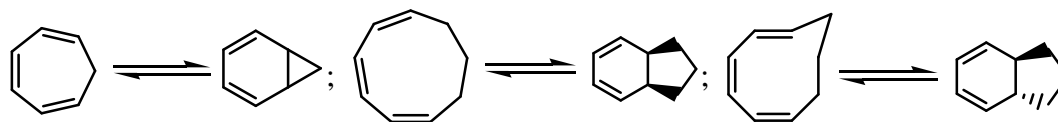
respectively is:

(a) Disrotory, disrotatory, disrotatory

(b) Conrotatory, conrotatory, conrotatory

(c) Disrotatory, disrotatory, conrotatory

(d) Disrotatory, conrotatory, disrotatory.

67. The molecules (s) that exist as meso structure (s).

(K)　　　　(L)　　　　(M)
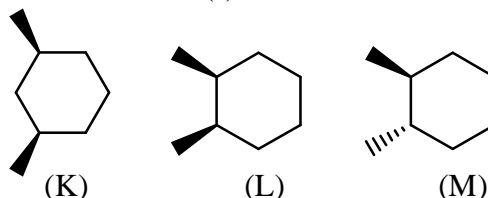
is/are:

(a) Only M　　　(b) Both K and L　　　(c) Only L　　　(d) Only K

68. Stereochemical descriptors for the atoms labeled H_a and H_b in the structures.

(X)　　　　(Y)　　　　(Z)
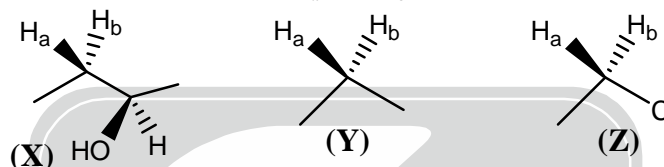
respectively are:

(a) X-homotopic, Y-enantiotopic and Z-diastereotopic

(b) X-enantiotopic, Y-homotopic and Z-diastereotopic

(c) X-diastereotopic, Y-homotopic and Z-enantiotopic

(d) X-homotopic, Y-diastereotopic and Z-enantiotopic.

69. Treatment of the pentapeptide Gly-Arg-Phe-Ala-Ala, in separate experiments, with the enzymes Trypsin, Chyemotrypsin and Carboxypeptidase A respectively, gives :

(a) Gly-Arg + Phe-Ala-Ala; Gly-Arg-Phe+Ala-Ala; Gly-Arg-Phe-Ala+Ala

(b) Gly-Arg-Phe+Ala-Ala; Gly-Arg-Phe+Ala-Ala; Gly-Arg-Phe-Ala+Ala

(c) Gly-Arg+Phe-Ala-Ala; Gly-Arg-Phe-Ala+Ala; Gly-Arg-Phe+Ala-Ala

(d) Gly-Arg + Phe-Ala-Ala; Gly-Arg-Phe+Ala-Ala; Gly+ Arg-Phe- Ala + Ala

70. Hordenine (x), an alkaloid, undergoes Hoffmann degradation to give compound (Y).

(X)
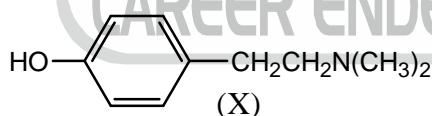
(Y) on treatment with alkaline permanganate (Z). Y and Z respectively are
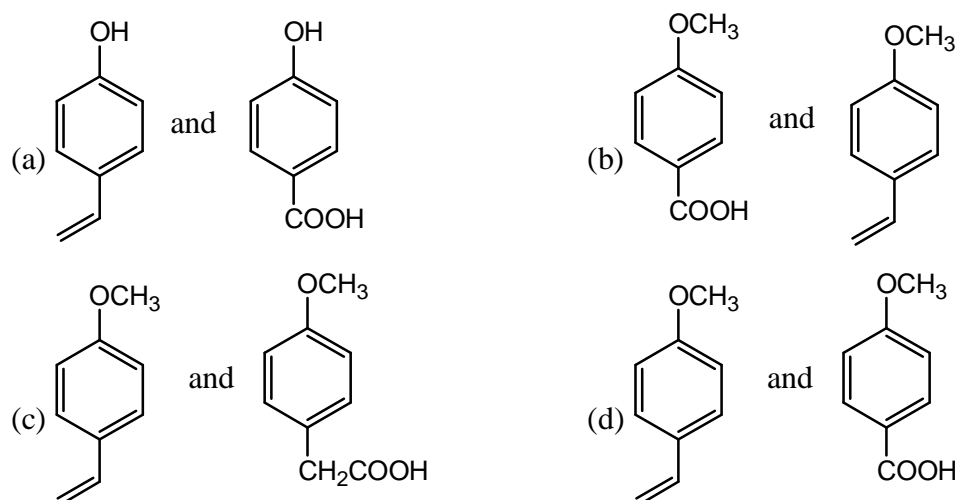
Common data for Q.71, Q.72, Q.73:

Trans 1, 2–difluoroethylene molecule has a 2-fold rotational axis, a symmetry plane perpendicular to the rotatinal axis and an inversion centre.

71. The number of distinct symmetry operations that can be performed on the molecule is:
    (a) 2   (b) 4   (c) 6   (d) 8

72. The number of irreducible representations of the point group of the molecule is:
    (a) 1   (b) 2   (c) 3   (d) 4

73. If two H atoms of the above molecule are also replaced by F atoms, the point group of the resultant molecule will be

    (a) C_i (b) C_{2h} (c) C_{2v} (d) D_{2h}

Common Data for Q.74 and Q.75 :

Reactivity of aryl amines towards electrophilic aromatic substitution is much higher than that of aliphatic amines. Hence differential reactivity of the amino group is desirable in many reactions.

74. The compound which on reacting with aniline will NOT form an acetanilide is

(a)

(b)

(c)

(d)

75. Aniline can be distinguished from methylamine by its reaction with
    (a) p-toluene sulphonyl chloride/KOH
    (b) (i) $NaNO_2$/HCl, 0-5ºC (ii) alkaline β -napthol
    (c) Sn/HCl
    (d) acetyl chloride

Linked Answer Q.76 and Q.77:

76. In the reaction,

$$\xrightarrow[\text{H}^+, \text{H}_2\text{O}]{\text{O}_3} \text{(X)} + \text{Acetone} + \text{2 Formaldehyde}$$

Compound X is

(a)

(b)

(c)

(d)
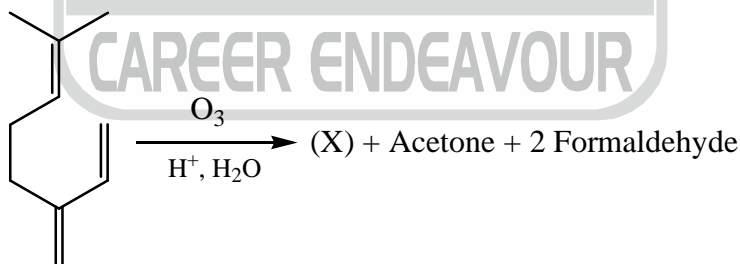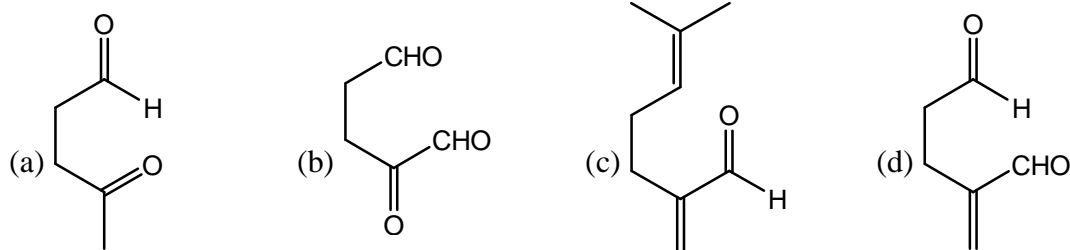
77. Oxidation of X with chromic acid chiefly gives

(a) COOH ... COOH

(b) COOH ... COOH ... O

(c) ... COOH

(d) COOH ... COOH
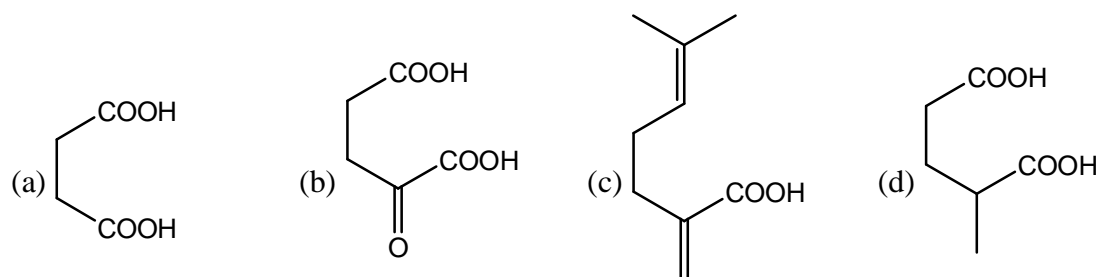
Linked Answer Type Q. 78 and Q.79:

78. In the reaction, $AMP \xrightarrow[\text{175°C}]{\text{aq. NH}_3} (X) + H_3PO_4$

Compound X is
(a) Adenine   (b) Xanthine
(c) 2, 6 - diaminopurine   (d) Adenosine

79. Compound X on treatment with conc. HCl gives
(a) Uric acid   (b) Adenine   (c) Hypoxanthine   (d) Guanine

Linked Answer Type Q.80 and Q.81.

80. The reaction of ammonium chloride with BCl_3 at 140°C at followed by treatment with $NaBH_4$ gives the product X. The formula of X is

(a) $B_3N_3H_3$ (b) $B_3N_3H_6$ (c) $B_3N_3H_{12}$ (d) $[BH-NH]_n$

81. Which of the following statement(s) is/are true for X?
(I) X is not isoelectronic with benzene
(II) X undergoes addition reaction with HCl.
(III) Electrophilic substitution reaction on X is much faster than that of benzene
(IV) X undergoes polymerization at 90°C
(a) I and II   (b) Only II   (c) II and III   (d) I and IV

Linked Answer Type Q.82 and Q.83.

82. Consider a particle of mass m moving in a one-dimensional box under the potential V = 0 for $0 \le x \le a$ and $V = \infty$ outside the box. When the particle is in its lowest energy state the average momentum ($< p_x >$ of the particle is

(a) $< p_x > = 0$ (b) $< p_x > = \dfrac{h}{a}$ (c) $< p_x > = \dfrac{h}{2a}$ (d) $< p_x > = \dfrac{h}{2\pi a}$

83. The uncertainty in the momentum (Δp_s) of the particle in its lowest energy state is:

(a) $\Delta p_x = 0$ (b) $\Delta p_x = \dfrac{h}{a}$ (c) $\Delta p_x = \dfrac{h}{2a}$ (d) $\Delta p_x = \dfrac{h}{2\pi a}$

Linked Answer Type Q. 84 and Q.85.

84. In the mixture obtained by mixing 25.0 mL 1.2×10^{-3} M $MnCl_2$ and 35.0 mL of 6.0×10^{-4} M KCl solution, the concentrations (M) of Mn^{2+}, K^+ and Cl^- ions respectively are
(a) $6.0 \times 10^{-4}, 3.0 \times 10^{-4}, 1.5 \times 10^{-3}$ (b) $6.0 \times 10^{-4}, 3.0 \times 10^{-4}, 9.0 \times 10^{-4}$
(c) $5.0 \times 10^{-4}, 3.5 \times 10^{-4}, 1.35 \times 10^{-3}$ (d) $5.0 \times 10^{-4}, 3.5 \times 10^{-4}, 8.5 \times 10^{-4}$

85. The activity (M) of Mn^{2+} ions in the above solution is

(a) 1.0×10^{-4} (b) 2.0×10^{-4} (c) 3.0×10^{-4} (d) 4.0×10^{-4}

***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.20 : Carry ONE mark each.

1. The total number of isomers of $Co(en)_2Cl_2$ (en = ethylenediamine) is
   (a) 4   (b) 3   (c) 6   (d) 5

2. Metal-metal quadruple bonds are well-known for the metal
   (a) Ni   (b) Co   (c) Fe   (d) Re

3. The reaction of Al_4C_3 with water leads to the formation of
   (a) methane   (b) propyne   (c) propene   (d) propane

4. The correct statement about C_{60} is
   (a) C_{60} is soluble in benzene
   (b) C_{60} does not react with tert-butyllithium
   (c) C_{60} is made up of 10 five-membered and 15 six-membered rings
   (d) two adjacent five-membered rings share a common edge.

5. The lattice parameters for a monoclinic crystal are :
   (a) $a \neq b \neq c; \alpha = \gamma = 90^o$ (b) $a = b \neq c; \alpha = \beta \neq \gamma$
   (c) $a \neq b \neq c; \alpha \neq \beta \neq \gamma$ (d) $a = b = c; \alpha = \gamma = 90^o$

6. The magnetic moment of $\left[Ru(H_2O)_6\right]^{2+}$ corresponds to the presence of
   (a) four unpaired electrons   (b) three unpaired electrons
   (c) two unpaired electrons   (d) zero unpaired electrons

7. The compound that is **NOT** aromatic is

8. The order of stability for the following cyclic olefins is

       I   II   III   IV

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

9. The most acidic species is:

10. The major product of the following reaction is

(a)   (b)

(c)   (d)
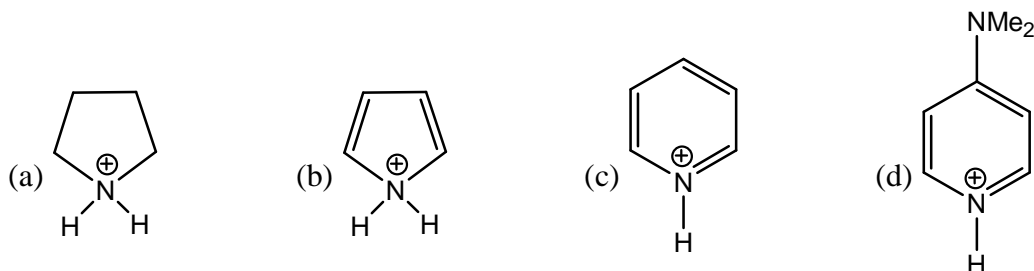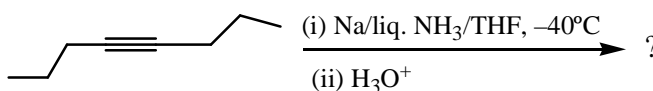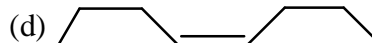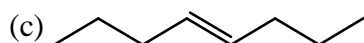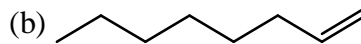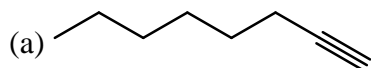
11. In the carbylamine reaction, R-X is converted to R-Y via the intermediate Z. R-X, R-Y and Z, respectively, are

(a) $R-NH_2$, R-NC, carbene   (b) $R-NH_2$, R-NC, nitrene

(c) R-NC, $R-NH_2$, carbene   (d) R-OH, R-NC, nitrene

12. The compound that is NOT oxidized by $KMnO_4$ is:

(a)   (b)   (c)   (d)
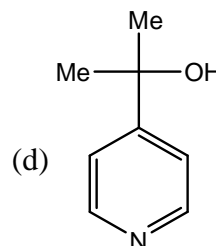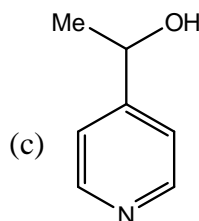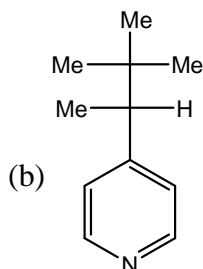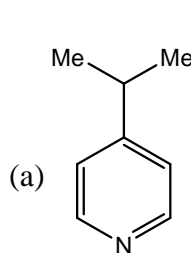
13. Cyanogen bromide (CNBr) specifically hydrolyses the peptide bond formed by the C-side of
(a) methionine   (b) glycine
(c) proline   (d) serine

14. The Hammett reaction constant ρ is based on
(a) the rates of alkaline hydrolysis of substituted ethyl benzoates
(b) the dissociation constants of substituted acetic acids
(c) the dissociation constants of substituted benzoic acids
(d) the dissociation constants of substituted phenols

15. The lifetime of a molecule in an excited electronic state is $10^{-10}\,s$. The uncertainty in the energy (eV) approximately is

(a) 2×10^{-5} (b) 3×10^{-6} (c) 0   (d) 10^{-14}

16. For a one component system, the maximum number of phases that can coexist at equilibrium is
(a) 3   (b) 2   (c) 1   (d) 4

17. At T = 300 K, the thermal energy ($k_B T$) in cm^{-1} is approximately
(a) 20000   (b) 8000   (c) 5000   (d) 200

18. For the reaction $2X_3 = 3X_2$, the rate of formation of X_2 is:

(a) $3\left(-d[X_3]/dt\right)$ (b) $\frac{1}{2}\left(-d[X_3]/dt\right)$ (c) $\frac{1}{3}\left(-d[X_3]/dt\right)$ (d) $\frac{3}{2}\left(-d[X_3]/dt\right)$

19. The highest occupied molecular orbital of HF is:
(a) bonding   (b) antibonding   (c) ionic   (d) nonbonding.

20. The residual entropy of the asymmetric molecule N_2O in its crystalline state is $5.8\ J\ K^{-1}\ mol^{-1}$ at absolute zero. The number of orientations that can be adopted by N_2O in its crystalline state is
(a) 4   (b) 3   (c) 2   (d) 1

Q.21 – Q.85 : Carry TWO marks each.

21. The spectroscopic ground state symbol and the total number of electronic transitions of $\left[Ti(H_2O)_6 \right]^{2+}$ are

    (a) $^3T_{1g}$ and 2   (b) $^3A_{2g}$ and 3   (c) $^3T_{1g}$ and 3   (d) $^3A_{2g}$ and 2

22. The structures of the complexes $[Cu(NH_3)_4](ClO_4)_2$ and $[Cu(NH_3)_4](ClO)_4$ in solution respectively
    (a) square planar and tetrahedral   (b) octahedral and square pyramidal
    (c) octahedral and trigonal bipyramidal   (d) tetrahedral and square planar

23. In biological systems, the metal ions involved in electron transport are

    (a) Na^+ and K^+ (b) Zn^{2+} and Mg^{2+}

    (c) Ca^{2+} and Mg^{2+} (d) Cu^{2+} and Fe^{3+}

24. In a homogeneous catalytic reaction, 1.0 M of a substrate and 1.0 µM of a catalyst yields 1.0 mM of a product in 10 seconds. The turnover frequency (TOF) of the reaction (s^{-1}) is
    (a) 10^{-2} (b) 10^2 (c) 10^{-3} (d) 10^3

25. The expected magnetic moments of the first-row transition metal complexes and those of the lanthanide metal complexes are usually calculated using

    (a) $\mu_{s.o}$ equation (s.o. = spin only) for both lanthanide and transition metal complexes

    (b) $\mu_{s.o}$ equation for lanthanide metal complexes and μ_J equation for transition metal complexes

    (c) $\mu_{s.o}$ equation for transition metal complexes and μ_J equation for lanthanide metal complexes

    (d) μ_{L+S} equation for transition metal complexes and $\mu_{s.o}$ equation for lanthanide metal complexes

26. The Bronsted acidity of boron hydrides follows the order
    (a) $B_2H_6 > B_4H_{10} > B_5H_9 > B_{10}H_{14}$ (b) $B_2H_6 = B_4H_{10} > B_5H_9 = B_{10}H_{14}$

    (c) $B_{10}H_{14} > B_5H_9 > B_4H_{10} > B_2H_6$ (d) $B_5H_9 > B_4H_{10} > B_2H_6 > B_{10}H_{14}$

27. NaCl is crystallised by slow evaporation of its aqueous solution at room temperature. The correct statement is
    (a) The crystals will be non-stoichiometric
    (b) The crystals should have Frenkel defects
    (c) The percentage of defects in the crystals will depend on the concentration of the solution and its rate of evaporation
    (d) The nature of defects will depend upon the concentration of the solution and its rate of evaporation

28. CaTiO$_3$ has a perovskite crystal structure. The coordination number of titanium in CaTiO$_3$ is :
    (a) 9   (b) 6   (c) 3   (d) 12

29. If CIF$_3$ were to be stereochemically rigid, its ^{19}F NMR spectrum (I for $^{19}F = \dfrac{1}{2}$) would be (assume that Cl is not NMR active)
    (a) a doublet and a triplet   (b) a singlet
    (c) a doublet and a singlet   (d) two singlets.

30. The point group of NSF$_3$ is:
    (a) D_{3d} (b) C_{3h} (c) D_{3h} (d) C_{3v}

31. When NiO is heated with a small amount of Li_2O in air at 1200°C, a non-stoichiometric compound $Li_x Ni_{(1-x)}O$ is formed. This compound is

    (a) an n-type semiconductor containing only Ni^{1+}

    (b) an n-type semiconductor containing Ni^{1+} and Ni^{2+}

    (c) a p-type semiconductor containing Ni^{2+} and Ni^{3+}

    (d) a p-type semiconductor containing only Ni^{3+}

32. White phosphorus, P_4, belongs to the
    (a) closo system   (b) nodo system   (c) arachno system   (d) hypho system

33. Among the compounds Fe_3O_4, $NiFe_2O_4$ and Mn_3O_4

    (a) $NiFe_2O_4$ and Mn_3O_4 are normal spinels   (b) Fe_3O_4 and Mn_3O_4 are normal spinels

    (c) Fe_3O_4 and Mn_3O_4 are inverse spinels   (d) Fe_3O_4 and $NiFe_2O_4$ are inverse spinels

34. The number of M-M bonds in $Ir_4(CO)_{12}$ are
    (a) four   (b) six   (c) eight   (d) zero

35. Schrock carbenes are
    (a) Triplets and nucleophilic   (b) Triplets and electrophilic
    (c) Singlets and nucleophilic   (d) Singlets and electrophilic.

36. The INCORRECT statement about linear dimethylpolysiloxane, $[(CH_3)_2 SiO]_n$, is
    (a) it is extremely hydrophilic

    (b) it is prepared by a KOH catalysed ring-opening reaction of $[Me_2SiO]_4$

    (c) it has a very low glass transition temperature
    (d) it can be reinforced to give silicon elastomers

37. Match the entries a-d with their corresponding structures P-S

    (A) bridged system   (P)
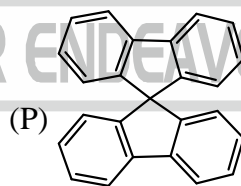
    (B) atropisometric system   (Q)
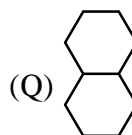
    (C) spiro system   (R)
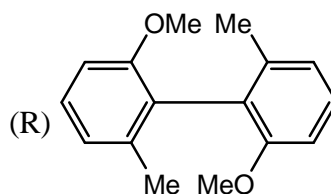
(D) Fused system   (S)
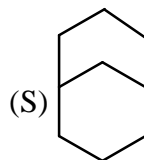
(a) A-S, B-R, C-Q, D-P   (b) A-P, B-S, C-Q, D-R

(c) A-Q B-P, C-S, D-R   (d) A-S, B-R, C-P, D-Q

38.   The reaction between X and Y to give Z proceeds via
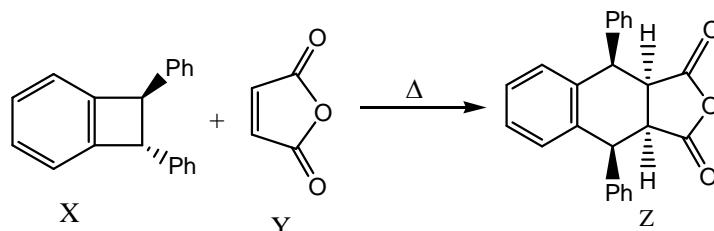
(a) 4π – conrotatory opening of X followed by endo Diels-Alder cycloaddition.

(b) 4π – distortary opening of X followed by endo Diels-Alder cycloaddition.

(c) 4π – conrotatory opening of X followed by exo Diels-Alder cycloaddition

(d) 4π – disrotatory opening of X followed by exo Diels -Alder cycloaddition.

39.   The Major products P_1 and P_2, respectively, in the following reaction sequenc are
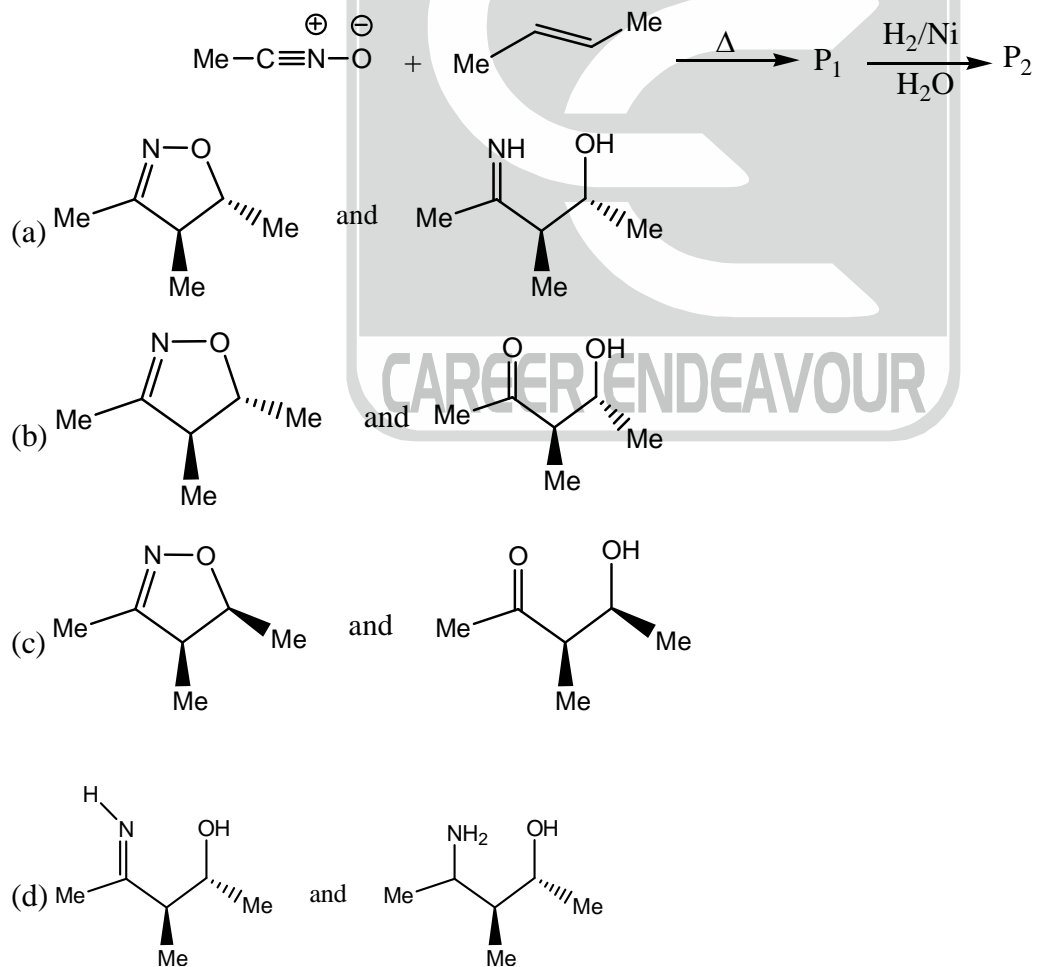
40. The products Y and Z are formed, respectively, from X via
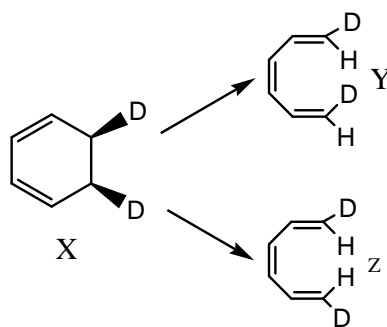
(a) hυ. conrotatory opening and Δ, disrotatory opening.
(b) hυ, disrotatory opening and Δ, controtatory opening.
(c) Δ, conrotatory opening and hυ, disrotatory opening.
(d) Δ, disrotatory opening and hυ, conrotatory opening.

41. o-Bromophenol is readily prepared from phenol using the following conditions

(a) (i) $(CH_3CO)_2O$;   (ii) Br_2;   (iii) $HCl-H_2O$, Δ

(b) (i) H_2SO_4, 100ºC   (ii) Br_2 (iii) H_3O^+, 100ºC

(c) N-Bromosuccinimide, dibenzoyl peroxide, CCl_4, Δ

(d) Br_2 / $FeBr_3$

42. The major product of the following reaction is
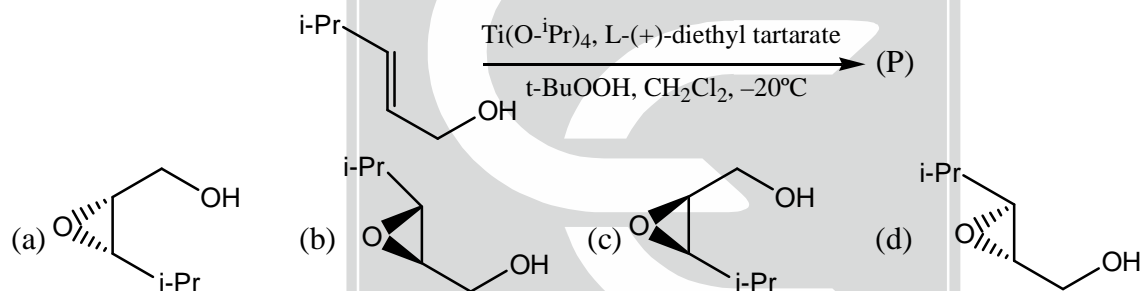
43. The photochemical reaction of 2-methylpropane with F_2 gives 2-fluoro-2-methylpropane and 1-fluoro-2-methylpropane in 14:86 ratio. The corresponding ratio of the bromo products in the above reaction using Br_2 is most likely to be
(a) 14 : 86   (b) 50 : 50   (c) 1 : 9   (d) 99 : 1

44. The major product P of the following reactions is

(c)

(d)
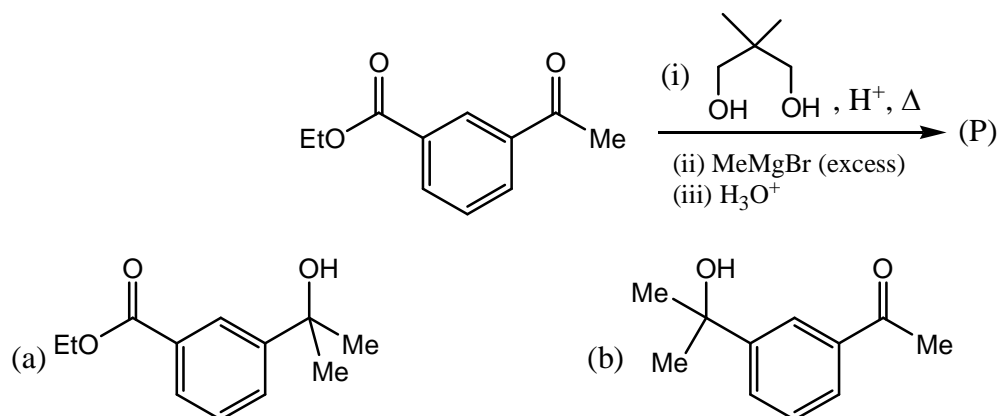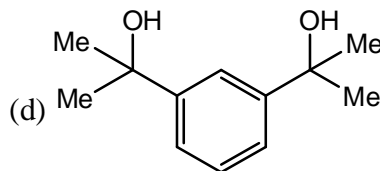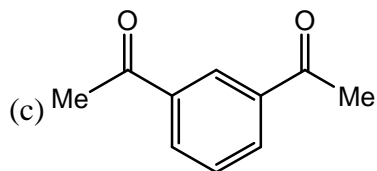
45. The reagent X in the following reaction is
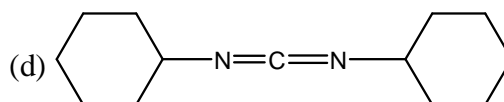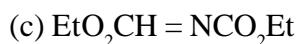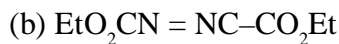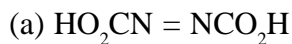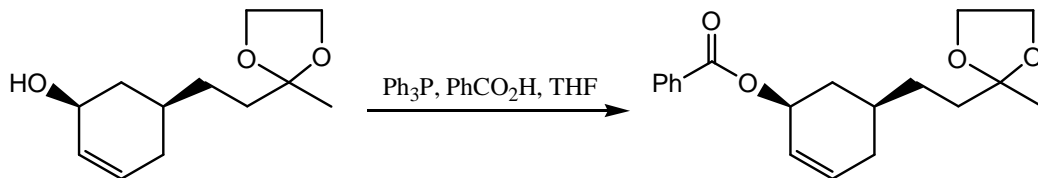
(a) $HO_2CN = NCO_2H$

(b) $EtO_2CN = NC–CO_2Et$

(c) $EtO_2CH = NCO_2Et$

(d)

46. The major product of the following reactions is

(a)

(b)

(c)

(d)

47. The major product of the following reaction is:

(a)

(b)

(c)

(d)
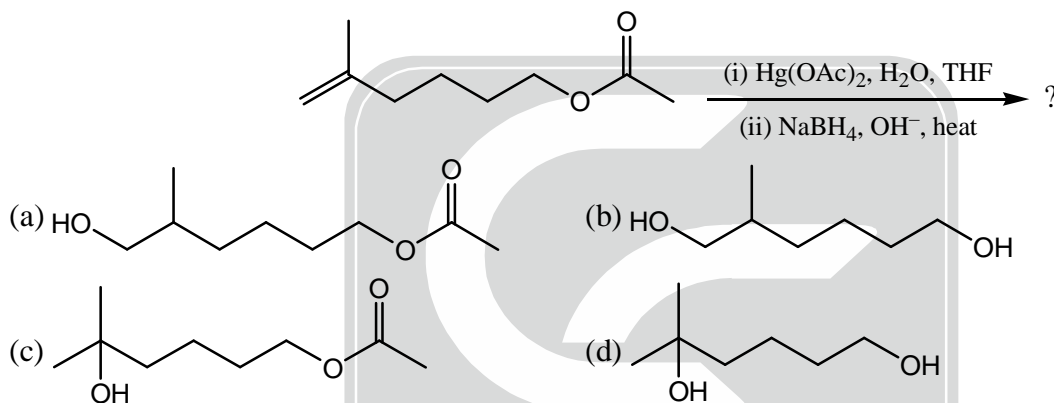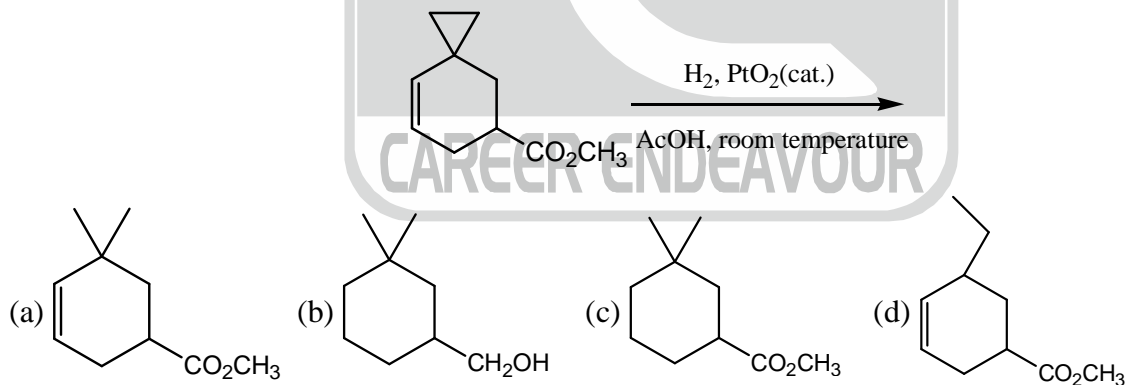
48. In the following compound, the hydroxy group that is most readily methylated with CH_2N_2 is:
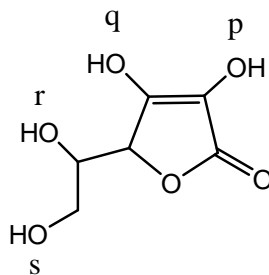
(a) p   (b) q   (c) r   (d) s

49. The most appropriate sequence of reactions for carrying out the following transformations.
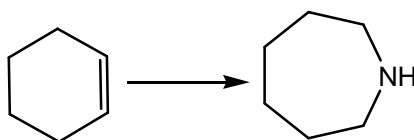
   (a) (i) O_3/H_2O_2; (ii) excess $SOCl_2$/pyridine ; (iii) excess NH_3; (iv) $LiAlH_4$
   (b) (i) O_3/Me_2S; (ii) excess $SOCl_2$/pyridine; (iii) $LiAlH_4$; (iv) excess NH_3
   (c) (i) O_3/H_2O_2; (ii) excess $SOCl_2$/pyridine; (iii) $LiAlH_4$; (iv) excess NH_3
   (d) (i) O_3/Me_2S; (ii) excess $SOCl_2$/pyridine; (iii) excess NH_3; (iv) $LiAlH_4$

50. The number of optically active stereoisomers possible for 1,3-cyclohexanediol in its chair conformation is
    (a) 4   (b) 3   (c) 2   (d) 1

51. The major product of the following reactions is
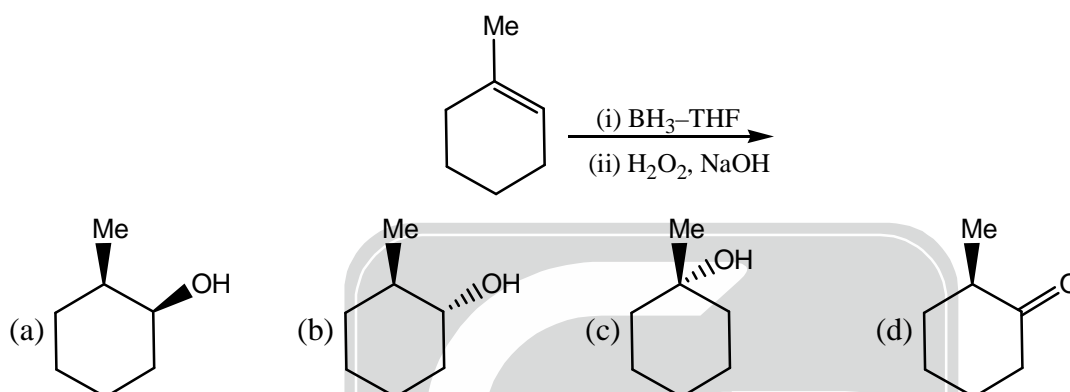
52. In the following reaction,
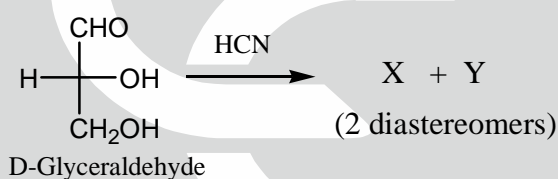
    The absolute configurations of the chiral centres in X and Y are
    (a) 2S, 3R and 2R, 3R   (b) 2R, 3R and 2R, 3S
    (c) 2S, 3S and 2R, 3R   (d) 2S, 3R and 2S, 3R

53. The IR stretching frequencies (cm^{-1}) for the compound X are as follows: 3300-3500 (s, br); 3000 (m); 2225 (s); 1680(s).
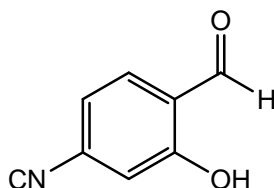
    The correct assignment of the absorption bands is:

    (a) $\overline{v}_{(OH)} = 3300 - 3500; \overline{v}_{(CH)} = 3000; \overline{v}_{(CN)} = 2225; \overline{v}_{(CO)} = 1680$

    (b) $\overline{v}_{(OH)} = 3000; \overline{v}_{(CH)} = 3300 - 3500; \overline{v}_{(CN)} = 2225; \overline{v}_{(CO)} = 1680$

    (c) $\overline{v}_{(OH)} = 3300 - 3500; \overline{v}_{(CH)} = 3000; \overline{v}_{(CN)} = 1680; \overline{v}_{(CO)} = 2225$

    (d) $\overline{v}_{(OH)} = 3000; \overline{v}_{(CH)} = 3300 - 3500; \overline{v}_{(CN)} = 1680; \overline{v}_{(CO)} = 2225$

54. The Td point group has 24 elements and 5 classes. Given that it has two 3-dimensional irreducible representation, the number of one dimensional irreducible representation is:

(a) 1   (b) 2   (c) 0   (d) 3

55. The total number of ways in which two nonidentical spin-½ particles can be oriented relative to a constant magnetic field is;

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

56. Approximately one hydrogen atom per cubic meter is present in interstellar space. Assuming that the H-atom has a diameter of 10^{-10} m, the mean free path (m) approximately is

(a) 10^{10} (b) 10^{19} (c) 10^{24} (d) 10^{14}.

57. The wavefunction of a diatomic molecule has the form $\psi = 0.89\, \varphi_{convalent} + 0.45\, \varphi_{ionic}$. The chance that both electrons of the bond will be found on the same atom in 100 inspections of the molecule approximately is

(a) 79   (b) 20   (c) 45   (d) 60

58. For the reaction given below, the relaxation time is 10^{-6} s. Givem that 10% of A remains at equilibrium, the value of $k_1 (s^{-1})$ is

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$
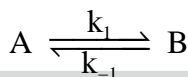
(a) 9×10^5 (b) 10^{-5} (c) 10^5 (d) 9×10^{-5}

59. The minimum number of electrons needed to form a chemical bond between two atoms is

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

60. The ground state electronic energy (Hartree) of a helium atom, neglecting the inter-electron repulsion, is

(a) –1.0   (b) –0.5   (c) –2.0   (d) –4.0

61. A particle is confined to a one-dimensional box of length 1 mm. If the length is changed by 10^{-9} m, the % change in the ground state energy is

(a) 2×10^{-4} (b) 2×10^{-7} (c) 2×10^{-2} (d) 0

62. A certain molecule can be treated as having only a doubly degenerate state lying at 360 cm^{-1} above the non-degenerate ground state. The approximate temperature (K) at which 15% of the molecules will be in the upper state is

(a) 500   (b) 150   (c) 200   (d) 300

63. A box of volume V contains one mole of an ideal gas. The probability that all N particles will be found occupying one half of the volume leaving the other half empty is

(a) 1/2   (b) 2/N   (c) $(1/2)^N$ (d) $(1/2)^{6N}$

64. According to the Debye-Huckel limiting law, the mean activity coefficient of 5×10^{-4} mol kg^{-1} aqueous solution of $CaCl_2$ at 25°C is (the Debye-Huckel constant 'A' can be taken to be 0.509)

(a) 0.63   (b) 0.72   (c) 0.80   (d) 0.91

65. The operation of the commutator $[x, d/dx]$ on a function f(x) is equal to

(a) 0   (b) f(x)   (c) –f(x)   (d) x df/dx

66. If a gas obeys the equation of state $P(V - nb) = nRT$, the ratio $\dfrac{(C_P - C_V)}{(C_P - C_V)_{ideal}}$ is:

(a) >1   (b) <1   (c) 1   (d) (1–b)

67. Physisorbed particles undergo desorption at 27 °C with an activation energy of 16.628 kJ mol^{-1}. Assuming first-order process and a frequency factor of 10^{12} Hz, the average residence time (in seconds) of the particles on the surface is

    (a) 8×10^{-10} (b) 8×10^{-11} (c) 2×10^{-9} (d) 1×10^{-12}

68. The rotational constants for CO in the ground and the first excited vibrational states are 1.9 and 1.6 cm^{-1}, respectively. The % change in the internuclear distance due to vibrational excitation is

    (a) 9   (b) 30   (c) 16   (d) 0

69. The mechanism of enzyme (E) catalysed reaction of a substrate (S) to yield product (P) is:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [ES] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P; \qquad \frac{-d[S]}{dt} = \frac{k_1 k_2 [S]_0 + k_2 k_{-2} [P]}{k_1 [S]_0 + k_{-2} [P] + k_{-1} + k_2} [E]_0$$

    If a small amount of S is converted to P, the maximum rate for the reaction will be observed for

    (a) $(k_1 + k_2) >> k_1 [S]_0$ (b) $(k_{-1} + k_2) << k_1 [S]_0$

    (c) $(k_1 + k_2) >> k_1 (s)_1$ (d) $k_2 << k_1$

70. The lowest energy state of the $(1s)^2 (2s)^1 (3s)^1$ configuration of Be is:

    (a) $^1S_0$ (b) $^1D_2$ (c) $^3S_1$ (d) $^3P_1$

Common Data for Q. 71 , Q.72 and Q.73

An electron accelerated through a potential difference of φ volts impinges on a nickel surface, whose (100) planes have a spacing $d = 351.5 \times 10^{-12}$ m (351.5 pm)

71. The de-Broglie wavelength of the electron is $\dfrac{\lambda}{pm} = \left(\dfrac{a}{\varphi}\right)^{1/2}$. The value of 'a' in volts is

    (a) 1.5×10^{-18} (b) 1.5×10^6 (c) 6.63×10^{-5} (d) 2.5×10^{18}

72. The condition for observing diffraction from the nickel surface is

    (a) $\lambda >> 2d$ (b) $\lambda \leq 2d$ (c) $\lambda \leq ad$ (d) $\lambda \geq ad$

73. The minimum value of $\varphi (V)$ for the electron to diffract from the (100) planes is

    (a) 3000   (b) 300   (c) 30   (d) 3

Common Data for Q. 74 and Q.75

An iron complex $[FeL_6]^{2+}$ (L = neutral monodentate ligand) catalyses the oxidation of $(CH_3)_2 S$ by perbenzoic acid.

74. The formation of the organic product in the above reaction can be monitored by
    (a) gas chromatography   (b) cyclic voltammetry
    (c) electron spin resonance   (d) fluorescence spectroscopy

75. The oxidation state of the metal ion in the catalyst can be deducted by
    (a) Atomic absorption spectroscopy   (b) Mossbauer spectroscopy
    (c) HPLC   (d) Gas Chromatography

Linked Answer type Q. 76 and Q. 77:

In the reaction, $(PPh_3)_3 RhCl \xrightarrow{CH_3CN} X + Y$

76.   Compound X is

(a)
$$
\begin{array}{c}
PPh_3 \\
| \\
Ph_3P-Rh-Cl \\
| \\
H_3C\equiv\!\!\!\equiv N
\end{array}
$$
(b)
$$
\begin{array}{c}
PPh_3 \\
| \\
Ph_3P-Rh-PPh_3 \\
| \\
N\equiv\!\!\!\equiv CCH_3
\end{array}
$$
(c)
$$
\begin{array}{c}
Cl \\
| \\
Ph_3P-Rh-PPh_3 \\
| \\
H_3C\equiv\!\!\!\equiv N
\end{array}
$$
(d)
$$
\begin{array}{c}
Cl \\
| \\
Ph_3P-Rh-PPh_3 \\
| \\
N\equiv\!\!\!\equiv CCH_3
\end{array}
$$
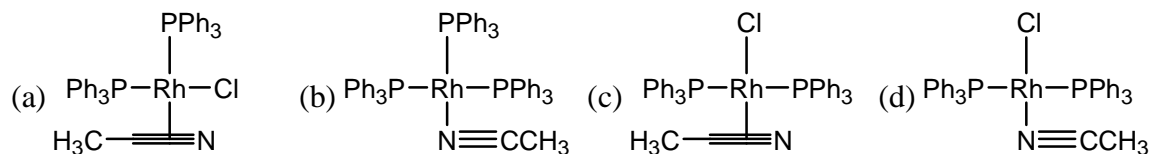
77. $Rh(PPh_3)_3 Cl$ reacts very fast with a gaseous mixture of H_2 and C_2H_4 to immediately give Z. The structure of Z is

(a) $H_3C - CH_3$

(b)
$$
\begin{array}{c}
Ph_3P \\
\diagdown \\
Rh \!\!=\!\! \\
\diagup \\
Ph_3P
\end{array}
$$

(c) $(PPh_3)_2 RhCl(\eta^2 - C_2H_4)$

(d)
$$
\begin{array}{c}
PPh_3 \\
| \\
Ph_3P-Rh-PPh_3 \\
\| \\

\end{array}
$$
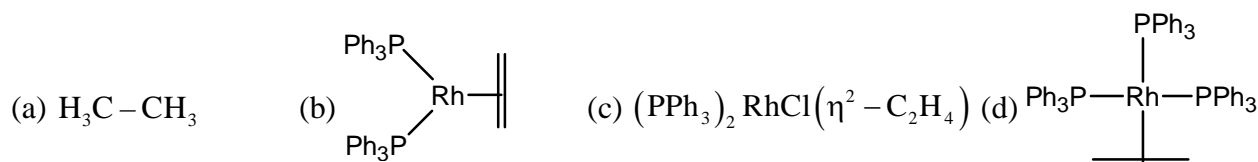
Linked Answer Type for Q. 78 and Q. 79:

The reaction of PCl_3 with methanol in the presence of triethylamine affords compound X. EI mass spectrum of X shows a parent ion peak at m/z = 124. Microanalysis of X shows that it contains C, H, O and P. The ^{1}H NMR spectrum of X shows a doublet at 4.0 ppm The separation between the two lines of the doublet is approximately 15 Hz (I for ^{1}H and ^{31}P$=\dfrac{1}{2}$).

78.   Compound X is:

(a) $(CH_3O)_3 P$ (b) $(CH_3O)_2 P(O)$

(c) $(CH_3O)_2 P(O)(OH)$ (d) $(CH_3O)_3 PH$

79.   Upon heating, compound X is converted to Y, which has the same molecular formula as that of X. The ^{1}H NMR spectrum of Y shows two doublets centered at 3.0 ppm (separation of two lines ~ 20 Hz) and 4.0 ppm (separation of two lines ~ 15 Hz) respectively.
Compound Y is:

(a) $(CH_3O)_2 P(O)(OH)$ (b) $(CH_3O)_3 P(O)$

(c) $(CH_3O)_2 (CH_3)P(O)$ (d) $(CH_3O)_2 (CH_3)P(OH)$

Linked Answer Type Q.80 and Q. 81.

For butyrophenone $(PhCOCH_2CH_2CH_3)$,

80.   The most probable fragmentation observed in the electron impact ionization (EI) mass spectrometry is:

(a)
$$
\left[\begin{array}{c} O \\ \| \\ Ph \diagup \diagdown \end{array} \right]^{.+} + H_2C\!=\!CH_2
$$

(b)
$$
\left[\begin{array}{c} O \\ \| \\ Ph \diagup \diagdown \end{array} \right]^{.-} + H_2C\!=\!CH_2
$$

(c)
$$
\begin{array}{c} O \\ \| \\ Ph \diagup \diagdown \diagup \end{array} + {}^\bullet CH_3
$$

(d)
$$
\begin{array}{c} O \\ \| \\ Ph \diagup \diagdown H \end{array} + H_2C \diagdown \diagup CH_3
$$
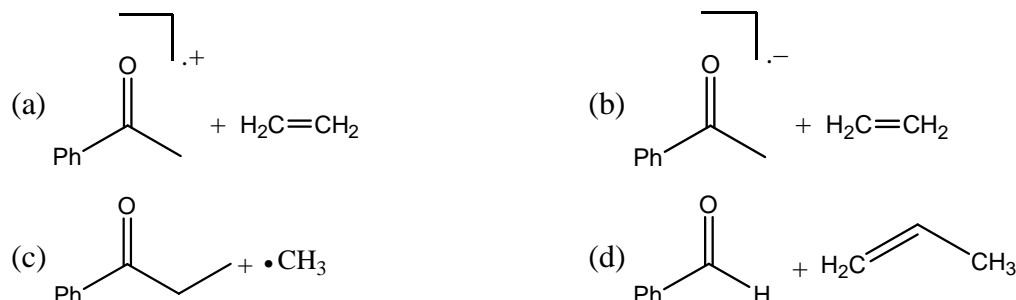
81.   Photoirradiation leads to the following set of products:

(a) Ph—CHO + H_2C=CH—CH$_3$ (b) benzene + butanal

(c) Ph—CO—CH$_3$ + H_3C—CH$_3$ (d) Ph-cyclobutanol + Ph—CO—CH$_3$ + H_2C=CH$_2$
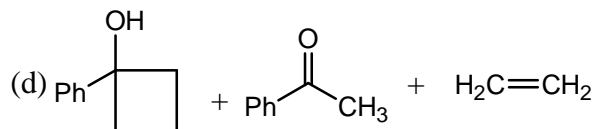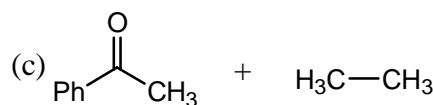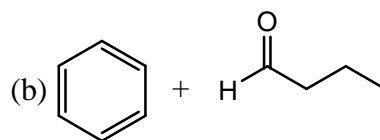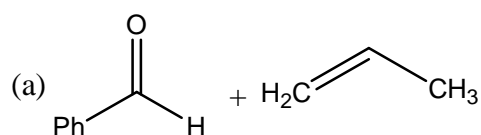
Linked Answer Q. 82 and Q. 83

In the following reaction,

$$\text{CH}_2=\text{CH-CH}_2\text{-CH-}\overset{\oplus}{\text{N}}\equiv\text{N} \xrightarrow{hv} [\text{I}] \longrightarrow [\text{P}]$$
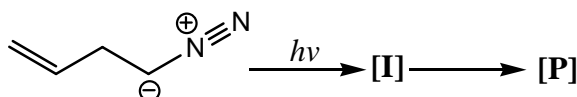
82.   The reactive intermediate I and the product P are

(a) carbene and (bicyclo structure with H's)

(b) radical and (hexatriene chain)

(c) carbene and (diene chain)

(d) radical and (bicyclopropyl structure)
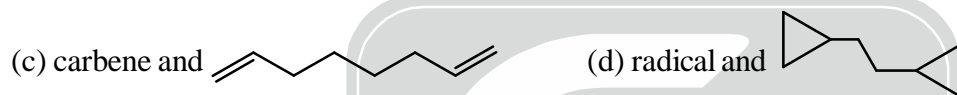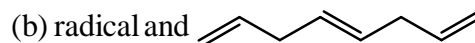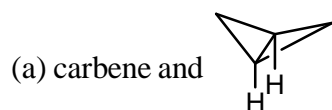
83.   The product P shows 'm' and 'n' number of signals in ^{1}H and ^{13}C NMR spectra, respectively. The values of 'm' and 'n' are

(a) m = 3 and n = 2   (b) m = 2 and n = 3   (c) m = 2 and n = 2   (d) m = 4 and n = 3

Linked Answer Type Q.84 and Q. 85:

The infrared spectrum of a diatomic molecule exhibits transitions at 2144, 4262 and 6354 cm^{-1} corresponding to excitations from the ground state to the first, second and, third vibration states respectively.

84.   The fundamental transition (cm^{-1}) of the diatomic molecule is at:

(a) 2157   (b) 2170   (c) 2183   (d) 2196

85.   The anharmonicity constant (cm^{-1}) of the diatomic molecule is:

(a) 0.018   (b) 0.012   (c) 0.006   (d) 0.003

***** END OF THE QUESTION PAPER *****
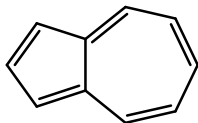
CHEMISTRY-CY

Q.1 – Q.20 : Carry ONE mark each.

1. The ^{31}P NMR spectrum of P_4S_3 consists of
   (a) a singlet
   (b) a doublet and a triplet
   (c) a doublet and a quartet
   (d) two doublets.

2. The geometry around the central atom in ClF_4^+ is
   (a) square planar
   (b) square pyramidal
   (c) octahedral
   (d) trigonal bipyramidal

3. The correct statement about the Cu-N bond distances in $\left[Cu\left(NH_3\right)_6\right]^{2+}$ is :
   (a) all the bond distances are equal
   (b) the axial bonds are longer than the equatorial ones.
   (c) the equatorial bonds are longer than the axial ones.
   (d) all the bond distances are unequal.

4. The reaction of phosgene with an excess of NH_3 produces
   (a) $HN = C = O$
   (b) $H_2N - C(Cl) = O$
   (c) $(H_2N)_2 C = O$
   (d) $(H_2N)_2 CCl_2$

5. The number of metal – metal bonds in $[(C_5H_5)Fe(CO)]_2$ is
   (a) zero
   (b) one
   (c) two
   (d) three

6. The coordination number of the Ba^{2+} ions in barium fluoride is 8. The coordination number of the fluoride ion is:
   (a) 8
   (b) 4
   (c) 1
   (d) 2.

7. In the transformation of oxyhaemoglobin to deoxyhaemoglobin
   (a) Fe^{2+} in the low spin state changes to Fe^{2+} in the high spin state
   (b) Fe^{2+} in the low spin state changes to Fe^{3+} in the low spin state.
   (c) Fe^{2+} in the high spin state changes to Fe^{2+} in the low spin state
   (d) Fe^{2+} in the high spin state changes to Fe^{3+} in the high spin state.

8. For the compound
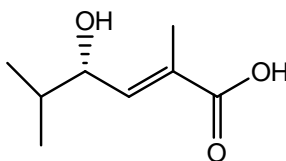
   the stereochemical notations are
   (a) 2Z, 4R
   (b) 2Z, 4S
   (c) 2E, 4R
   (d) 2E, 4S

9. The compound is

   (a) aromatic and has high dipole moment
   (b) aromatic and has no dipole moment
   (c) non-aromatic and has high dipole moment
   (d) anti-aromatic and has no dipole moment.

10. In the reaction,

the major product X is:

(a)

(b)

(c)

(d)
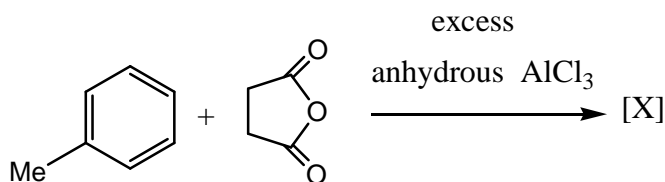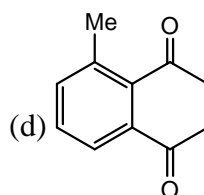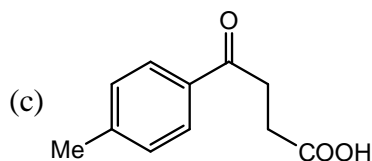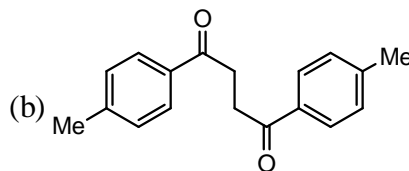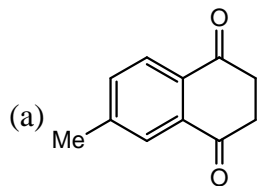
11. In the reaction

the major products X and Y are

(a) and

(b) and

(c) and

(d) None of these

12. In the reaction,
the major product X is:

(a)

(b)

(c)

(d)
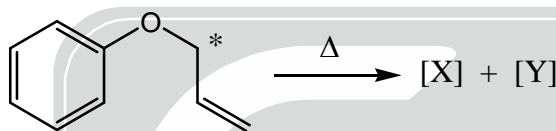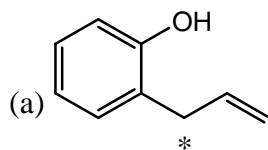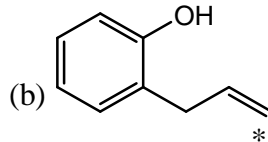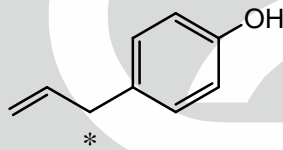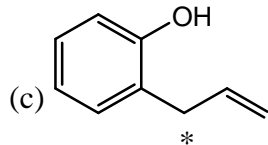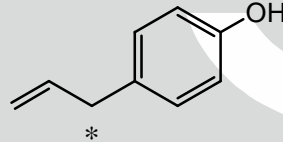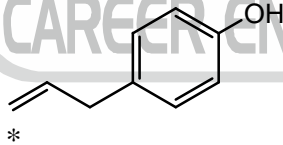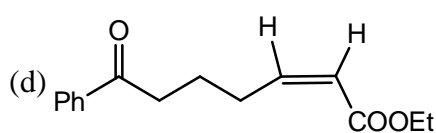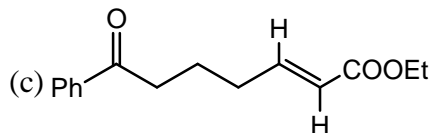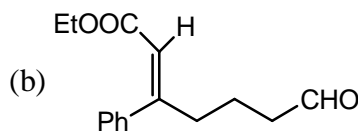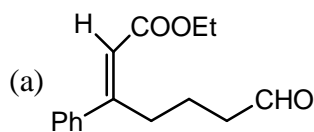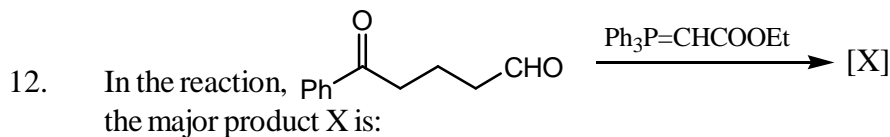
13. The most suitable reagent combination to bring out the following transformation
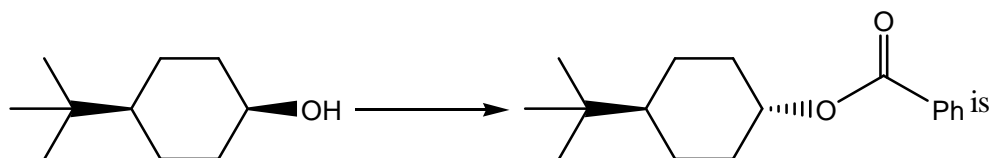
 (a) PhCOCl and pyridine   (b) DCC and PhCOOH
 (c) PhBr, CO and $Pd(PPh_3)_4$ (d) EtOOC–N=N–COOEt, PPh_3 and PhCOOH

14. In the two steps reaction sequence :
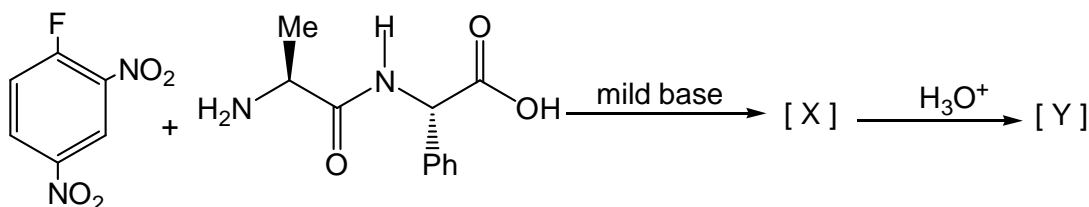
 the major product Y is :
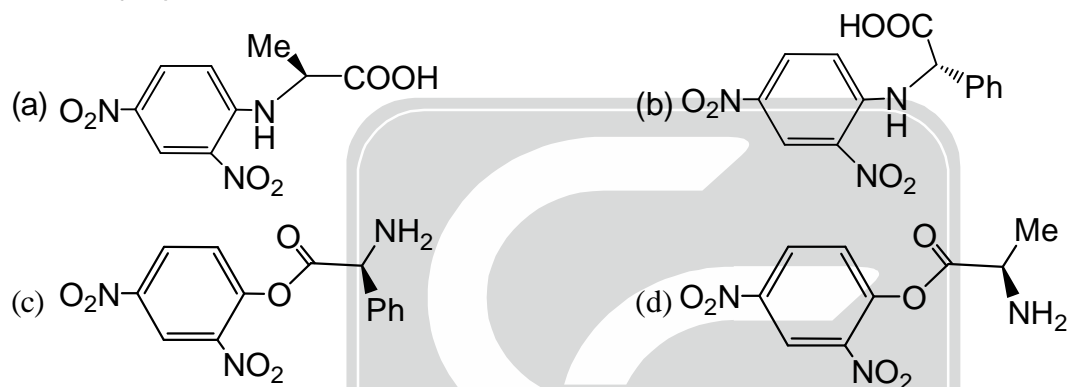
15. Among the following the system that would require the least amount of thermal energy to bring its temperature to 80°C is:
 (a) 200 gm of water at 40°C   (b) 100 gm of water at 20°C
 (c) 150 gm of water at 50°C   (d) 300 gm of water at 30°C.

16. Among the following, the reaction that is accompanied by a decrease in the entropy is
 (a) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ (b) $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$
 (c) $PCl_5(s) \rightarrow PCl_3(l) + Cl_2(g)$ (d) $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

17. The number of degrees of freedom of a system consisting of solid sucrose in equilibrium with an aqueous solution of sucrose is
 (a) 0   (b) 1   (c) 2   (d) 3

18. The lowest allowed energy is equal to zero for
 (a) the hydrogen atom   (b) a rigid rotor
 (c) a harmonic oscillator   (d) a particle in a 3-dimensional box

19. According to the Debye-Hückel limiting law, if the concentration of a dilute aqueous solution of KCl is increased 4-fold, the value of $\ln \gamma_\pm$ ($\gamma_\pm$ is the molal mean ionic activity coefficient) will
 (a) decrease by a factor of 2   (b) increase by a factor of 2
 (c) decrease by a factor of 4   (d) increase by a factor of 4.

20. For the parallel first order reaction shown below
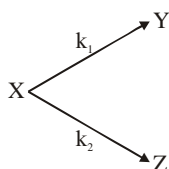
the value of k_1 is $1 \times 10^{-4} \, s^{-1}$. If the reaction starts from X, the ratio of the concentrations of Y and Z at any given time during the course of the reaction is found to be $\dfrac{[Y]}{[Z]} = \dfrac{1}{4}$

The value of k_2 is:

(a) $1 \times 10^{-4} \, s^{-1}$ (b) $2.5 \times 10^{-5} \, s^{-1}$ (c) $4 \times 10^{-4} \, s^{-1}$ (d) $4 \times 10^{4} \, s^{-1}$

Q.21 – Q.60 : Carry TWO marks each.

21. The correct order of ν_{CO} for the compounds $\left[Mo(CO)_3 (NMe_3)_3 \right]$, $\left[Mo(CO)_3 \left(P(OPh)_3 \right)_3 \right]$, $\left[Mo(CO)_3 (PMe_3)_3 \right]$, $\left[Mo(CO)_3 (PCl_3)_3 \right]$ in the IR spectrum is:

(a) $\left[Mo(CO)_3 (NMe_3)_3 \right] > \left[Mo(CO)_3 \left(P(OPh)_3 \right)_3 \right] > \left[Mo(CO)_3 (PMe_3)_3 \right] > \left[Mo(CO)_3 (PCl_3)_3 \right]$

(b) $\left[Mo(CO)_3 (PCl_3)_3 \right] > \left[Mo(CO)_3 (NMe_3)_3 \right] > \left[Mo(CO)_3 \left(P(OPh)_3 \right)_3 \right] > \left[Mo(CO)_3 (PMe_3)_3 \right]$

(c) $\left[Mo(CO)_3 (PCl_3)_3 \right] > \left[M0(CO)_3 \left(P(OPh)_3 \right)_3 \right] > \left[Mo(CO)_3 (PMe_3)_3 \right] > \left[Mo(CO)_3 (NMe_3)_3 \right]$

(d) $\left[Mo(CO)_3 (PMe_3)_3 \right] > \left[Mo(CO)_3 (NMe_3)_3 \right] > \left[Mo(CO)_3 (PCl_3)_3 \right] > \left[Mo(CO)_3 \left(P(OPh)_3 \right)_3 \right]$

22. 2.5 g of an iron compound upon suitable treatment yielded 0.391 g of iron (III) oxide. The percentage of iron in the compound is

(a) 10.94   (b) 12.15   (c) 11.31   (d) 9.11

23. In the reaction, $Ph_3P \xrightarrow{\text{MeI}} [X] \xrightarrow{\text{n-BuLi}} [Y]$, the compounds X and Y, respectively are

(a) $\left[Ph_3P(Me)I \right]$; $Ph_3P = CH - CH_2 - CH_2 - CH_3$

(b) $\left[Ph_3P(Me) \right][I]$; $Ph_3P = CH_2$

(c) $\left[Ph_3P(Me)_2 \right]$; $Ph_3P = CH_2$

(d) $\left[Ph_3P(Me) \right][I]$; Ph_3P

24. The ^1H NMR spectrum of HD consists of a

(a) singlet   (b) 1:1 doublet   (c) 1:1:1 triplet   (d) 1:2:1 triplet.

25. The X-ray powder pattern of NaCl shows an intense cone at $\theta = 15.87°$ using X-rays of wavelength 1.54×10^{-8} cm. The spacing between the planes (in Å) of NaCl crystal is

(a) 1.41   (b) 2.82   (c) 4.23   (d) 5.63

26. Among the following, the isoelectronic and isostructural pair is

(a) CO_2 and SO_2 (b) SO_3 and SeO_3 (c) NO_2^+ and TeO_2 (d) SiO_4^{4-} and PO_4^{3-}

27. Two samples have been given to you : $[NiCl_2(PPh_3)_2]$ and $[PdCl_2(PPh_3)_2]$. A physical method that can be used to identify these compounds unambiguously is
    (a) HPLC   (b) magnetic susceptibility
    (c) ^{13}C NMR spectroscopy   (d) Mössbauer spectroscopy

28. In the reaction $HSO_4^-(aq) + OH^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2O(\ell)$, the conjugate acid-base pairs are

    (a) HSO_4^- and SO_4^{2-}; H_2O and OH^- (b) HSO_4^- and H_3O^+; SO_4^{2-} and OH^-

    (c) HSO_4^- and OH^-; SO_4^{2-} and H_2O (d) HSO_4^- and OH^-; SO_4^{2-} and H_3O^+

29. Designate the following complexes X, Y and Z as inert or labile:

    $$X = \left[Al(C_2O_4)_3\right]^{3-}, \quad Y = \left[V(H_2O)_6\right]^{2+}, \quad Z = \left[Cr(C_2O_4)_3\right]^{3-}$$
    (a) X and Y are inert; Z is labile   (b) X and Z are labile; Y is inert.
    (c) X is inert; Y and Z are labile   (d) X is labile; Y and Z are inert.

30. In the reaction sequence :

X and Y, respectively, are
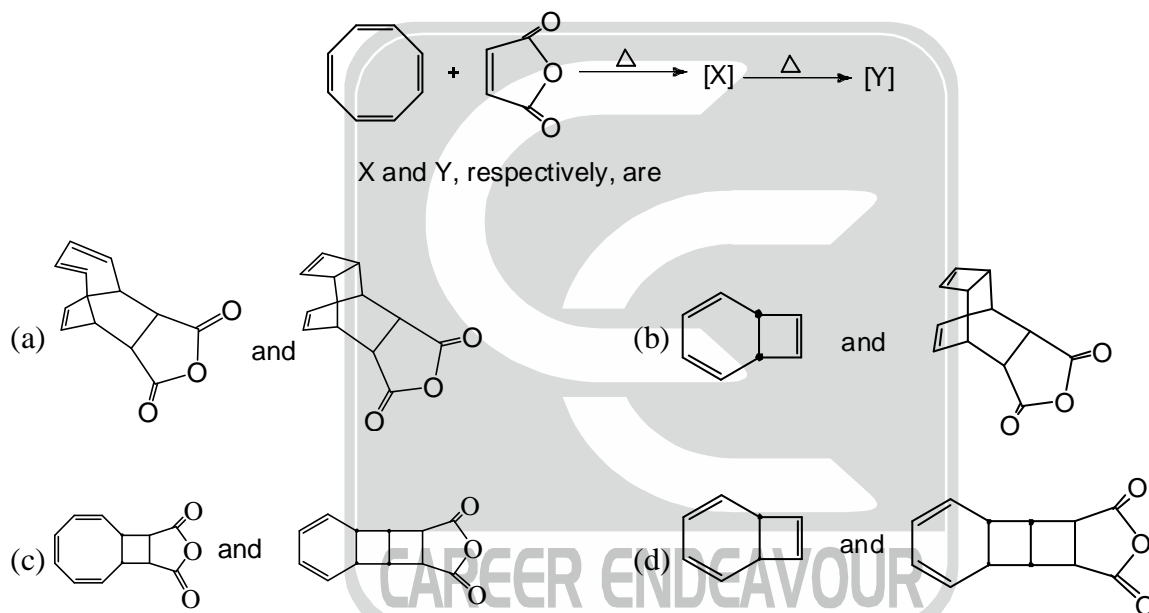
31. The major product X (based on the preferred conformation) in the reaction
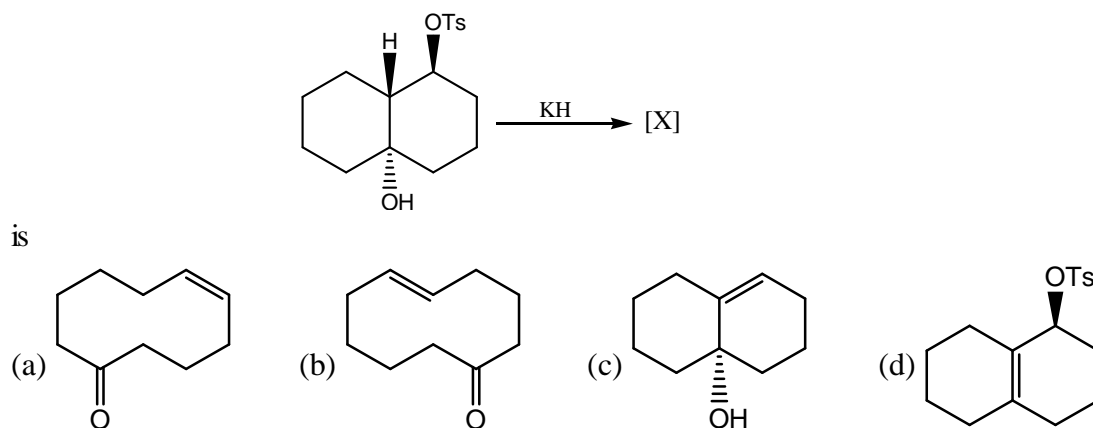
is

32. In the reactions,
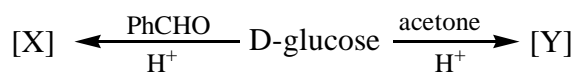
$$[X] \xleftarrow[\text{H}^+]{\text{PhCHO}} \text{D-glucose} \xrightarrow[\text{H}^+]{\text{acetone}} [Y]$$

The major products X and Y, respectively are

(a) and

(b) and

(c) and

(d) and

33. In the reaction

$$\text{Ph} \equiv\!\!\!\!\!\equiv D \xrightarrow[\text{2. CH}_3\text{COOH}]{1.} [X]$$

the major product X is

(a)

(b)

(c)

(d)
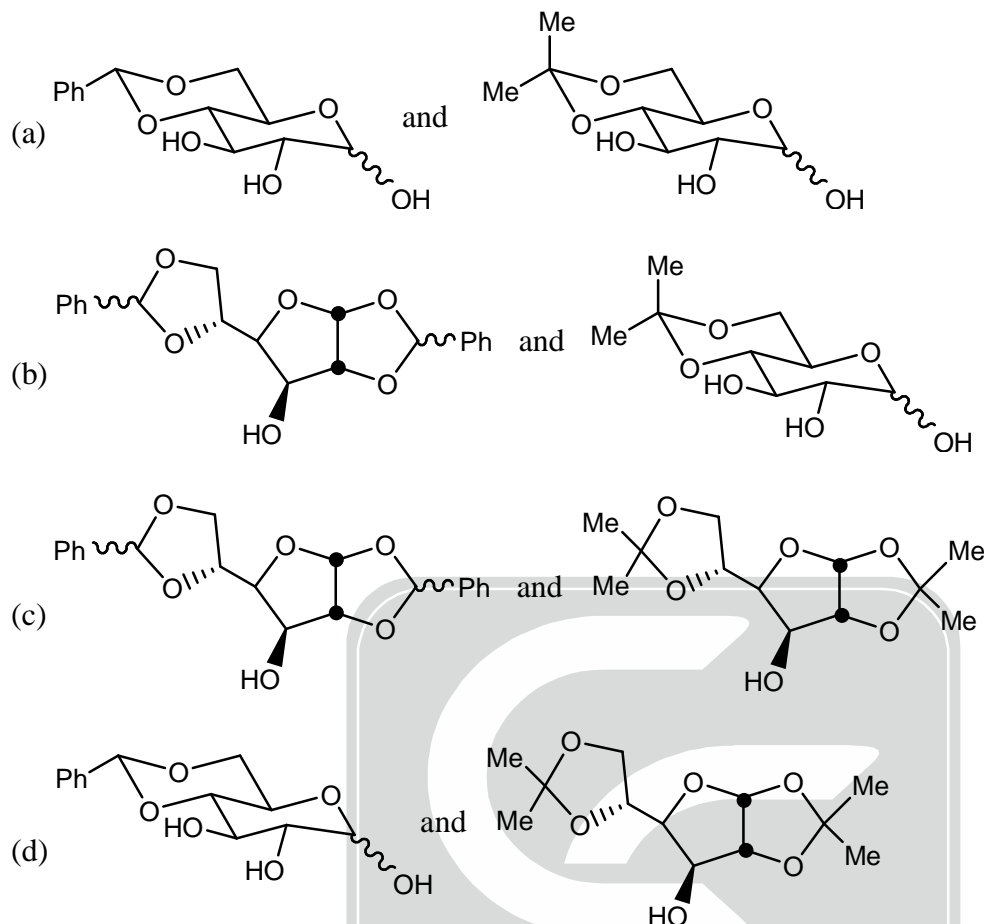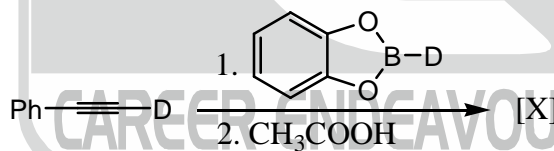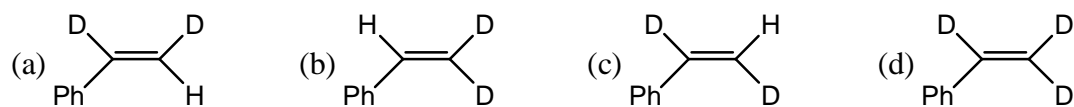
34. Reaction of m-methylanisole with lithium in liquid ammonia and t-butyl alcohol at –33ºC generates compound X as the major product. Treatment of the compound X with dilute sulphuric acid produces compound Y as the major product. The compounds X and Y, respectively, are

(a) and

(b) and

(c) and   (d) and
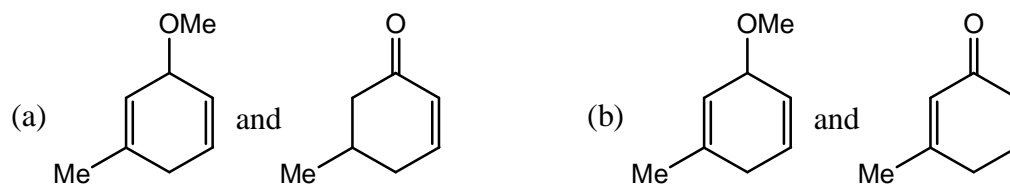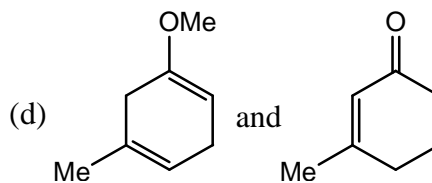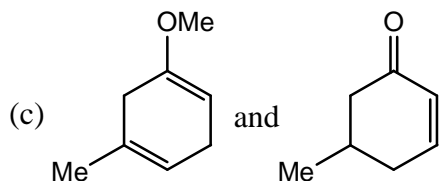
35. The number of signals that appear in the broad-band decoupled ^{13}C NMR spectrum of ortho-, meta- and para-dichlorobenzenes, respectively, are

(a) 3, 4 and 2   (b) 3, 3 and 2   (c) 4, 4 and 2   (d) 3, 4 and 4

36. In the reaction seqeunce,   **[GATE 2009]**
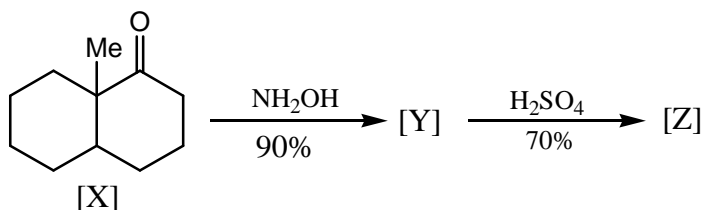
the structure of the major product Z and the overall yield for its formation from the ketone X, are

(a) and 80%   (b) and 63%

(c) and 63%   (d) and 80%
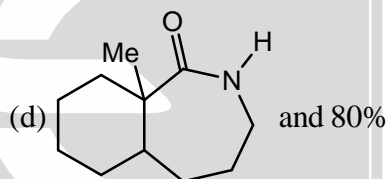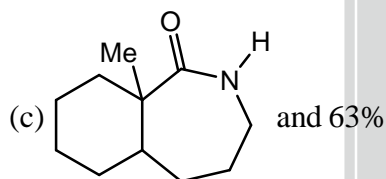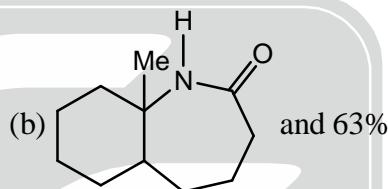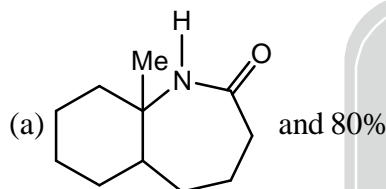
37. In the reaction sequence
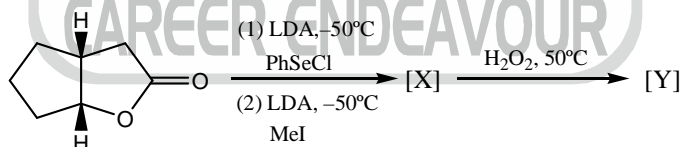
the major product respectively, are:

(a) and   (b) and

(c) and (d) and
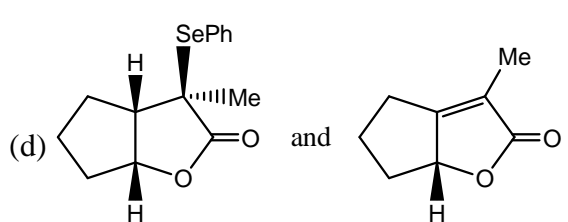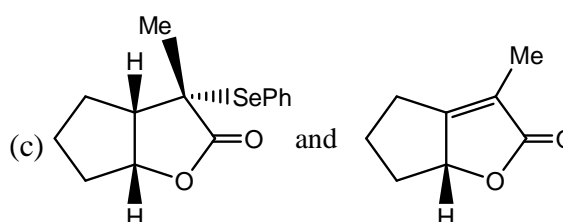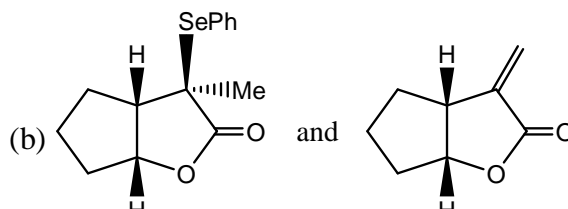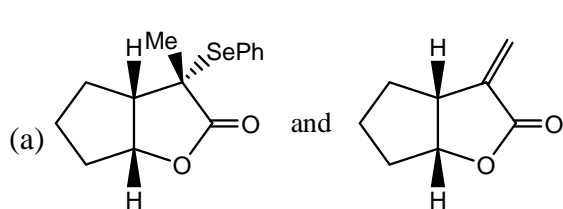
38. In the reaction sequence the major products X and Y, respectively are   **[GATE 2009]**

(a) and

(b) and

(c) and

(d) and

39. In the reaction sequence

The major products X and Y, respectively are

(a) and

(b) and

(c) and

(d) and
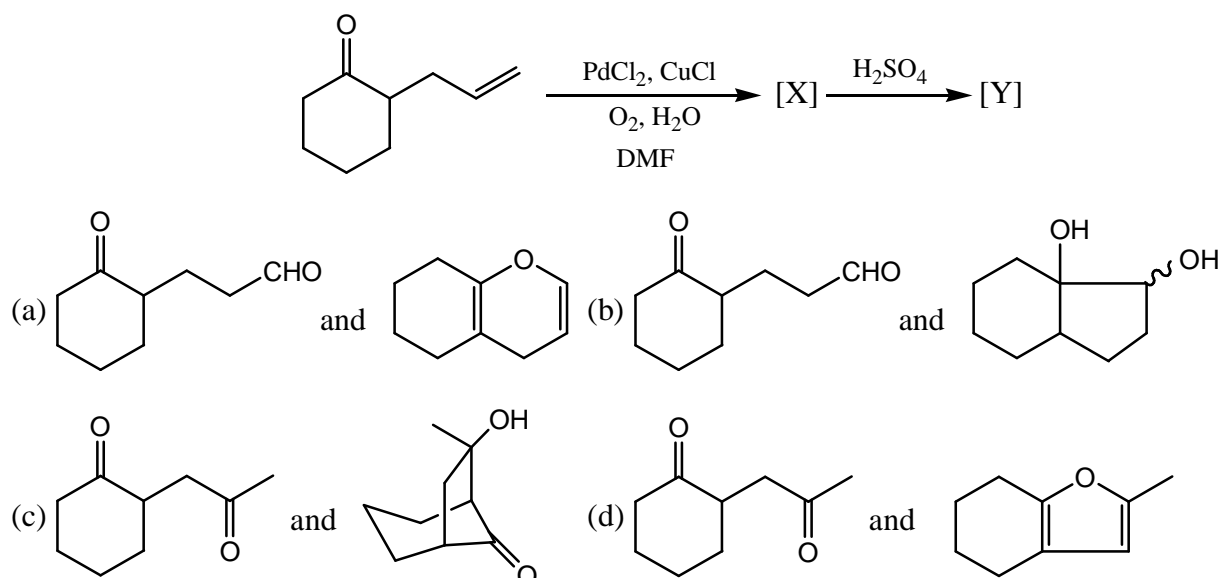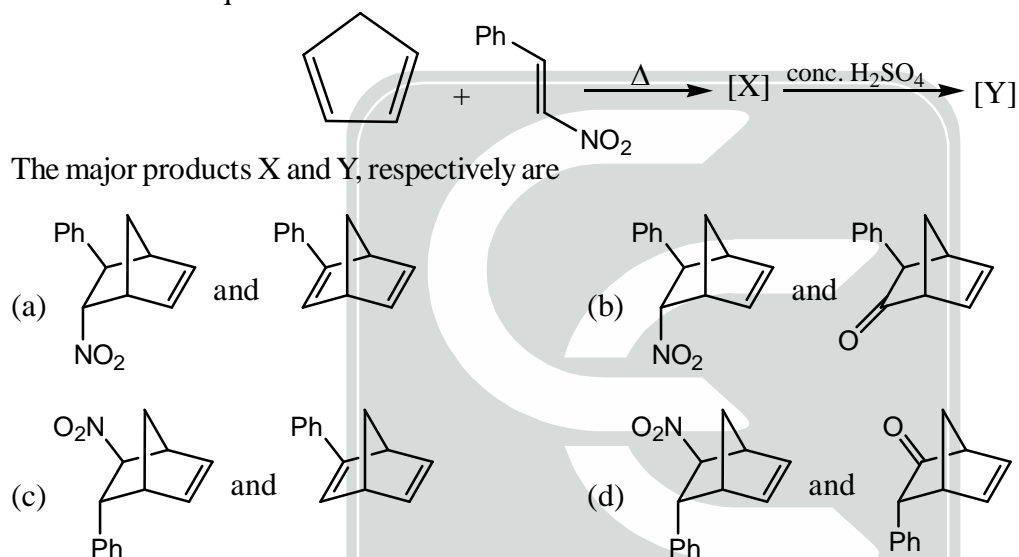
40. In the photochemical reaction
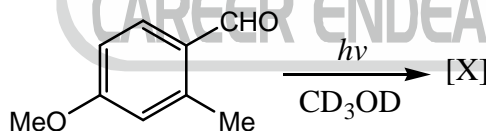
formation of the compound X can be inferred by the disappearance of the ^{1}H NMR signal at ^{1}H NMR spectrum of the starting material:

$$\delta\, 9.7\,(1H, s), 7.8\,(1H, d, J = 8.0\ Hz), 7.1 - 6.8\,(2H, m), 3.9\,(3H, s), 2.5\,(3H, s)\,ppm\,]$$

(a) $\delta\, 9.7$ ppm   (b) $\delta\, 7.8$ ppm   (c) $\delta\, 3.9$ ppm   (d) $\delta\, 2.5$ ppm

41. The half-life $(t_{1/2})$ for the hydrolysis of an ester varies with the initial concentration of the reactant $([E]_0)$ as follows:

$[E]_0 / 10^{-2}$ mol L^{-1}	5.0	4.0	3.0
$t_{1/2} / s$	240	300	400

The order of the reaction is:

(a) 0   (b) 1   (c) 2   (d) 3

42. The fluorescene lifetime of a molecule in solution is 10 ns. If the fluorescence quantum yield is 0.1, the rate constant of fluorescence decay is:

(a) $1 \times 10^9 \, s^{-1}$ (b) $1 \times 10^8 \, s^{-1}$ (c) $1 \times 10^7 \, s^{-1}$ (d) $9 \times 10^7 \, s^{-1}$

43. The fundamental vibrational wavenumbers for H_2 and I_2 are 4403.2 cm^{-1} and 214.5 cm^{-1}, respectively. The relative population of the first excited vibrational states of these two molecules compared to their respective ground states at 300 K are respectively:

(a) 6.75×10^{-1} and 3.57×10^{-1} (b) 6.75×10^{-10} and 3.57×10^{-1}

(c) 3.57×10^{-6} and 6.75×10^{-1} (d) 3.57×10^{-1} and 6.75×10^{-1}

44. The degeneracy of a quantum particle in a cubic box having energy four times that of the lowest energy is

(a) 3   (b) 6   (c) 1   (d) 4

45. The rotational Raman spectrum of $^{19}F_2$ shows a series of Stokes lines at 19230.769 cm^{-1}, 19227.238 cm^{-1} and 19223.707 cm^{-1}. The rotational constant for $^{19}F_2$ in GHz is:

(a) 26.484   (bv) 52.968   (c) 105.936   (d) 3.531

46. The de-Broglie wavelength for a He atom travelling at 1000 ms^{-1} (typical speed at room temperature) is

(a) $99.7 \times 10^{-12} \, m$ (b) $199.4 \times 10^{-12} \, m$ (c) $199.4 \times 10^{-18} \, m$ (d) $99 \times 10^{-6} \, m$

47. Given that the standard molar enthalpies of formation of NO(g) and NO_2(g) are, respectively, 90.3 kJ mol^{-1} and 33.2 kJ mol^{-1}, the enthalpy change for the reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ is

(a) 16.6 kJ   (b) –57.1 kJ   (c) –114.2 kJ   (d) 57.1 kJ

48. Among the following, the equilibrium which is NOT affected by an increase in pressure is

(a) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ (b) $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$

(c) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$ (d) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

49. The free energy change (ΔG) of 1 mole of an ideal gas that is compressed isothermally from 1 atm to 2 atm is:

(a) RTln2   (b) –2RT   (c) –RTln2   (d) 2RT

50. Two liquids B and C form an ideal solution. In the figure below, the vapour pressure P of this solution is shown as a function of the mole fraction, X_B, of component B.
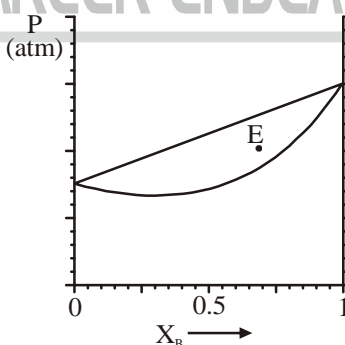
Given a state of this vapour-liquid mixture whose overall composition corresponds to point E in the figure, the mole fraction of B in the vapour phase is approximately

(a) 0.25   (b) 0.53   (c) 0.65   (d) 0.80

Common data for Q. 51 and Q. 52:

Treatment of $W(CO)_6$ with 1 equivalent of $Na(C_5H_5)$ in THF solution gives the ionic compound M. Reaction of M with glacial acetic acid results in product N. The ^1H NMR spectrum of N displays two singlets of relative intensity 5:1. When N is heated, hydrogen gas is evolved and O is produced; O may also be prepared by refluxing $W(CO)_6$ with cyclopentadiene and H_2 is also produced. Treatment of O with an equivalent of Br_2 produces P. (Use the 18 electron rule as your guide).

51. The compounds M and N, respectively, are

    (a) $\left[(C_5H_5)W(CO)_3\right]Na$ and $\left[(C_5H_5)W(CO)_3H\right]$

    (b) $\left[(C_5H_5)W(CO)_4\right]Na$ and $\left[(C_5H_5)W(CO)_4H\right]$

    (c) $\left[(C_5H_5)W(CO)_3\right]Na$ and $\left[(C_5H_5)W(CO)_4H\right]$

    (d) $\left[(C_5H_5)W(CO)_4\right]Na$ and $\left[(C_5H_5)W(CO)_3H\right]$

52. The compounds O and P, respectively, are

    (a) $\left[(C_5H_5)W(CO)_3\right]_2$ and $\left[(C_5H_5)W(CO)_3Br\right]$

    (b) $\left[(C_5H_5)W(CO)_4\right]$ and $\left[(C_5H_5)W(CO)_2Br(THF)\right]$

    (c) $\left[(C_5H_5)W(CO)_2(THF)_2\right]$ and $\left[(C_5H_5)W(CO)_3Br\right]$

    (d) $\left[(C_5H_5)W(CO)_3\right]_2$ and $\left[(C_5H_5)W(CO)_2Br(THF)\right]$

Common data for Q. 53 and Q. 54:

An organic compound $X(C_9H_{10}O)$ exhibited the following spectral data.
IR : 1680 cm^{-1}.

^1H NMR : $\delta 7.8(2H, d, J\ 7.5\ Hz),\ 7.2(2H, d, J = 75\ Hz),\ 2.7(3H, s)$ and $2.4(3H, s)$

Compound X on treatment with m-chloroperbenzoic acid produced two isomeric compounds Y (major) and Z (minor).

53. Compounds Y and Z, respectively, are

    (a) and

    (b) and

(c) and
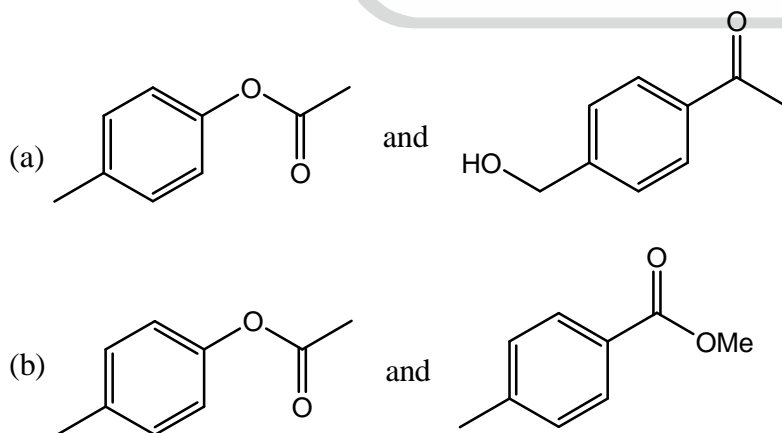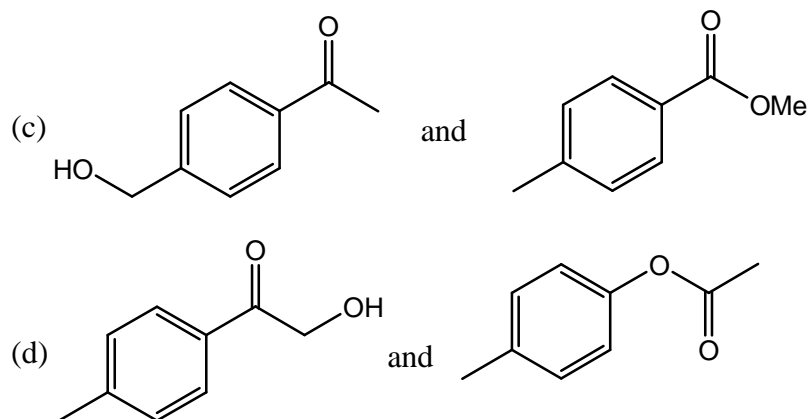
(d) and

54. Compounds Y and Z can be differentiated by carrying out basic hydrolysis, because   **[GATE 2009]**
(a) Y produces 4-methylphenol and Z is unaffected.
(b) Y produces 4-methylphenol and Z produces 4-methylbenzoic acid.
(c) Y is unaffected and Z produces 4-methylbenzoic acid.
(d) Y is unaffected and Z produces 4-methylphenol.

Common data for Q. 55 and Q. 56.

Character table for the point group C_{2v} is given below:

C_{2v}	E	C_2	$\sigma_y(xz)$	$\sigma_y(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^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

55. The reducible representation corresponding to the three translational degrees of freedom, $\Gamma_{u'}$ is:

(a) 3, 1, 1, 1   (b) 3, −1, 1, 1   (c) 3, −1, −1, −1   (d) 3, 1, −1, −1.

56. The asymmetric stretching mode of the H_2O is shown below. The molecular plane is yz and the symmetry axis of H_2O is z.
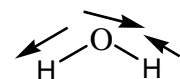
This vibration transforms as the irreducible representation

(a) A_1 (b) B_1 (c) A_2 (d) B_2

Linked Answer type Q.57 and Q.58.

Triphosphazene is prepared by reacting X and Y in equimolar ratio at 120–150°C using appropriate solvents   **[GATE 2009]**

57. The reaction X and Y, respectively, are

(a) PCl_3; NH_3 (b) PCl_5; NH_3 (c) PCl_5; NH_4Cl (d) PCl_3; NH_4Cl

58. The structure of triphosphazene is

(a)   (b)

(c)

(d)
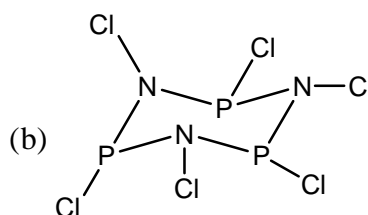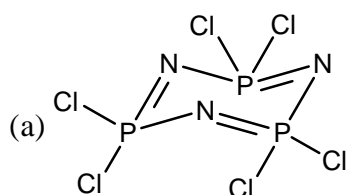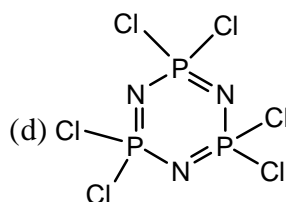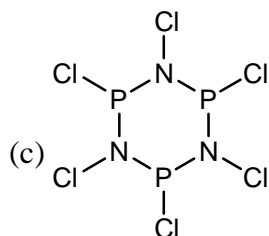
Statement for Linked Q.59 and Q.60:

In the reaction mechanism given , $X + Y \underset{k_2, E_{A,2}}{\overset{k_1, E_{A,1}}{\rightleftharpoons}} Z \xrightarrow{k_3, E_{A,3}} P$

$'k's$ represent rate constants, 'E_A's represent activation energies, and $k_2 \gg k_3$

59. The overall rate constant $(k_{overall})$ for the formation of P can be expressed as

(a) $k_1 k_3 / k_2$ (b) k_1 (c) $k_1 / (k_2 + k_3)$ (d) $k_1 / (k_2 - k_3)$

60. The overall activation energy $(E_{A, overall})$ for the formation of P can expressed as

(a) $\dfrac{E_{A,1}.E_{A,3}}{E_{A,2}}$ (b) $E_{A,1}$ (c) $E_{A,1} + E_{A,3} - E_{A,2}$ (d) $\dfrac{E_{A,1}}{E_{A,2} + E_{A,3}}$

***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.25 : Carry ONE mark each.

1. The Lewis acidity of BF_3 is less than BCl_3 even though fluorine is more electronegative than chlorine. It is due to
    (a) stronger 2p(B)-2p(F) σ-bonding
    (b) stronger 2p(B)-2p(F) π-bonding
    (c) stronger 2p(B)-2p(Cl) σ-bonding
    (d) stronger 2p(B)-2p(Cl) π-bonding

2. Pyrozenes are a class of silicate minerals, which exhibit a polymeric chain structure, as shown below

    • = Silicon
    O = Oxygen
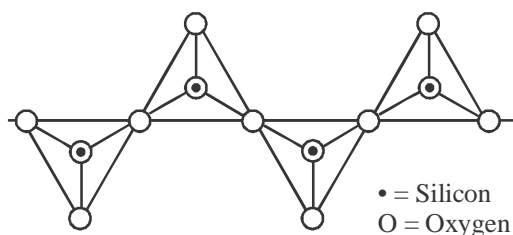
    Its simplest repeat unit is

    (a) $\left[SiO_4\right]^{4-}$ (b) $\left[SiO_3\right]^{2-}$ (c) $\left[Si_2O_7\right]^{6-}$ (d) $\left[Si_4O_{11}\right]^{6-}$

3. Among the following pentachlorides the one which does not exist due to the 'inertpair effect' is
    (a) PCl_5 (b) $BiCl_5$ (c) $SbCl_5$ (d) $AsCl_5$

4. Band theory predicts that magnesium is an insulator. However, in practice it acts as a conductor due to
    (a) presence of filled 3s orbital   (b) overlap of filled 2p and filled 3s orbital
    (c) overlap of filled 3s and emtpy 3p orbital   (d) presence of unfilled 3p orbital

5. The number of 'framework electron pairs' present in the borane cluster $[B_{12}H_{12}]^{2-}$ is:
    (a) 10   (b) 11   (c) 12   (d) 13

6. The reaction between $\{PdCl_4\}^{2-}$ and C_2H_4 produces a new compound. Compare to free C_2H_4, the C–C bond order of the product is:
    (a) between 1 and 2   (b) less than 1
    (c) unaltered   (d) greater than 2

7. Among the following pair of metal ions present in Nature, the first one functions as an electrontransfer agent and the second one catalyzes the hydrolysis reactions. The correct pair is
    (a) Fe and Zn   (b) Mg and Fe   (c) Co and Mo   (d) Ca and Cu

8. Structurally nickellocene is similar to ferrocene. Nickellocene attains stability due to the formation of
    (a) a monocation   (b) a dication
    (c) a monoanion   (d) a dianion

9. The absolute configurations for compounds X and Y, respectively are
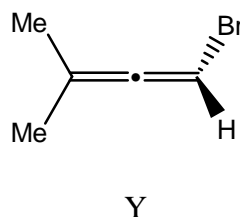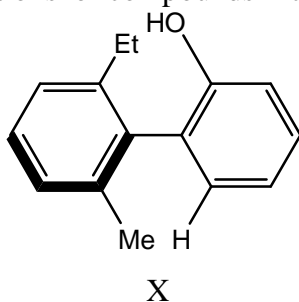
    (a) R, S   (b) S, R   (c) R, R   (d) S, S

10. In the reaction,

the major product [X] is

(a)   (b)   (c)   (d)
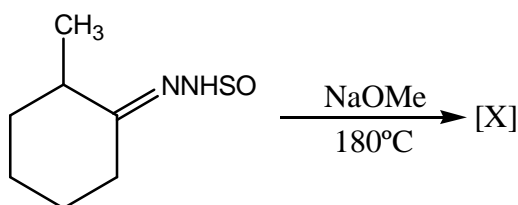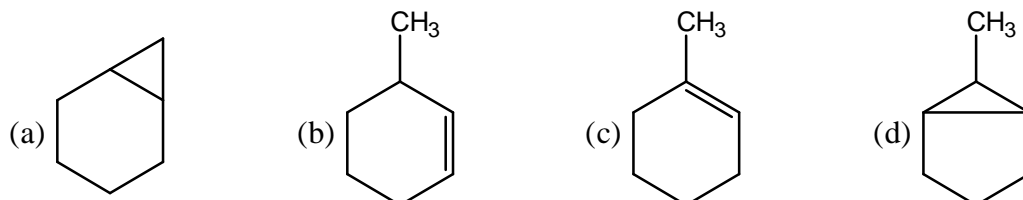
11. Among the following, a pair of resolvable configurational enantiomers is given by
    (a) cis-1, 2-dimethylcyclohexane   (b) cis-1, 3-dimethylcyclohexane
    (c) cis-1, 4-dimethylcyclohexane   (d) trans-1, 3-dimethylcyclohexane

12. In the reaction,

the major product [X] is:

(a)   (b)   (c)   (d)
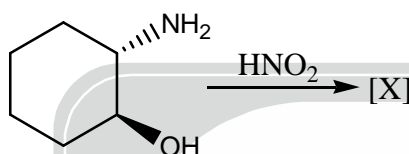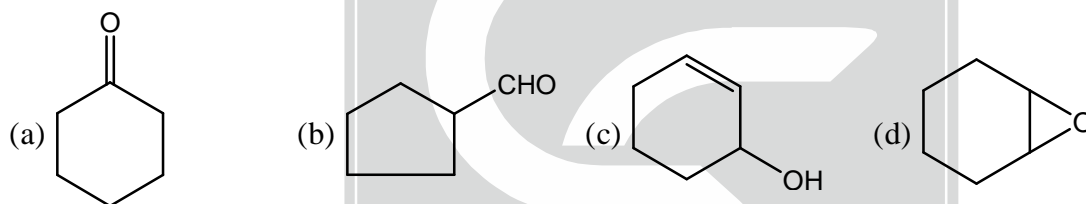
13. The decreasing order of isoelectric point for the following α – amino acids is

   Lysine   Alanine   Glutamic acid
   (I)   (II)   (III)
(a) I > II > III   (b) II > I > III   (c) III > I > II   (d) I > III > II

14. The decreasing order of the reactivity of the following compounds towards electrophiles is
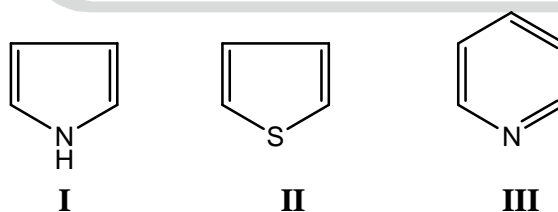
         I   **II**   **III**

(a) II > I > III   (b) II > III > I   (c) III > I > II   (d) I > II > III
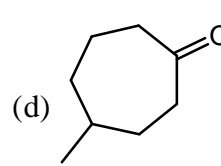
15. In the reaction,

the major product [X] is

(a)   (b)   (c)   (d)
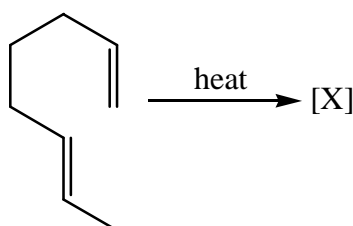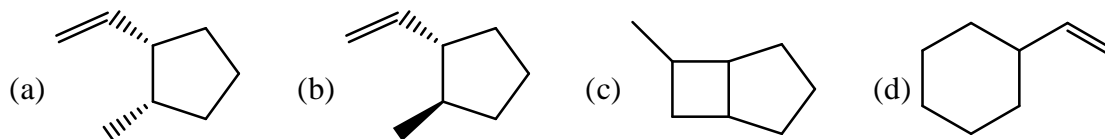
16.   The decreasing order of acidity of marked **H** of the following molecules is
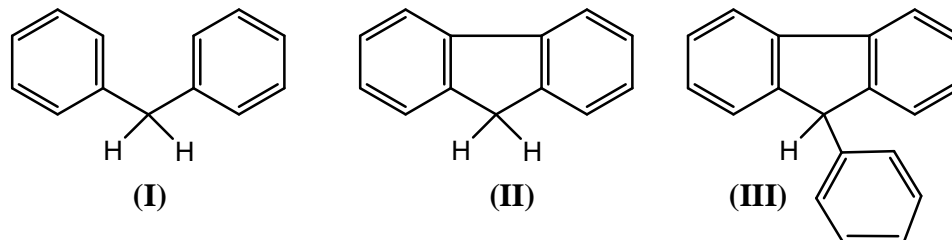
(I)   **(II)**   **(III)**

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

17.   The decreasing order of nucleophilicity for the following anions is

$CH_3CO_2^-, CH_3O^-, C_6H_5O^-, NO_3^-$
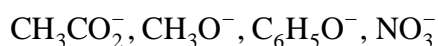
(a) $CH_3CO_2^- > CH_3O^- > C_6H_5O^- > NO_3^-$ (b) $CH_3O^- > NO_3^- > C_6H_5O^- > CH_3CO_2^-$

(c) $CH_3O^- > C_6H_5O^- > CH_3CO_2^- > NO_3^-$ (d) $C_6H_5O^- > CH_3O^- > NO_3^- > CH_3CO_2^-$

18.   The molar entropy of crystallline CO at absolute zero is
(a) Zero   (b) $-R\ln 2$ (c) $R\ln 2$ (d) $2R\ln 2$

19.   For an ideal gas

(a) $\left(\dfrac{\partial P}{\partial T}\right)_V \left(\dfrac{\partial T}{\partial V}\right)_P \left(\dfrac{\partial V}{\partial P}\right)_T = 0$ (b) $\left(\dfrac{\partial P}{\partial T}\right)_V \left(\dfrac{\partial T}{\partial V}\right)_P \left(\dfrac{\partial V}{\partial P}\right)_T = -1$

(c) $\left(\dfrac{\partial P}{\partial T}\right)_V \left(\dfrac{\partial T}{\partial V}\right)_P \left(\dfrac{\partial V}{\partial P}\right)_T = +1$ (d) $\left(\dfrac{\partial P}{\partial T}\right)_V \left(\dfrac{\partial T}{\partial V}\right)_P \left(\dfrac{\partial V}{\partial P}\right)_T = +2$

20.   Among W (work), Q (heat), U(internal energy) and S(entropy)
(a) W and U are path functions but Q and S are state functions.
(b) W and S are path functions but Q and U are state functions.
(c) S and U are path functions but Q and W are state functions.
(d) W and Q are path functions but U and S are state functions.

21.   For eigen functions $\psi_1 = \sqrt{\dfrac{1}{b}}\sin\left(\dfrac{\pi x}{b}\right)$ and $\psi_2 = \sqrt{\dfrac{2}{b}}\sin\left(\dfrac{2\pi x}{b}\right)$ of particle in a 1-D box of length

$b\left(0 \le x \le b\right)$

(a) ψ_1 is normalized but not orthogonal to ψ_2

(b) ψ_1 is normalized but not orthogonal to ψ_2

(c) ψ_2 is normalized and orthogonal to ψ_1

(d) ψ_2 is neither normalized nor orthogonal to ψ_1

22.   The bond order of C_2 molecule is
(a) 0   (b) 1   (c) 2   (d) 3

23. Sulfur can exist in four phases. The possible number of triple points is
    (a) 1   (b) 2   (c) 3   (d) 4

24. The standard reduction potentials at 298K for single electrodes are given below:

Electrode	Electrode Potential (volt)
Mg^{2+}/Mg	–2.34
Zn^{+2}/Zn	–0.76
Fe^{+2}/Fe	–0.44

    From this we can infer that
    (a) Zn can reduce both Mg^{2+} and Fe^{2+} (b) Fe can reduce both Mg^{2+} and Zn^{2+}
    (c) Mg can reduce both Zn^{2+} and Fe^{2+} (d) Mg can reduce Zn^{2+} but not Fe^{2+}.

25. For the pair of reactions given below

    (i) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

    (ii) $\dfrac{1}{2}N_2(g) + \dfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$
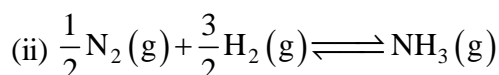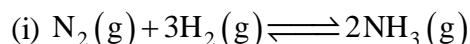
    If at a particular temperature, K_{P1} and K_{P2} are the equilibrium constants for reactions (i) and (ii) respectively, then

    (a) $K_{P1} = 2K_{P2}$ (b) $K_{P1} = 2K_{P2}^2$ (c) $K_{P1} = K_{P2}^2$ (d) $K_{P1}^2 = K_{P2}$

Q.26 – Q.55 : Carry TWO marks each.

26. According to VSEPR model, the shape of $[XeOF_5]^-$ is
    (a) Octahedral   (b) Trigonal bipyramidal
    (c) square pyramidal   (d) pentagonal monopyramidal

27. The number of unpaired electron(s) present in the species $[Fe(H_2O)_5(NO)]^{2+}$ which is formed during 'brown ring test' is:
    (a) 2   (b) 3   (c) 4   (d) 5

28. Fe_3O_4 and Co_3O_4 are metal oxides having spinel structure. Considering their CFSEs, the correct statment regarding their structure is
    (a) both have normal spinel structure
    (b) both have inverse spinel structure
    (c) Fe_3O_4 has normal and Co_3O_4 has inverse spinel structure
    (d) Fe_3O_4 has inverse and Co_3O_4 has normal spinel structure.

29. The mechanism of the reaction between $[Fe(CN)_6]^{4-}$ and $[Fe(bpy)_3]^{3+}$ (bpy = 2, 2'–bipyridine) is
    (a) outer-sphere electron-transfer   (b) inner-sphere electron-transfer
    (c) self-exchange reaction   (d) ligand-exchange followed by electron transfer.

30. The d-d absorption band of $[Fe(H_2O)_6]^{2+}$ is split due to
    (a) presence of octahedral geometry
    (b) static Jahn-Teller distortion
    (c) dynamic Jahn-Teller distortion
    (d) presence of trigonal bipyramidal geometry.

31. The crystal-field symbol for the ground-state of $[Mn(CN)_6]^{4-}$ is

    (a) $^2T_{2g}$ (b) $^1A_{1g}$ (c) ^5E_g (d) $^6A_{1g}$

32. In the following reactions:
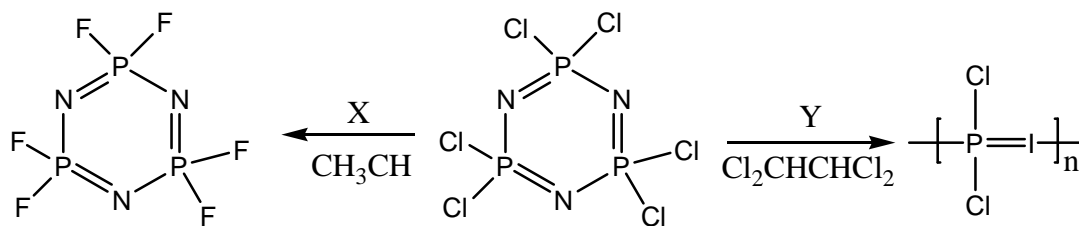
the reagent/conditions X and Y are

(a) X = BF$_3$; Y = heating at 1250ºC   (b) X = NaF; Y = heating at 25ºC

(c) X = NH$_4$F; Y = HCl   (d) X = CF$_3$SO$_3$H; Y = H$_2$SO$_4$

33. [CoCl$_4$]$^{2-}$ is a blue coloured complex. Controlled-treatment of this complex with water generates two isomeric light pink coloure complexes of composition [Co(H$_2$O)$_4$Cl$_2$].

              Identify the correct point groups for [CoCl$_4$]$^{2-}$ and two isomeric complexes [Co(H$_2$O)$_4$Cl$_2$].

(d) D$_{2h}$ and (C$_{2v}$ and C$_{2h}$)   (b) T$_d$ and (C$_{2v}$ and D$_{4h}$)

(c) D$_{4h}$ and (C$_{2v}$ and D$_{4h}$)   (d) T$_d$ and (C$_{2v}$ and C$_{4v}$)

34. In the reaction
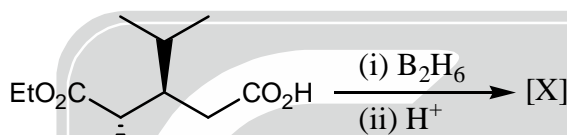
the major product [X] is:
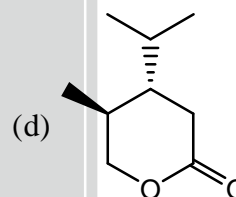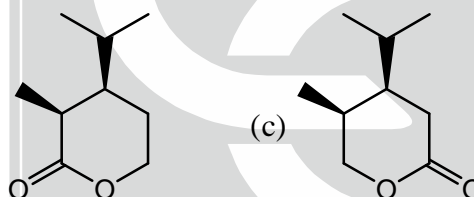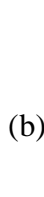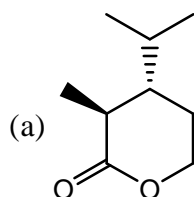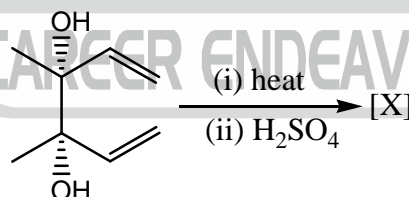
(a)   (b)   (c)   (d)

35. In the reaction,

the major product [X] is:
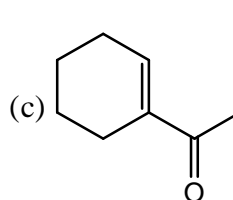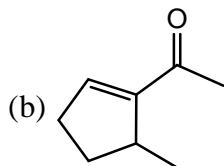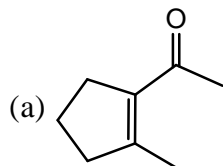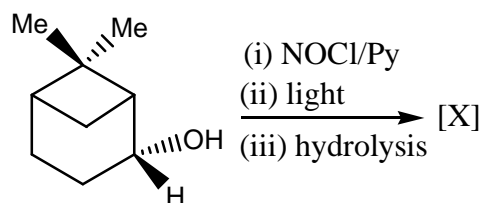
(a)   (b)   (c)   (d)

36. In the following reaction sequence

(i) NOCl/Py

(ii) light

(iii) hydrolysis   → [X]

the major product [X] is

(a) ![structure a] HOOC, Me ...OH, H

(b) ![structure b] OHC, Me ...OH, H

(c) ![structure c] Me, CHO ...OH, H

(d) ![structure d] Me, COOH ...OH, H

37. In the reaction,

$$[Y] \xleftarrow{\text{HNO}_3} \text{(camphor structure)} \xrightarrow{\text{mCPBA}} [X]$$

the major products, [X] and [Y], respectively, are

(a) ![lactone structure] and ![diacid structure] COOH, COOH

(b) ![lactone structure] and ![diacid structure] COOH, COOH

(c) ![lactone structure] and ![diacid structure] COOH

(d) ![lactone structure] and ![acid structure] COOH

38. In the reaction,

$$\text{(bicyclic chloride)} \xrightarrow{\text{SnCl}_4} [X]$$

the major product [X] is

(a) Cl (b) Cl (c) Cl (d) Cl

39. In the reaction sequence

$$\text{(glycal structure with CH}_2\text{OH, OH, OH)} \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OAc)}_2/\text{MeOH}} [X] \xrightarrow[\text{HCl}]{(\text{CH}_3)_2\text{CO}} [Y]$$

the major products, [X] and [Y] respectively, are

(a) [structure] and [structure]

(b) [structure] and [structure]

(c) [structure] and [structure]
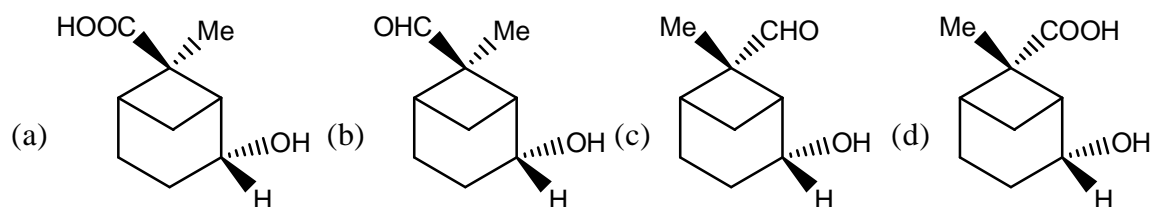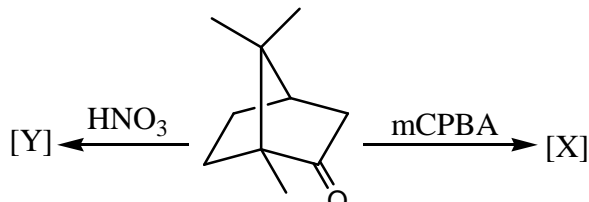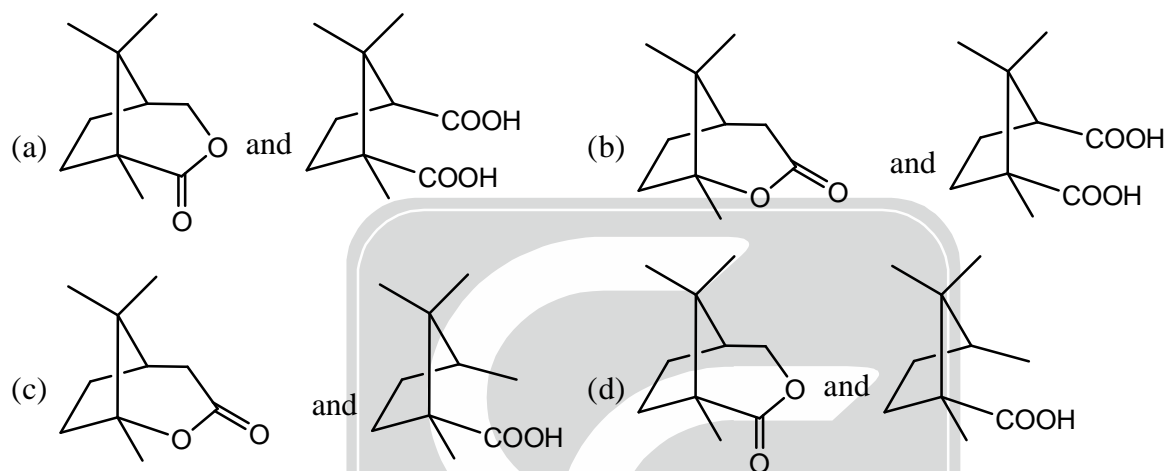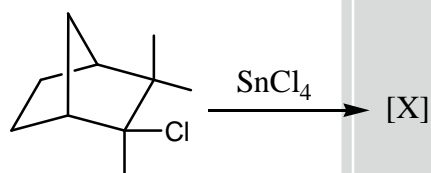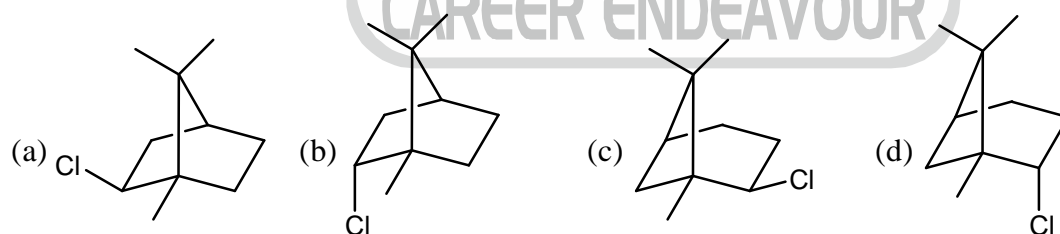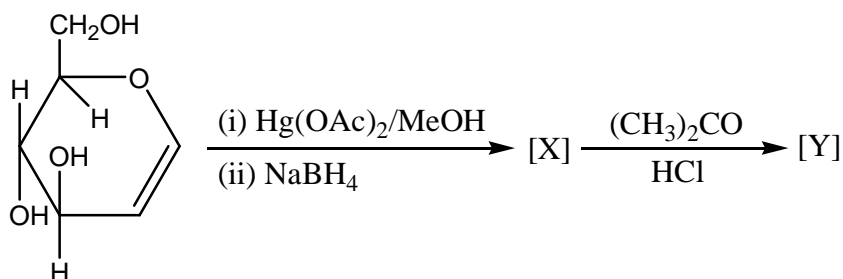
(d) [structure] and [structure]
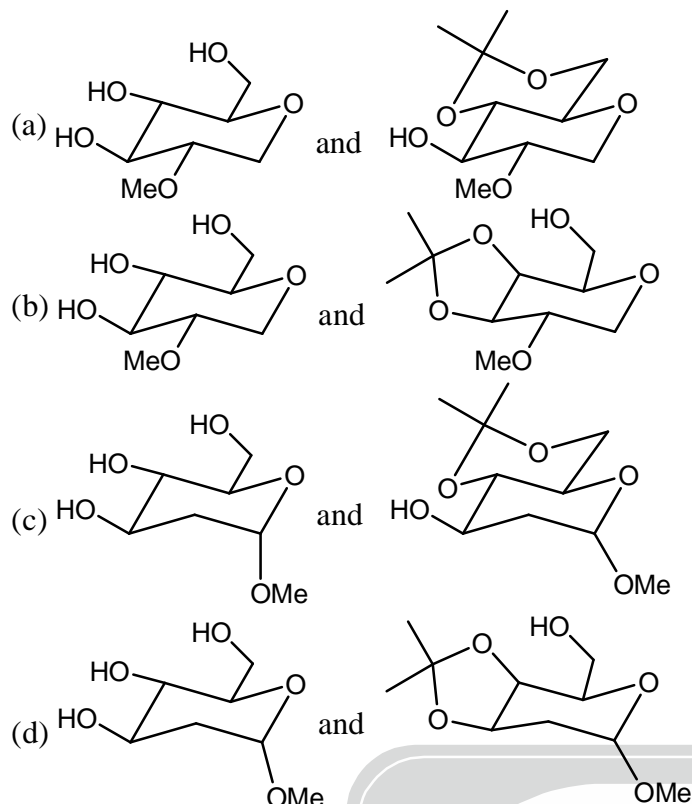
40. The change in entropy when two moles of Argon gas are heated at constant volume from 300K to 500K is:
(a) -12.74 J K^{-1} mole^{-1} (b) -6.37 J K^{-1} mole^{-1}
(c) 6.37 J K^{-1} mole^{-1} (d) 12.74 J K^{-1} mole^{-1}

41. At any temperature T, the fugacity coefficient (γ) is given by

$$\ln \gamma = \int_0^P \frac{Z-1}{P'} dP'$$

where Z is the compressiblity factor. The fugacity coefficient of a real gas governed by equations of state, $P(V-b) = RT$ with 'b' a constant is given by

(a) $\dfrac{RT}{bP}$ (b) $e^{\frac{RT}{bP}}$ (c) $\dfrac{bP}{RT}$ (d) $e^{\frac{bP}{RT}}$

42. The specific rate constant of decomposition of a compound is represented by

$\ln k = 5.0 - \dfrac{12000}{T}$

The activation energy of decomposition for this compound at 300K is
(a) 24 kcal/mole   (b) 12 kcal/mole   (c) 24 cal/mole   (d) 12 cal/mole

43. The commutator $\left[x^3, p_x \right]$ is equal to

(a) $-\dfrac{3hx^2}{2\pi i}$ (b) $\dfrac{hx}{2\pi i}$ (c) $\dfrac{hx^2}{2\pi i}$ (d) $\dfrac{3hx^2}{2\pi i}$

44. An electron of mass 'm' is confined to a one dimensional box of length 'b'. If it makes a radiative transition from second excited state to the ground state, the frequency of the photon emitted is

(a) $\dfrac{9h}{8mb^2}$ (b) $\dfrac{3h}{8mb^2}$ (c) $\dfrac{h}{mb^2}$ (d) $\dfrac{2h}{mb^2}$

45. The point group of CIF_3 molecule and its corresponding number of irreducible representation are respectively.
    (a) C_{3v} and 4   (b) C_{2v} and 4   (c) C_{3v} and 3   (d) C_{2v} and 3

46. The most populated rotational state for $HCl(B = 8.5 \text{ cm}^{-1})$ at 300 K is:
    (a) 2   (b) 3   (c) 5   (d) 7

47. The ratio of life times of two states that gives rise to line widths of 1.0 cm^{-1} and 0.2 cm^{-1} respectively is:
    (a) 1 : 2   (b) 1 : 5   (c) 2 : 1   (d) 5 : 1

Commond Data Questions:
Commond data for Q.48 and Q.49:
A six-coordinate transition-metal complex is ESR and Mossbauer active. The effective magnetic moment of this complex is –5.9 B.M.

48. The metal-ion along with its oxidation state and the number of unpaired electron present are
    (a) Fe(II) and 4   (b) Mn(II) and 5   (c) Fe(III) and 1   (d) Fe(III) and 5

49. The complex is
    (a) $[Mn(H_2O)_6]^{2+}$ (b) $[Fe(CN)_6]^{3-}$ (c) $[Fe(H_2O)_6]^{2+}$ (d) $[Fe(H_2O)_6]^{3+}$

Common data for Q.50 and Q.51:
An organic compound [X] $(C_{12}H_{16}O_3)$ exhibits the following spectral data IR: -1720 cm^{-1}
^{1}H NMR: 2.35 (s, 6H), 3.30 (s, 3H), 3.83 (t, 2H), 4.42 (t, 2H), 7.07 (s, 1H), 7.58 (s, 2H)
The compound [X] with an excess of MeMgBr gives a 1 : 1 mixture of compounds [Y] and [Z]. The compound [Z] exhibits the following ^{1}H NMR data: 2.0(bs, 1H), 3.30 (s, 3H), 3.56(t, 2H), 3.70 (t, 2H)

50. The compound [X] is:
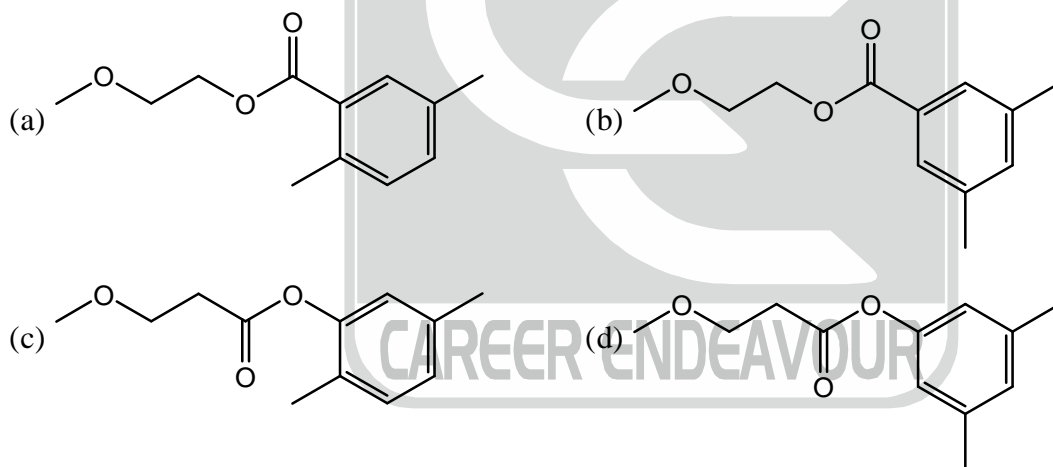
51. The compound [Y[is:
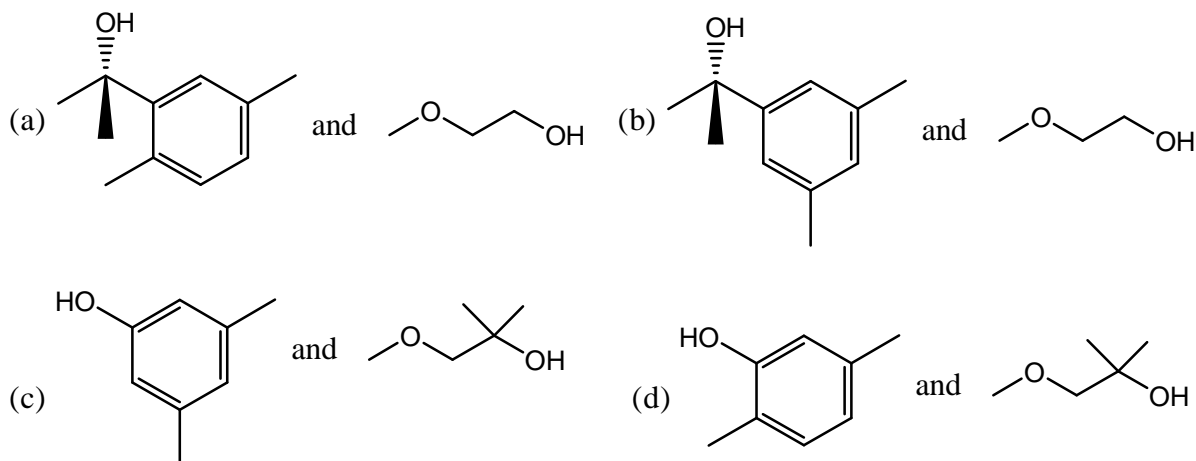
Linked Answer Q.52 and Q.53:

In the reaction sequence

$$\text{Ph} \quad \text{CHO}$$

$$\xrightarrow[\text{H}_3\text{O}^+]{\text{MeMgBr}} \quad [\text{X}] \text{ (major)} + [\text{Y}] \text{ (minor)}$$

$$[\text{X}] \xrightarrow[\text{(ii) NaOEt/EtOH}]{\text{(i) TsCl/Py}} [\text{Z}]$$

52.　　The compound [X] is:

(a)
$$
\begin{array}{c}
\text{Ph} \\
\text{H} \!-\!\!|\!-\! \text{CH}_3 \\
\text{H}_3\text{C} \!-\!\!|\!-\! \text{H} \\
\text{OH}
\end{array}
$$

(b)
$$
\begin{array}{c}
\text{Ph} \\
\text{H}_3\text{C} \!-\!\!|\!-\! \text{H} \\
\text{H} \!-\!\!|\!-\! \text{CH}_3 \\
\text{OH}
\end{array}
$$

(c)
$$
\begin{array}{c}
\text{Ph} \\
\text{H}_3\text{C} \!-\!\!|\!-\! \text{H} \\
\text{H}_3\text{C} \!-\!\!|\!-\! \text{H} \\
\text{OH}
\end{array}
$$

(d)
$$
\begin{array}{c}
\text{CH}_3 \\
\text{Ph} \!-\!\!|\!-\! \text{H} \\
\text{HO} \!-\!\!|\!-\! \text{H} \\
\text{CH}_3
\end{array}
$$
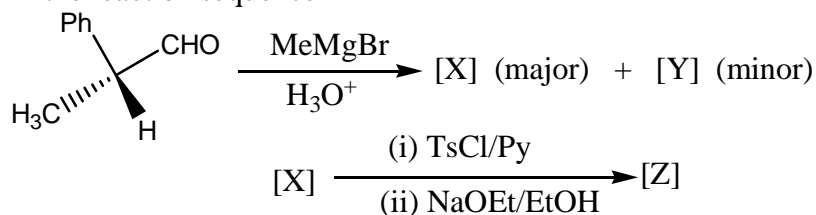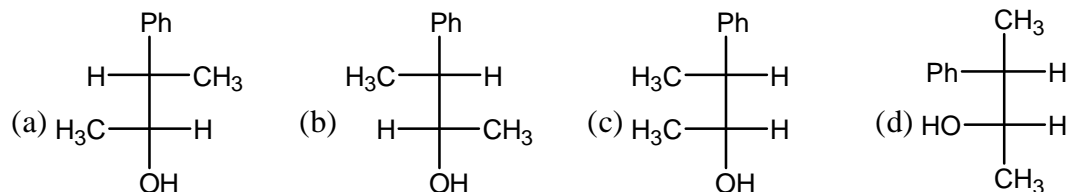
53.　　The compound [Z] is:

(a)
$$
\begin{array}{c}
\text{Me} \\
\text{Me} \quad \diagdown \quad \text{H} \\
\text{EtO} \quad \text{H} \quad \text{Ph}
\end{array}
$$

(b)
$$
\begin{array}{c}
\text{Me} \\
\text{EtO} \quad \diagdown \quad \text{H} \\
\text{Me} \quad \text{H} \quad \text{Ph}
\end{array}
$$

(c) Me—C(Me)=CH—Ph type:
$$
\begin{array}{c}
\text{Me} \\
\text{Me} \diagdown \diagup \text{Ph} \\
\text{H}
\end{array}
$$

(d)
$$
\begin{array}{c}
\text{Ph} \\
\text{Me} \diagdown \diagup \text{Me} \\
\text{H}
\end{array}
$$
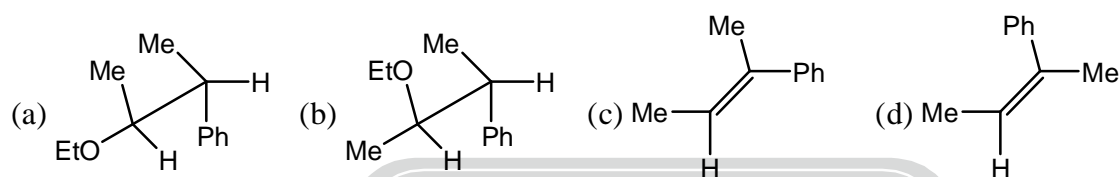
Statement for Linked Answer Q.54 and Q.55:

In the m vs T diagram for different phases of the same substance at one atmospheric pressure, the lines A, B and C compound to
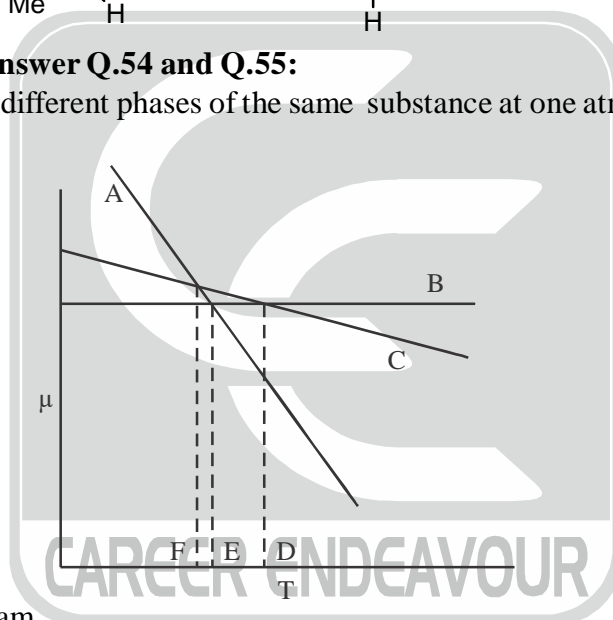
54.　　Based on the above diagram.
　　(a) A represents the change in chemical potential as a function of temperature for the solid phase, B for the liquid and C for the gas.
　　(b) A represents the change in chemical potential as a function of temperature for the gas phase, B for the gas and C for the solid
　　(c) A represents the change in chemical potential as a function of temperature for the liquid phase, B for the gas and C for the solid
　　(d) A represents the change in chemical potential as a function of temperature for the gas phase, B for the gas and C for the liquid.

55.　　From the same diagram
　　(a) D represents boiling point, E sublimation point and F melting point.
　　(b) E represents boiling point, D sublimation point and F melting point.
　　(c) E represents melting point, F sublimation point and D boiling point.
　　(d) D represents melting point, F boiling point and E sublimation point.

***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.25 : Carry ONE mark each.

1. Jahn-Teller distortion of $CuSO_4.5H_2O$ acts to
   (a) Raise symmetry
   (b) Remove an electronic degeneracy
   (c) Cause loss of H_2O ligand
   (d) Promote a d-electron to an antibonding molecular orbital.

2. Among the following, the group of molecules that undergoes rapid hydrolysis is:
   (a) SF_6, Al_2Cl_6, $SiMe_4$ (b) BCl_3, SF_6, $SiCl_4$
   (c) BCl_3, $SiCl_4$, PCl_5 (d) SF_6, Al_2Cl_6, $SiCl_4$

3. The reaction of solid XeF_2 with AsF_5 in 1:1 ratio affords
   (a) XeF_4 and AsF_3 (b) XeF_6 and AsF_3
   (c) $[XeF]^+[AsF_6]^-$ (d) $[Xe_2F_3]^+[AsF_6]^-$

4. A well known naturally occuring organometallic compound is:
   (a) vitamin B_{12} coenzyme   (b) chlorophyll
   (c) cytochrome P-450   (d) myoglobin

5. The complex that exists as a pair of enantiomers is
   (a) trans-$[Co(H_2NCH_2CH_2NH_2)_2Cl_2]^+$ (b) cis-$[Co(NH_3)_4Cl_2]^+$
   (c) $[Pt(PPh_3)(Cl)(Br)(CH_3)]^-$ (d) $[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$

6. The region of electromagnetic spectrum employed in the electron spin resonance (ESR) spectroscopy is:
   (a) radiowave   (b) microwave   (c) infrared   (d) visible

7. The red color of oxyhaemoglobin is mainly due to the
   (a) d-d transition   (b) metal to ligand charge transfer transition
   (c) ligand to metal charge transfer transition   (d) intraligand $\pi - \pi^*$ transition.

8. The band structure in an n-type semiconductor is
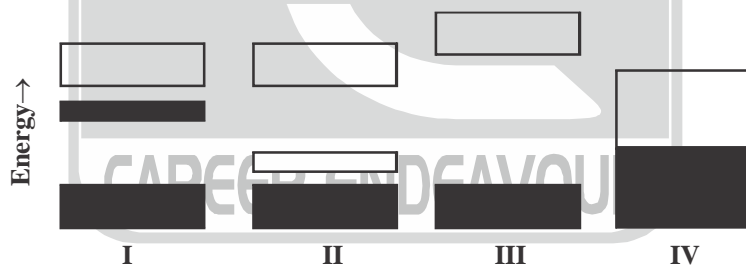
   (a) I   (b) II   (c) III   (d) IV

9. In the following reaction
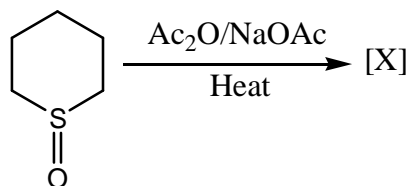
   The major product [X] is:

10. In the following reaction sequence

(i) NH$_2$OH.HCl
(ii) ArSO$_2$Cl, Py
(iii) Heat
(iv) H$_2$O

→ [X]

the major product [X] is:

(a)

(b)

(c)

(d)
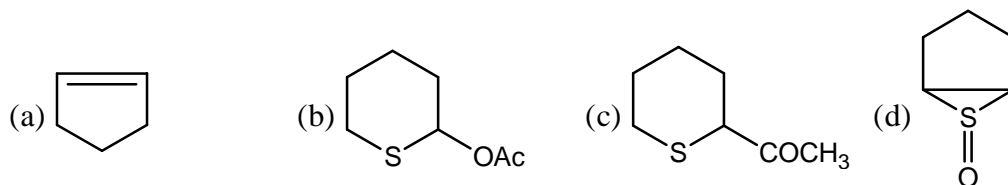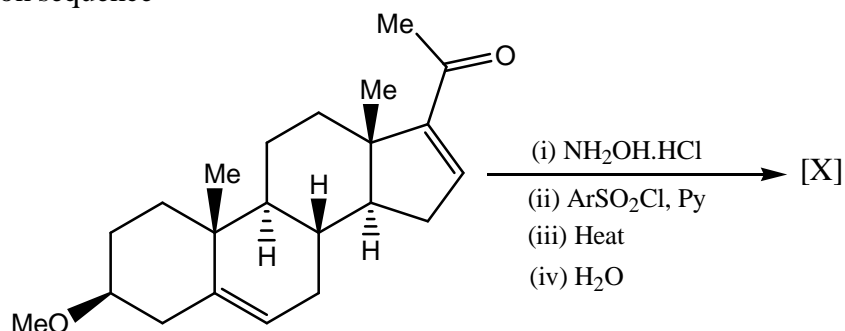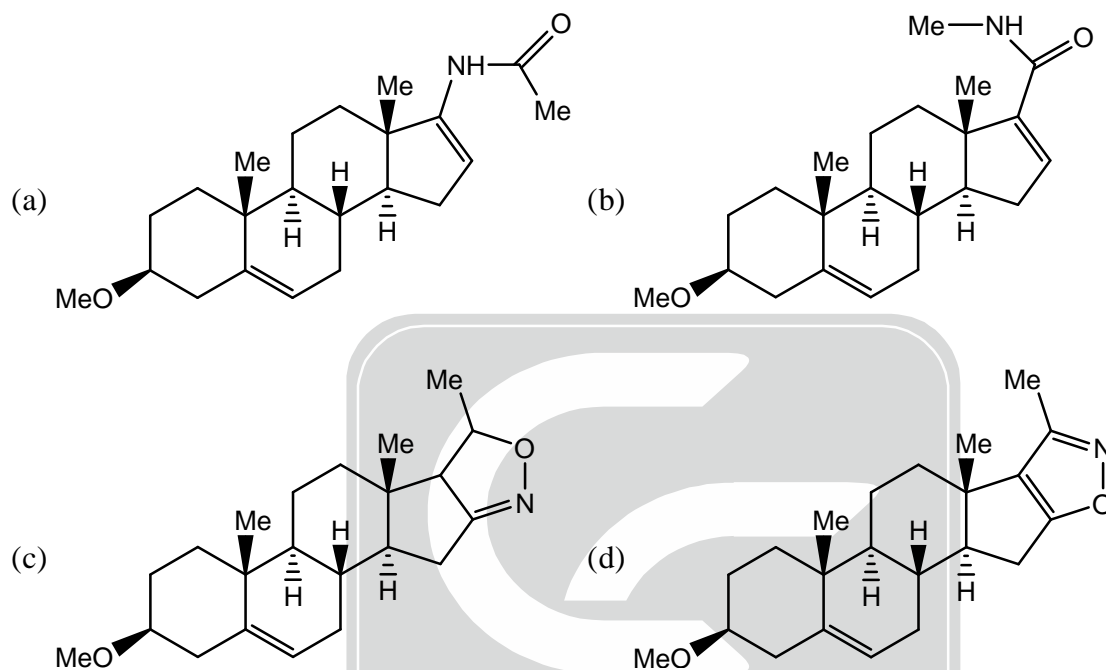
11. The diene which undergoes Diels-Alder reaction with maleic anhydride is:

(a) 　　(b) 　　(c) 　　(d)

12. The sequence of an mRNA molecule produced from a DNA template strand with the composition
   $5'-AGCTACACT-3'$ is

   (a) $5'-AGUGUAGCU-3'$ 　　　　(b) $5'-UCGAUGUGA-3'$

   (c) $5'-AGTGTAGCT-3'$ 　　　　(d) $5'-TCGATGTGA-3'$

13. In the following reaction,

$\xrightarrow[-CO_2]{\text{Heat}}$ [X]

the major product [X] is:

(a) 　　　　(b)

(c) Me ⌐ Me (with Me and O substituents)
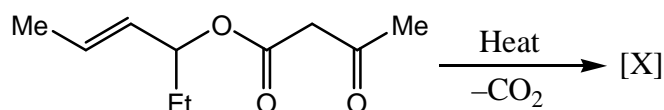
(d) with Et, Me, O, Me groups
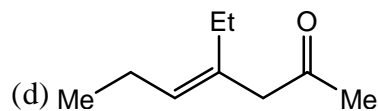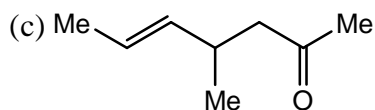
14. The structure of the dipeptide Ala-Pro derived from the natural amino acids is:

(a) H$_2$N— structure with Me, N, O, CO$_2$H

(b) HO$_2$C— structure with HN, O, N, H, Me

(c) HO$_2$C— Me, H$_2$N, N, O structure

(d) H$_2$N— structure with Me, N, CO$_2$H

15. In the following reaction

Me-substituted cyclopentane with N–N(H)–Ts group

(i) 2 eq. n-BuLi
   -78ºC to 0ºC
───────────────→ [X]
(ii) DMF

the major product [X] is:

(a) cyclopentanone with CH$_2$CHO group (O, CHO)

(b) Me— cyclopentanone with CHO group (O, Me, CHO)

(c) cyclopentene with Me and CHO groups

(d) Me— cyclopentene with CHO group

16. In the following reaction,

bicyclic decalone structure with Me (top), O, and Me (bottom)

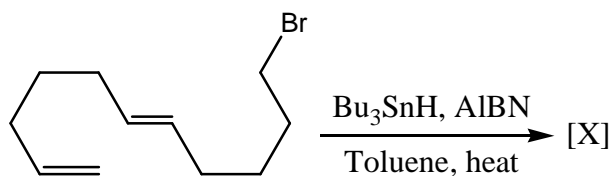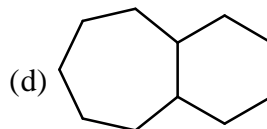   H$^+$
───────────────→ [X]

the major product [X] is:

(a) HO— tetrahydronaphthalene with Me (top), Me (bottom)

(b) tetrahydronaphthalene with Me (top), OH, Me (bottom)

(c) [structure with Me, Me substituents and OH]

(d) [structure with Me, Me substituents and HO]

17. For a given first order reaction, the reactant reduces to $1/4^{th}$ its initial value in 10 minutes. The rate constant of the reaction is:
    (a) 0.1386 min^{-1}
    (b) 0.0693 min^{-1}
    (c) 0.1386 mol L^{-1} min^{-1}
    (d) 0.0693 mol L^{-1} min^{-1}.

18. The freezing point constant for water is 1.86 K (mol kg^{-1})$^{-1}$. The change in freezing point when 0.01 mol glucose is added to 1 kg water is:
    (a) 1.86 K
    (b) -1.86 K
    (c) 0.186 K
    (d) -0.0186 K

19. On the pressure-temperature diagram for a one-component system, the point where the solid-liquid and the liquid-gas curves intersect is:
    (a) triple point
    (b) critical point
    (c) melting point
    (d) boiling point

20. The wave function for a harmonic oscillator described by $Nx \exp\left(-\alpha x^2/2\right)$ has
    (a) One maximum only
    (b) One maximum, one minimum only
    (c) Two maxima, one minimum only
    (d) Two maxima, two minima only

21. If an arbitrary wave function is used to calculate the energy of a quantum mechanical system, the value calculated is never less than the true energy.
    The above statement relates to
    (a) Perturbation theory
    (b) Variation principle
    (c) Heisenberg's uncertainty principle
    (d) quantization of energy

22. The point group symmetry of the given planar shape is:

    [structure image]
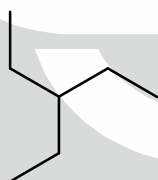
    (a) D_{3h}
    (b) C_3
    (c) C_{3h}
    (d) C_{3v}

23. $\left(\dfrac{\partial G}{\partial P}\right)_T =$
    (a) V
    (b) S
    (c) $-S$
    (d) $-V$

24. [graph: Volume vs Temperature]
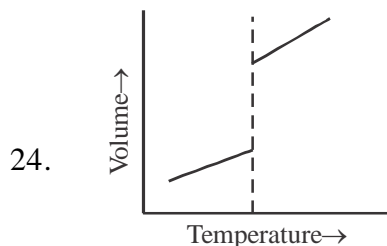
    According to Ehrenfest classification of phase transitions, the above diagram refers to
    (a) Zeroth order phase transition
    (b) First order phase transition
    (c) Second order phase transition
    (d) λ transition.

25. According to conventional transition state theory, for elementary bimolecular reactions, the molar entropy of activation $\Delta S^{0\dagger}_{\dagger}$ is :

    (a) Positive   (b) Zero   (c) Negative

    (d) Positive for endothermic and negative for exothermic reactions.

Q.26 – Q.55 : Carry TWO marks each.

26. The crystal field stabilization energy (CFSE) value for $[Ti(H_2O)_6]^{3+}$ that has an absorption maximum at 492 nm is:
    (a) 20, 325 cm^{-1} (b) 12, 195 cm^{-1} (c) 10, 162 cm^{-1} (d) 8, 130 cm^{-1}

27. For Et_2AlX $(X = PPh_2^-, Ph^-, Cl^-$ and $H^-)$, the tendency towards dimeric structure follows the order

    (a) $PPh_2^- > Cl^- > H^- > Ph^-$ (b) $Cl^- > PPh_2^- > H^- > Ph^-$

    (c) $Ph^- > H^- > Cl^- > PPh_2^-$ (d) $H^- > Ph^- > PPh_2^- > Cl^-$

28. In the isoelectronic series, VO_4^{3-}, CrO_4^{2-} and MnO_4^-, all members have intense charge transfer (CT) transitions. The **INCORRECT** statement is

    (a) CT transitions are attributed to excitations of electrons from ligand (σ) to metal (e)

    (b) MnO_4^- exhibits charge transfer at shortest wavelength among the three

    (c) The wavelength of transitions increase in the order $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$

    (d) The charge on metal nucleus increases in the order $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$

29. The increasing order of wavelength of absorption for the complex ions

    (i) $\left[Cr(NH_3)_6\right]^{3+}$ (ii) $\left[CrCl_6\right]^{3-}$ (iii) $\left[Cr(OH_2)_6\right]^{3+}$ (iv) $\left[Cr(CN)_6\right]^{3-}$, is
    (a) iv < ii < i < iii   (b) iv < iii < ii < i   (c) iv < i < iii < ii   (d) ii < iii < i < iv

30. The total number of metal-metal bonds in $Ru_3(CO)_{12}$ and $Co_4(CO)_{12}$, respectively, is
    (a) 3 and 6   (b) 4 and 5   (c) zero and 4   (d) 3 and 4

31. According to VSEPR theory the shapes of $[SF_2Cl]^+$ and $[S_2O_4]^{2-}$ should be
    (a) trigonal planar for $[S_2O_4]^{2-}$ and trigonal pyramidal for $[SF_2Cl]^+$
    (b) both trigonal planar
    (c) trigonal pyramidal for $[S_2O_4]^{2-}$ and trigonal planar for $[SF_2Cl]^+$
    (d) both trigonal pyramidal

32. The product of the reaction between $CH_3Mn(CO)_5$ and ^{13}CO is:
    (a) $(CH_3\,^{13}CO)Mn(CO)_5$ (b) $(CH_3CO)Mn(CO)_4(^{13}CO)$
    (c) $(^{13}CH_3CO)Mn(CO)_5$ (d) $CH_3Mn(CO)_4$

33. The correct pair of ^1H and ^{31}P NMR spectral patterns for $C(H)(F)(PCl_2)_2$ is:
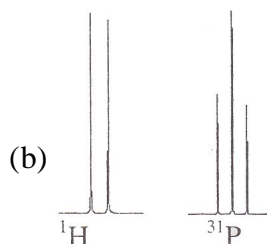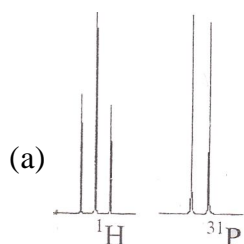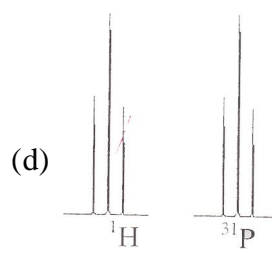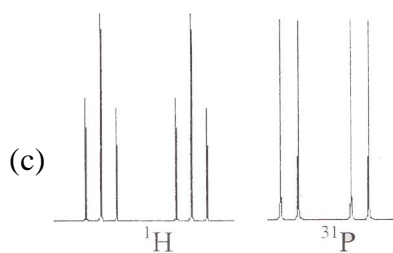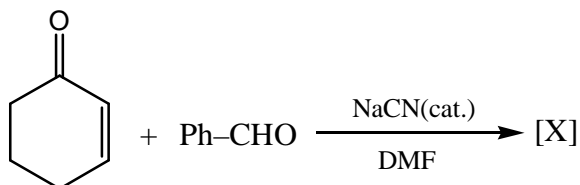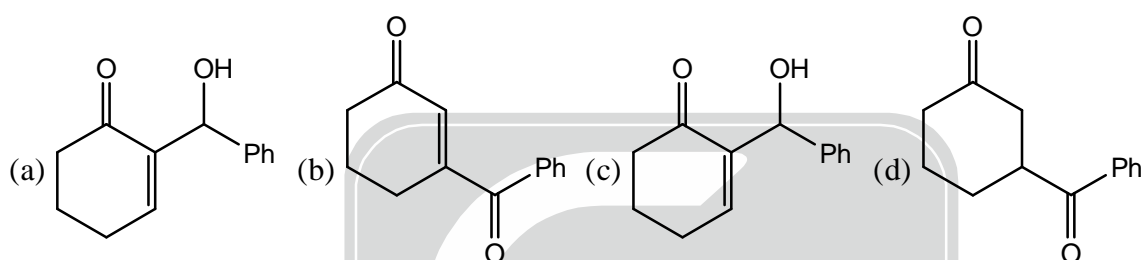
(a)   (b)

      ^1H ^{31}P ^1H ^{31}P

(c)

^{1}H ^{31}P

(d)

^{1}H ^{31}P

34. In the following reaction

$$+ \quad \text{Ph–CHO} \quad \xrightarrow[\text{DMF}]{\text{NaCN(cat.)}} \quad [X]$$

the major product [X] is:

(a)   (b)   (c)   (d)

35. In the following reaction,

$$\xrightarrow{\begin{array}{l}\text{(i) SeO}_2/\text{HOAc}\\ \text{(ii) NaOH}\\ \text{(iii) H}_3\text{O}^+\end{array}} \quad [X]$$

the major product [X] is:

(a)   (b)   (c)   (d)

36. In the following reaction,

$$\xrightarrow[\text{Toluene, heat}]{\text{Bu}_3\text{SnH, AIBN}} \quad [X]$$

the major product [X] is:

(a)

(b)

(c)

(d)
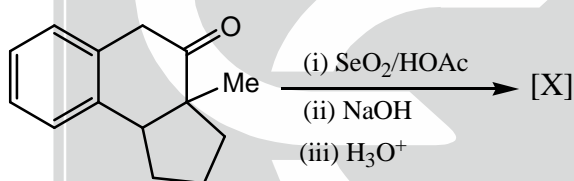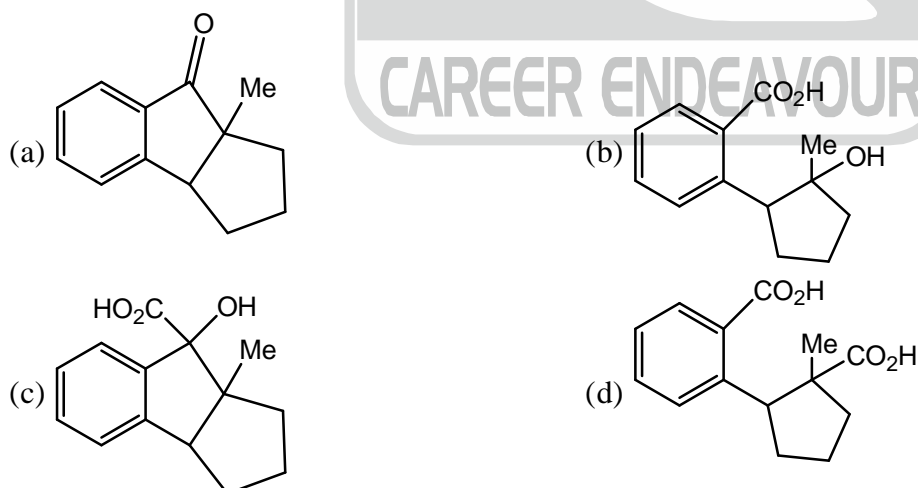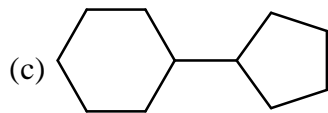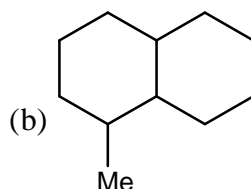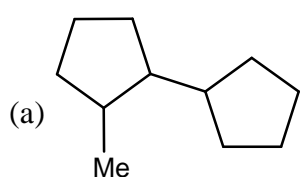
37.　The most appropriate sequence of reactions for carrying out the following conversion
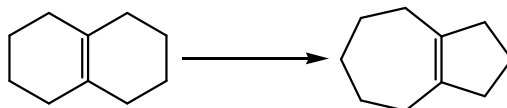
is

(a) (i) Peracid; (ii) H$^+$; (iii) Zn/dil. HCl
(b) (i) Alkaline KMnO$_4$; (ii) NaIO$_4$; (iii) N$_2$H$_4$/KOH
(c) (i) Alkaline KMnO$_4$; (ii) H$^+$; (iii) Zn/dil. HCl
(d) (i) O$_3$/Me$_2$S; (ii) NaOEt; (iii) N$_2$H$_4$/KOH

38.　In the following reaction sequence
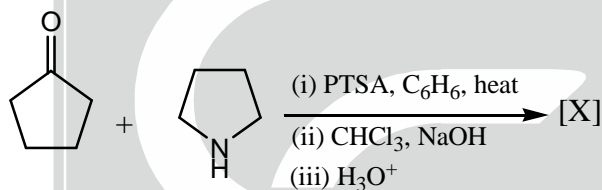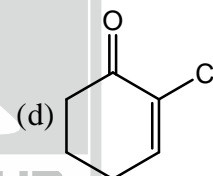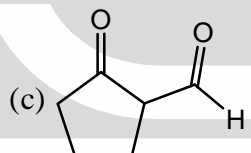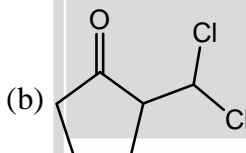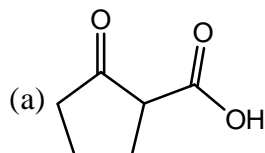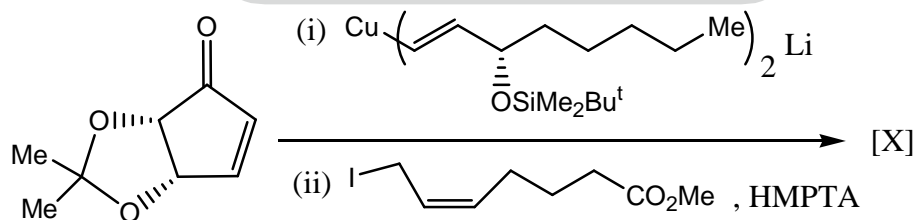
$$\text{cyclopentanone} + \text{pyrrolidine} \xrightarrow[\substack{\text{(ii) CHCl}_3\text{, NaOH} \\ \text{(iii) H}_3\text{O}^+}]{\text{(i) PTSA, C}_6\text{H}_6\text{, heat}} [X]$$

the major product [X] is:

(a)　(b)　(c)　(d)

39.　In the following conversion

$$\xrightarrow[\substack{\text{(ii) I}\text{—}\text{—CO}_2\text{Me , HMPTA}}]{\text{(i) Cu}\left(\text{—Me}\right)_2\text{Li, } \overset{}{O}\text{SiMe}_2\text{Bu}^t}} [X]$$

the major product [X] is:

(a)

(b)

(c)

(d)

40. In the following reaction,

$$\xrightarrow[\text{(ii) Raney Ni, EtOH}]{\text{(i) KO }^{t}\text{Bu}} [X]$$

the major product [X] is:

(a) (b) (c) (d)

41. In the reaction,

Optically pure (+)-trans-2-acetoxycyclohexyl tosylate $\xrightarrow[\Delta]{\text{HOAc,KOAc}}$ [X]
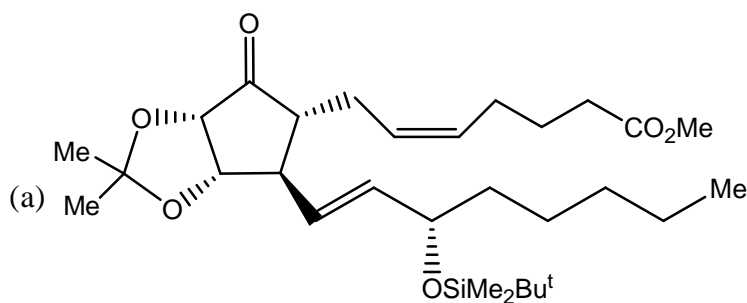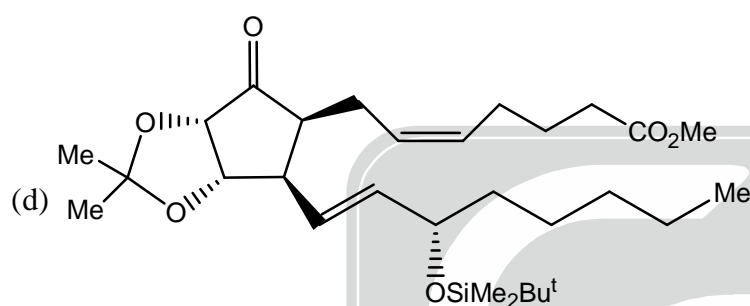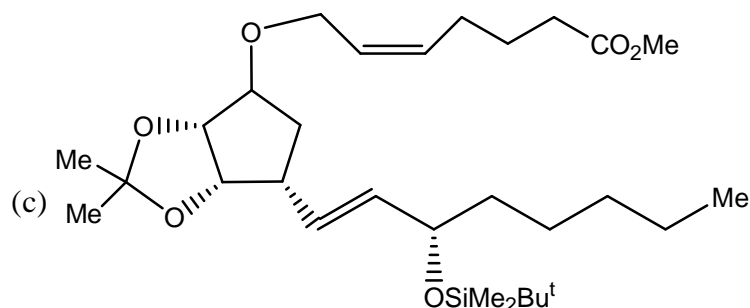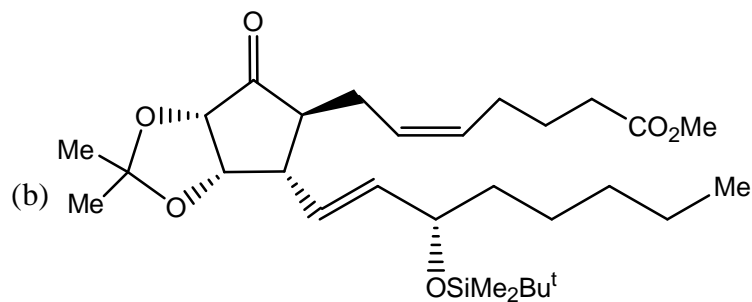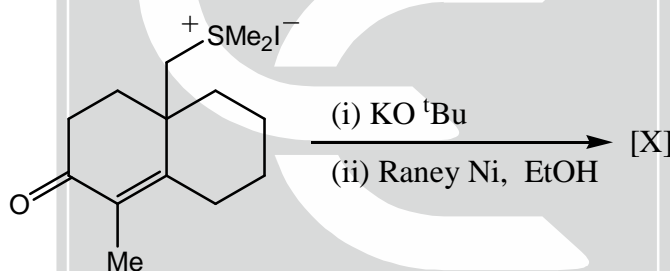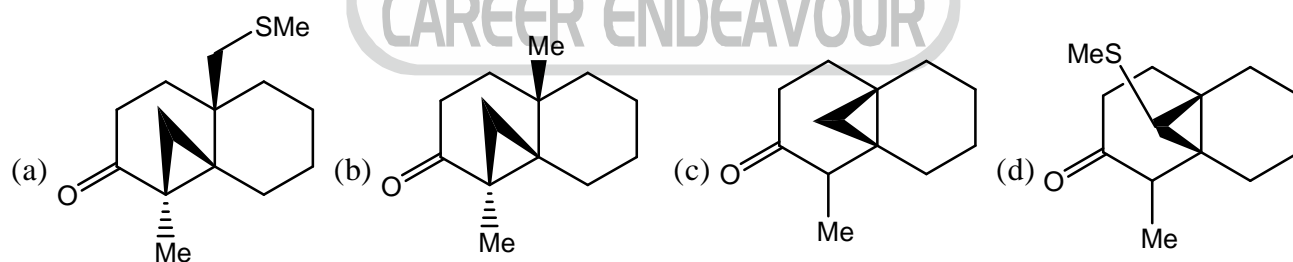
the major product [X] is:

(a) racemic trans-1, 2-cyclohexanediol diacetate
(b) optically active trans-1, 2-cyclohexanediol diacetate
(c) racemic cis-1, 2-cyclohexanediol diacetate
(d) optically active cis-1, 2-cyclohexanediol diacetate.

42. The activity of water at 11 bar and 298K is:

(a) 1.101   (b) 1.007   (c) 0.998   (d) 0.898

43. For the process

$$1\,Ar\,(300K, 1\,bar) \longrightarrow 1\,Ar\,(200K, 10\,bar)$$
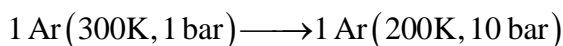
assuming ideal gas behavior, the change in molar entropy is:
(a) $-27.57\ J\ K^{-1}\ mol^{-1}$ (b) $+27.57\ J\ K^{-1}\ mol^{-1}$
(c) $-24.20\ J\ K^{-1}\ mol^{-1}$ (d) $+24.20\ J\ K^{-1}\ mol^{-1}$

44. The wave function for a quantum mechanical particle in a 1-dimensional box of length 'a' is given by

$$\psi = A \sin \frac{\pi x}{a}$$

The value of 'A' for a box of length 200 nm is

(a) $4 \times 10^4\ (nm)^2$ (b) $10\sqrt{2}\ (nm)^{\frac{1}{2}}$ (c) $\sqrt{2}/10\ (nm)^{-\frac{1}{2}}$ (d) $0.1\ (nm)^{-1/2}$

45. For 1 mole of a monoatomic ideal gas, the relation between pressure (p), volume (V) and average molecular kinetic energy $(\bar{\varepsilon})$ is

(a) $p = \dfrac{N_A \bar{\varepsilon}}{V}$ (b) $p = \dfrac{N_A \bar{\varepsilon}}{3V}$ (c) $p = \dfrac{2N_A \bar{\varepsilon}}{3V}$ (d) $p = \dfrac{2N_A}{3V\bar{\varepsilon}}$

46. For a 1 molal aqueous NaCl solution, the mean ionic activity coefficient $(\gamma_\pm)$ and the Deby-Huckel Limiting Law constant (A) are related as

(a) $\log \gamma_\pm = \sqrt{2}\,A$ (b) $\log \gamma_\pm = -\sqrt{2}\,A$ (c) $\gamma_\pm = 10^A$ (d) $\gamma_\pm = 10^{-A}$

47. For the concentration cell
M | M$^+$(aq, 0.01 mol dm^{-3}) || M$^+$(aq, 0.1 mol dm^{-3}) | M
the EMF (E) of the cell at a temperature (T) equals

(a) $2.303 \dfrac{RT}{F}$ (b) $-2.303 \dfrac{RT}{F}$

(c) $E^0_{M^+/M} + 2.303 \dfrac{RT}{F}$ (d) $E^0_{M^+/M} - 2.303 \dfrac{RT}{F}$

Commond Data Questions:
Commond data for Q.48 and Q.49:
A hypothetical molecule XY has the following properties
Reduced mass: 2×10^{-26} kg
X–Y bond length: 100 pm
Force constant of the bond: 8×10^2 N.m^{-1}

48. The frequency of radiation (in cm^{-1} units) required to vibrationally excite the molecule from v = 0 to v = 1 state is
(a) 3184.8   (b) 2123.2   (c) 061.6   (d) 840.0

49. The frequency of radiation (in cm^{-1} units) required to rotationally excite the molecule from J = 0 to J = 1 state is
(a) 1.4   (b) 2.8   (c) 3.2   (d) 3.6

Common data for Q.50 and Q.51:
Na_2HPO_4 and NaH_2PO_4 on heating at high temperature produce a chain sodium pentaphosphate quantitatively.

50. The ideal molar ratio of Na_2HPO_4 to NaH_2PO_4 is:
(a) 4 : 1   (b) 1 : 4   (c) 3 : 2   (d) 2 : 3

51. The total charge on pentaphosphate anion is:
(a) –5   (b) –3   (c) –7   (d) –9

Linked Answer Q.52 and Q.53:

The decomposition of ozone to oxygen $2O_3(g) \rightarrow 3O_2(g)$ occurs by mechanism

(i) $M(g) + O_3(g) \xrightarrow{k_1} O_2(g) + O(g) + M(g)$, 　　　　$E_{a,1}$

(ii) $O_2(g) + O(g) + M(g) \xrightarrow{k_2} M(g) + O_3(g)$, 　　　$E_{a,2}$

(iii) $O(g) + O_3(g) \xrightarrow{k_3} 2O_2(g)$, 　　　　　　　$E_{a,3}$
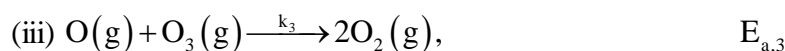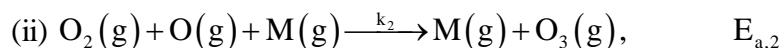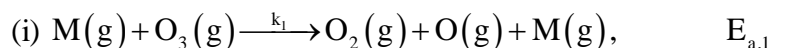
where, M is the catalyst molecule.

k_i' are rate constants and $k_{a,i}$'s the activation energies for the elementary steps,

52. Under the steady state approximation for the intermediates, the rate of decomposition of ozone, $-\dfrac{d[O_3]}{dt}$, is

(a) $\dfrac{2k_1k_3[O_3]^2[M]}{k_2[O_2][M] + k_3[O_3]}$　　　　　　(b) $\dfrac{2k_1k_3[O_3]^2[M]}{k_2[O_2][M] - k_3[O_3]}$

(c) $\dfrac{2k_2k_3[O_3][M]}{k_2[O_2][M] + k_3[O_3]}$　　　　　　(d) $\dfrac{2k_1k_2[O_3]^2[M]}{k_2[O_2][M] - k_3[O_3]}$

53. Assuming $k_3[O_3] \gg k_2[O_2][M]$, the activation of the overall reaction is

(a) $\dfrac{E_{a,1}E_{a,3}}{E_{a,2}}$　　　　(b) $E_{a,3} + E_{a,1} - E_{a,2}$　　　(c) $E_{a,2}$　　　　　(d) $E_{a,1}$

Statement for Linked Answer Q.54 and Q.55:

A ketone on treatment with bromine in methanol gives the corresponding monobromo compound[X] having molecular formula C_5H_9BrO. The compound [X] when treated with NaOMe in MeOH produces [Y] as the major product. The spectral data for compound [X] are: ^{1}H NMR: δ 1.17(d, 6H), 3.02 (m, 1H), 4.10(s, 2H); ^{13}C NMR: δ 17, 37, 39, 210.

54. The compound [X] is:
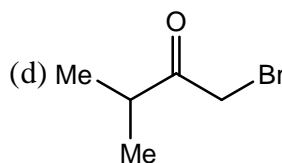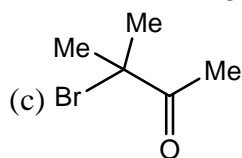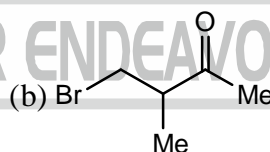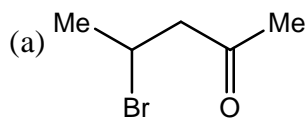
(a)

(b)

(c)

(d)

55. The major product [Y] is:

(a) 　(b) 　(c) 　(d)
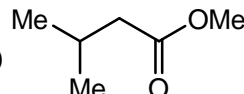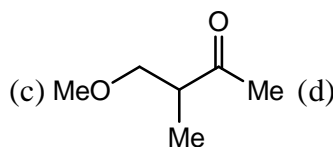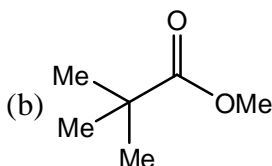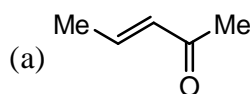
***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.25 : Carry ONE mark each.

1. In the proton decoupled ^{13}C NMR spectrum of 7-norbornanone, the number of signals obtained is
   (a) 7   (b) 3   (c) 4   (d) 5

2. Identify the most probable product in the given reaction
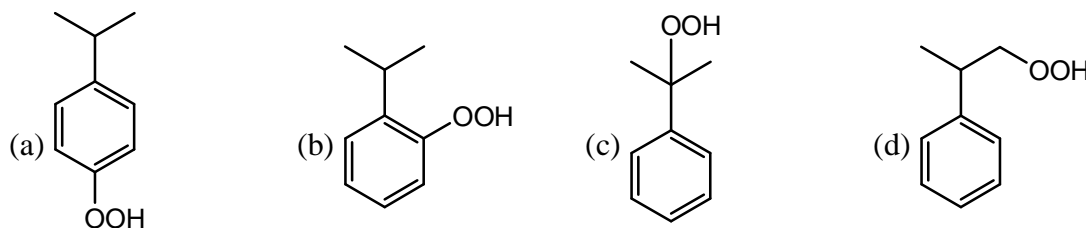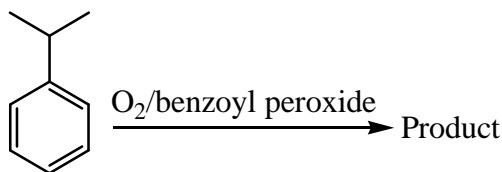
3. In the cyclization reaction given below, the most probable product formed is
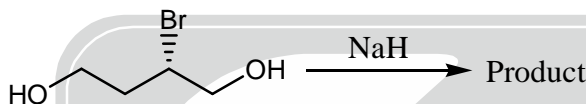
4. If Δy and ΔP_y are the uncertainties in the y-coordinate and the y component of the momentum of a particle respectively, then, according to uncertainty principle $\Delta y \Delta P_y$ is: $\left(\hbar = \dfrac{h}{2\pi} \text{ and h is Planck 's constant} \right)$

   (a) $\geq \hbar$ (b) $> \hbar / 2$ (c) $> \hbar$ (d) $\geq \hbar / 2$

5. The average length of a typical $\alpha - \text{helix}$ comprised of 10 amino acids is
   (a) 10Å   (b) 15Å   (c) 36Å   (d) 54Å

6. Number of thymine residues in a 5000 kb DNA containing 23% guanine residues is:
   (a) 2.70×10^6 (b) 2.70×10^7 (c) 1.35×10^6 (d) 1.35×10^7

7. Show below is a Hammett plot obtained for the reaction
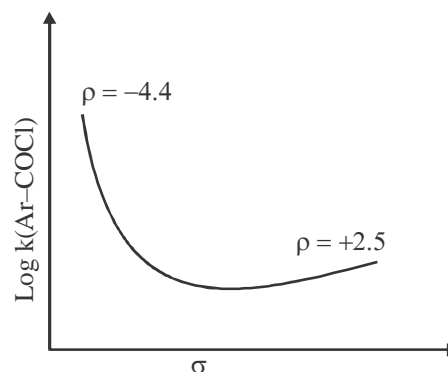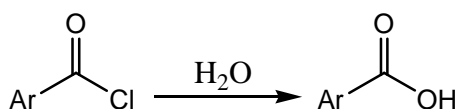
The change in slope of the plot indicates that

(a) The reaction does not follow linear free energy relationship

(b) electrons are being withdrawn from the transition state in the mechanism

(c) electrons are being donated to the transition state in the mechanism

(d) the mechanism of the reaction is changing

8. The ratio of relative intensities of the two molecular ion peaks of methyl bromide (CH_3Br) in the mass spectrum is:

(a) $M^+ : (M+2)^+ = 1:3$ (b) $M^+ : (M+2)^+ = 3:1$

(c) $M^+ : (M+2)^+ = 1:1$ (d) $M^+ : (M+2)^+ = 1:2$

9. A disaccharide that will not given Benedict's test and will not form osazone is

(a) maltose   (b) lactose   (c) cellobiose   (d) sucrose

10. Choose the allowed transition

(a) $^1\sum_g^+ \to {}^3\sum_u^+$ (b) $^1\sum_g^+ \to {}^3\sum_u^-$ (c) $^1\sum_g^+ \to {}^1\sum_u^+$ (d) $^1\sum_g^+ \to {}^1\sum_u^-$

11. The angular part of the wavefunction for the electron in a hydrogen atom is proportional to $\sin^2\theta \cos\theta \, e^{2i\phi}$. The values of the azimuthal quantum number l and the magnetic quantum number (m) are respectively.

(a) 2 and 2   (b) 2 and –2   (c) 3 and 2   (d) 3 and –2

12. Let ϕ_x^C and ϕ_z^C denote the wavefunctions of the $2p_x$ and $2p_z$ orbitals of carbon, respectively, and ϕ_x^0 and ϕ_z^0 represent the wavefunction of the $2p_x$ and $2p_z$ orbitals of oxygen, respectively. If c_1 and c_2 are constants used in linear combinations and the CO molecule is oriented along the z axis than, according to molecular orbital theory, the π – bonding molecular orbital has a wavefunction given by

(a) $c_1\phi_z^C + c_2\phi_x^0$ (b) $c_1\phi_z^C + c_2\phi_z^0$ (c) $c_1\phi_x^C + c_2\phi_z^0$ (d) $c_1\phi_x^C + c_2\phi_x^0$

13. The bond that gives the most intense band in the infrared spectrum for its stretching vibrations is

(a) C–H   (b) N –H   (c) O –H   (d) S–H

14. If x_A and x_B are the respective mole fractions of A and B in a ideal solution of the two and T_A, T_B, T are the fusion temperatures of pure A, and pure B and the ideal solution respectively, then

(a) $1 - x_B = \exp\left[\dfrac{-\Delta H_{fus(B)}^0}{R}\left(\dfrac{1}{T} - \dfrac{1}{T_B} \right) \right]$ (b) $1 - x_B = \exp\left[\dfrac{\Delta H_{fus(A)}^0}{R}\left(\dfrac{1}{T} - \dfrac{1}{T_A} \right) \right]$

(c) $1 - x_B = \exp\left[\dfrac{\Delta H_{fus(B)}^0}{R}\left(\dfrac{1}{T} - \dfrac{1}{T_B} \right) \right]$ (d) $1 - x_B = \exp\left[\dfrac{-\Delta H_{fus(A)}^0}{R}\left(\dfrac{1}{T} - \dfrac{1}{T_A} \right) \right]$

15. For a reaction involving two steps given below

First step : $G \rightleftharpoons 2H$

Second step : $G + H \longrightarrow P$

assume that the first step attains equilibrium rapidly. The rate of formation of P is proportional to

(a) $[G]^{1/2}$ (b) $[G]$ (c) $[G]^2$ (d) $[G]^{3/2}$

16. A metal chelate that can be used for separation and quantitative analysis of aluminium ions by gas chromatography is

    (a) EDTA   (b) ethylene glycol   (c) dinonyl phthalate   (d) trifluoroacetylacetone

17. The enthalpies of hydration of Ca^{2+}, Mn^{2+} and Zn^{2+} follow the order

    (a) $Mn^{2+} > Ca^{2+} > Zn^{2+}$ (b) $Zn^{2+} > Ca^{2+} > Mn^{2+}$

    (c) $Mn^{2+} > Zn^{2+} > Ca^{2+}$ (d) $Zn^{2+} > Mn^{2+} > Ca^{2+}$

18. The number of terminal carbonyl groups present in $Fe_2(CO)_9$ is

    (a) 2   (b) 5   (c) 6   (d) 3

19. Among the following substituted silanes, the one that gives cross-linked silicone polymer upon hydrolysis is

    (a) $(CH_3)_4 Si$ (b) CH_3SiCl_3 (c) $(CH_3)_2 SiCl_2$ (d) $(CH_3)_3 SiCl$

20. The plot of χT versus T (where χ is molar magnetic susceptibility and T is the temperature) for a paramagnetic complex which strictly follows Curie equation is:

    (a)   (b)   (c)   (d)
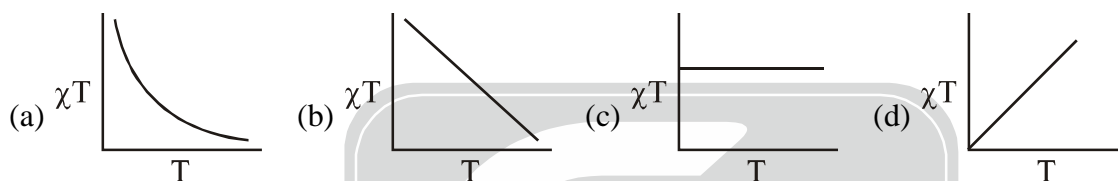
21. Among the following donors, the one that forms most stable adduct with the Lewis acid $B(CH_3)_3$ is:

    (a) 4-methylpyridine   (b) 2,6- dimethylpyridine
    (c) 4-nitropyridine   (d) 2, 6- di-tert-butylpyridine

22. The complex with inverse-spinel structure is

    (a) Co_3O_4 (b) Fe_3O_4 (c) $MgAlO_4$ (d) Mn_3O_4

23. The IUPAC nomenclature of $Na[PCl_6]$ is

    (a) sodium hexachlorophosphine (V)   (b) sodium hexachlorophosphate (V)
    (c) sodium hexachlorophosphine   (d) sodium hexachlorophosphite (V)

24. An intermediate formed during the hydroformylation of olefins using $Co_2(CO)_8$ as catalyst is

    (a) $HCo(CO)_6$ (b) $H_4Co(CO)_3$ (c) $H_2Co(CO)_4$ (d) $HCo(CO)_4$

25. The order of polarity of NH_3, NF_3 and BF_3 is:

    (a) $NH_3 < NF_3 < BF_3$ (b) $BF_3 < NF_3 < NH_3$

    (c) $BF_3 < NH_3 < NF_3$ (d) $NF_3 < BF_3 < NH_3$

Q.26 – Q.55 : Carry TWO marks each.

26. From a carboxymethyl-cellulose column at pH 6.0, arginine, valine and glutamic acid will elute in the order
    (a) arginine, valine, glutamic acid   (b) arginine, glutamic acid, valine
    (c) glutamic acid, arginine, valine   (d) glutamic acid, valine, arginine

27. Symmetry operations of the four C_2 axes perpendicular to the principal axis belong to the same class in the point group (s)

    (a) D_4 (b) D_{4d} (c) D_{4h} (d) D_{4h} and D_{4d}

28. At 298K, the EMF of the cell

$$pt \,|\, H_2\,(1bar)\,|\, H^+ \,(solution)\,||\, Cl^- \,|\, Hg_2Cl_2Hg$$

is 0.7530V. The standard potential of the calomel electrode is 0.2802V. If the liquid junction potential is zero, the pH of the solution is:

(a) 4.7   (b) 7.4   (c) 8.0   (d) 12.7

29. The wavefunction of a 1-D harmonic oscillator between $x = +\infty$ and $x = -\infty$ is given by $\psi(x) = N(2x^2 - 1)e^{-x^2/2}$. The value of N that normalizes the function $\psi(x)$ is:

$$\left(\text{Given} \int_{-\infty}^{+\infty} x^{2n} e^{-x^2} dx = \frac{1.3.5\ldots(2n-1)}{2^n}\sqrt{\pi} \right)$$

(a) $\left(\dfrac{1}{8\sqrt{\pi}} \right)^{\frac{1}{2}}$ (b) $\left(\dfrac{1}{3\sqrt{\pi}} \right)^{\frac{1}{2}}$ (c) $\left(\dfrac{1}{2\sqrt{\pi}} \right)^{\frac{1}{2}}$ (d) $\left(\dfrac{1}{4\sqrt{\pi}} \right)^{\frac{1}{2}}$

30. Consider the reaction, $\mathbf{H_2 + C_2H_4 \rightarrow C_2H_6}$

The molecular diameters of $\mathbf{H_2}$ and C_2H_4 are 1.8Å and 3.6Å respectively. The pre-exponential factor in the rate constant calculated using collision theory in $m^3\,(mole)^{-1}\,s^{-1}$ is approximately. (For this reaction at 300 K,

$\left(\dfrac{8k_B T}{\pi\mu} \right)^{\frac{1}{2}} N_A = 1.11 \times 10^{27}\, m\,(mole)^{-1}\,s^{-1}$, where the symbols have their usual meanings)

(a) 2.5×10^8 (b) 2.5×10^{14} (c) 9.4×10^{17} (d) 9.4×10^{23}

31. The molecular partition function of a system is given by $q(T) = \left(\dfrac{k_B T}{hc} \right)^{\frac{3}{2}} \left(\dfrac{8\pi^3 mk_B T}{h^2} \right)^{\frac{3}{2}}$, where the symbols have their usual meanings.

The heat capacity at constant volume for this system is

(a) 3R   (b) 6R   (c) 9R/2   (d) 3R/2

32. Consider the phase diagram given below .
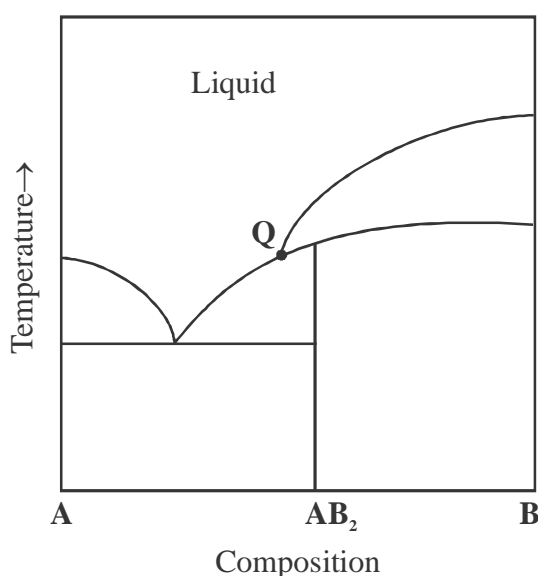
At the intersection point Q the phases that are in equilibrium are

(a) Solid **A**, solid **B** and Solid AB_2

(b) Solid A, solid AB_2 and liquid

(c) solid B, solid AB_2 and liquid

(d) solid A, solid B, solid AB_2 and liquid

33.   Identify the product from the following reaction

1. 9-BBN (1 eq)
2. H_2O_2, NaOH
→ Product
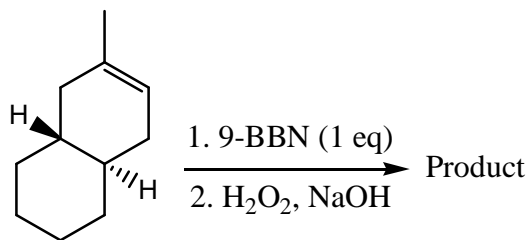
9-BBN= 9- Borabicyclo [3.3.1] nonane)

(a)

(b)

(c)

(d)
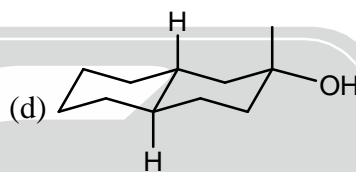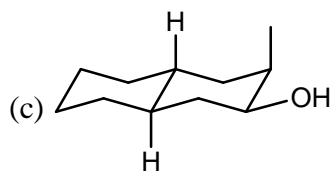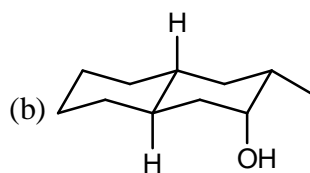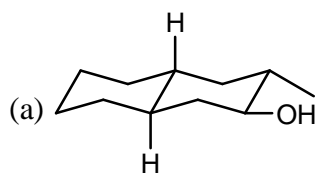
34.   The product from the following reaction is

$\xrightarrow{h\nu}$ Product

(a)

(b)

(c)

(d)
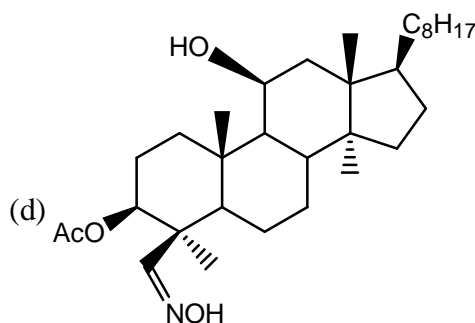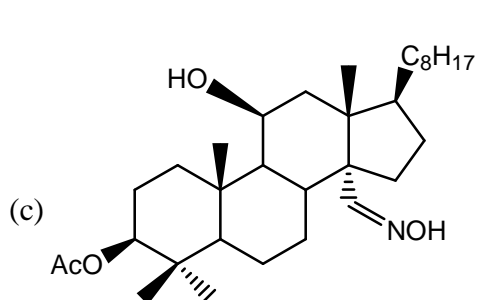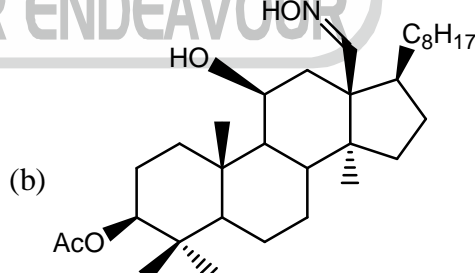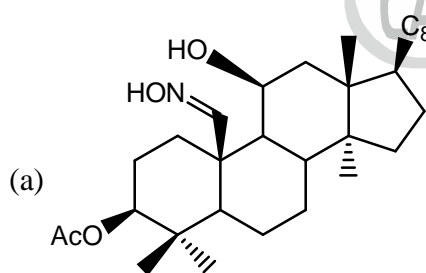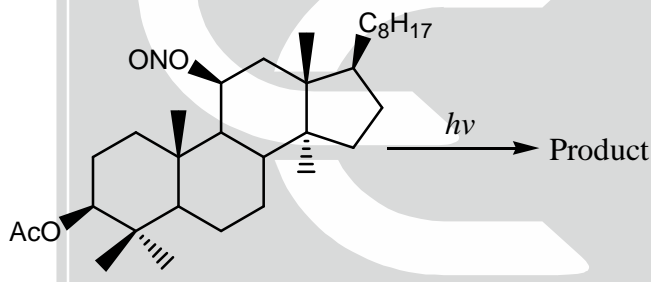
35. The acid catalyzed cyclization of 5-ketodecan-1,9-diol is given below
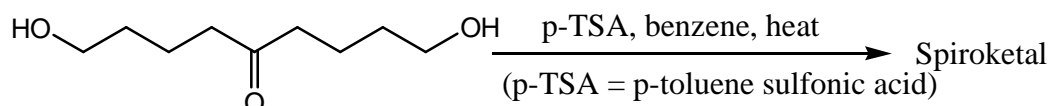
The most predominant spiroketal is

(a)   (b)   (c)   (d)
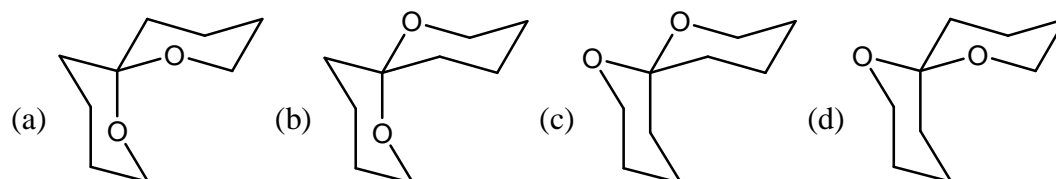
36. For a face centered cubic lattice, the Miller indices for the first Bragg's peak (smallest Bragg angle) are
(a) 002   (b) 111   (c) 001   (d) 110

37. For the titration of a 10 mL (aq) solution of $CaCO_3$, 2mL of 0.001 M Na_2 EDTA is required to reach the end point. The concentration of $CaCO_3$ (assume molecular weight of $CaCO_3 = 100$) is

(a) $5 \times 10^{-4} g / mL$ (b) $2 \times 10^{-4} g / mL$ (c) $5 \times 10^{-5} g/mL$ (d) $2 \times 10^{-5} g/mL$

38. In the reaction

the product formed is

(a)   (b)   (c)   (d)
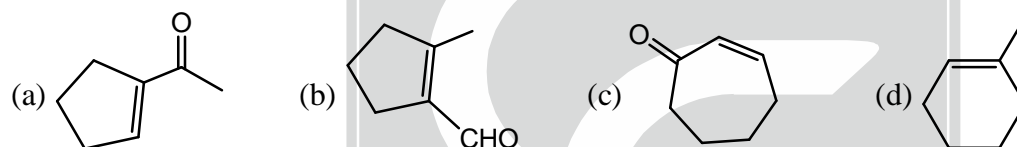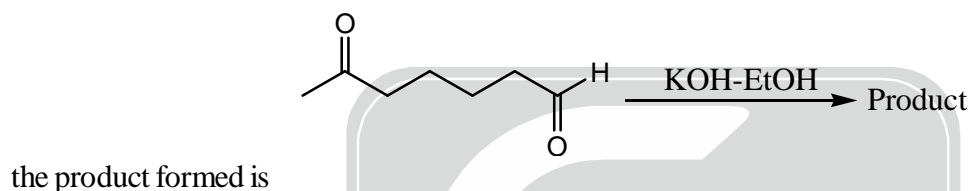
39. In the reaction given below, identify the product

1. $CH_2=CHMgBr$, THF
2. H_3O^+
3. excess $CH_3C(OMe)_3$, p-TSA, heat

(p-TSA = p-toluenesulfonic acid; THF = tetrahydrofuran)

(a) $OC(Me)(OMe)_2$ (b)

(c)   (d)
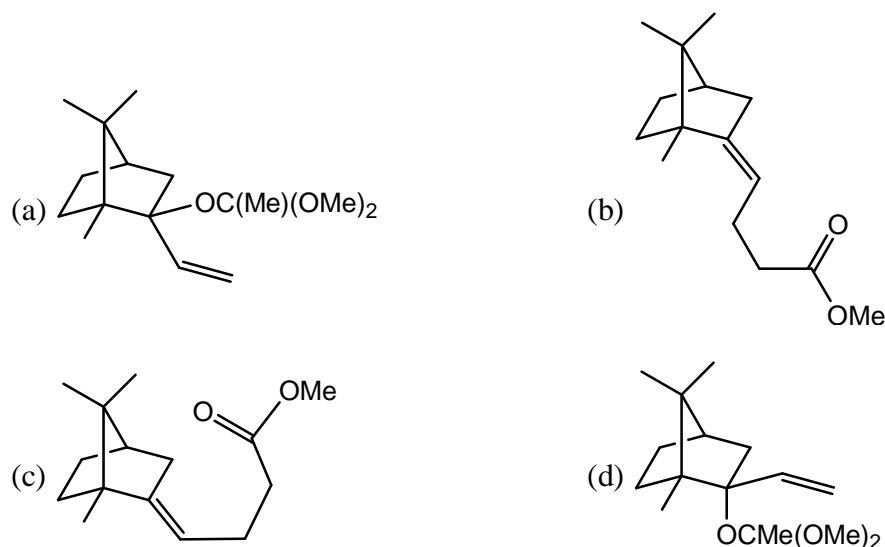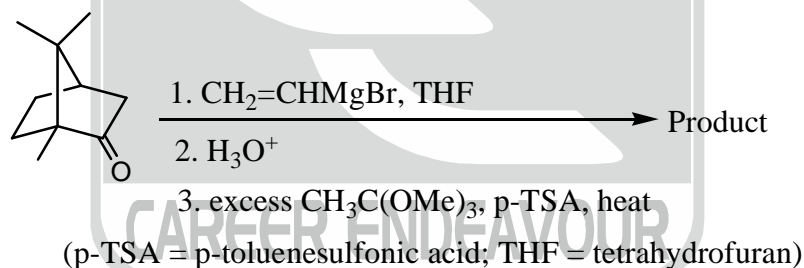
40. Consider the following pairs of complexes

$\left[CoF(NH_3)_5 \right]^{2+}$ and $\left[Cr(OH_2)_6 \right]^{2+}$; $\left[Co(NH_3)_5(OH_2) \right]^{3+}$ and $\left[Cr(OH_2)_6 \right]^{2+}$

$\left[Co(NH_3)_6 \right]^{3+}$ and $\left[Cr(OH_2)_6 \right]^{2+}$; $\left[CoI(NH_3)_5 \right]^{2+}$ and $\left[Cr(OH_2)_6 \right]^{2+}$
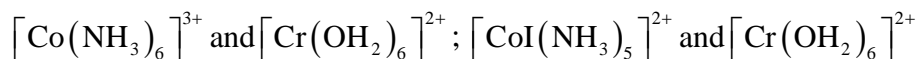
The electron transfer rate will be fastest in the pair .

(a) $\left[CoF(NH_3)_5 \right]^{2+}$ and $\left[Cr(OH_2)_6 \right]^{2+}$ (b) $\left[Co(NH_3)_5(OH_2) \right]^{3+}$ and $\left[Cr(OH_2)_6 \right]^{2+}$

(c) $\left[Co(NH_3)_6 \right]^{3+}$ and $\left[Cr(OH_2)_6 \right]^{2+}$ (d) $\left[CoI(NH_3)_5 \right]^{2+}$ and $\left[Cr(OH_2)_6 \right]^{2+}$
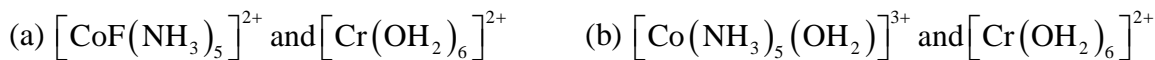
41. The extent of Mossbauer quadrupole splitting of iron follows the order

(a) $FeCl_2 \cdot 4H_2O > K_2\left[Fe(CN)_5(NO) \right] > FeCl_3 \cdot 6H_2O$

(b) $K_2\left[Fe(CN)_5(NO) \right] > FeCl_2 \cdot 4H_2O > FeCl_3 \cdot 6H_2O$

(c) $FeCl_3 \cdot 6H_2O > K_2\left[Fe(CN)_5(NO) \right] > FeCl_2 \cdot 4H_2O$

(d) $FeCl_2 \cdot 4H_2O > FeCl_3 \cdot 6H_2O > K_2\left[Fe(CN)_5(NO) \right]$
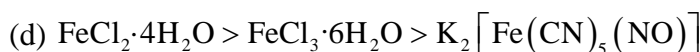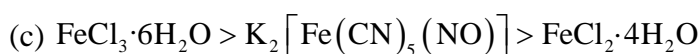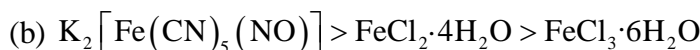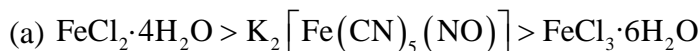
42. Hemoglobin is an oxygen carrying protein. The correct statement about oxy-hemoglobin is that

(a) the metal is low-spin in +3 oxidation state while dioxygen is in O_2^- form

(b) the metal is high-spin in +3 oxidation state while dioxygen is in O_2^- form

(c) The metal is low-spin in +3 oxidation state while dioxygen is in neutral form

(d) the metal is high-spin in +3 oxidation state while dioxygen is in neutral form

43. If a mixture of NaCl, conc. H_2SO_4 and $K_2Cr_2O_7$ is heated in a dry test tube, a red vapour (P) is formed. This vapour (P) dissolves in aqueous NaOH to form a yellow solution, which upon treatment with $AgNO_3$ forms a red solid (Q). P and Q are, respectively

(a) CrO_2Cl_2 and $Ag_2Cr_2O_7$ (b) $Na_2\left[CrOCl_5 \right]$ and Ag_2CrO_4

(c) $Na_2\left[CrOCl_5 \right]$ and $Ag_2Cr_2O_7$ (d) CrO_2Cl_2 and Ag_2CrO_4

44. For the following reaction

$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$
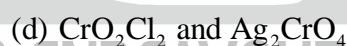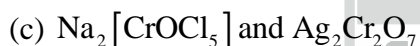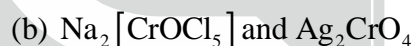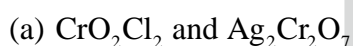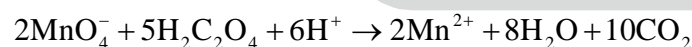
$E^0\left(MnO_4^-/Mn^{2+} \right) = +1.51V$ and $E^0\left(CO_2/H_2C_2O_4 \right) = -0.49V$.

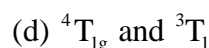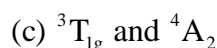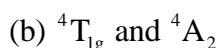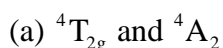At 298 K, the equilibrium constant is:

(a) 10^{500} (b) 10^{338} (c) 10^{38} (d) 10^{833}

45. The ground states of high-spin octahedral and tetrahedral Co(II) complexes are respectively

(a) $^4T_{2g}$ and $^4A_2$ (b) $^4T_{1g}$ and $^4A_2$ (c) $^3T_{1g}$ and $^4A_2$ (d) $^4T_{1g}$ and $^3T_1$

46. The INCORRECT statement about Zeise's salt is:
(a) Zeise salt is diamagnetic
(b) The oxidation state of Pt in Zeise's slat is +2
(c) All the Pt–Cl bond lengths in Zeise's salt are equal
(d) C–C bond length of ethylene moiety in Zeise's salt is longer than that of free ethylene molecule

47. The number of possible isomers for the square planar mononuclear complex $\left[(NH_3)_2 M(CN)_2 \right]$ of a metal M is:

    (a) 2   (b) 4   (c) 6   (d) 3
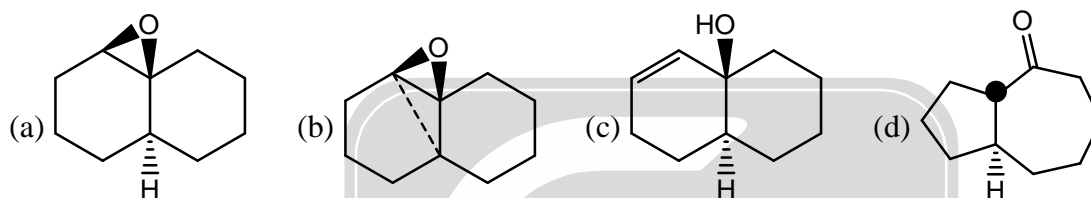
Common Data for Q. 48 and Q. 49 :
Consider the reaction sequence shown below :
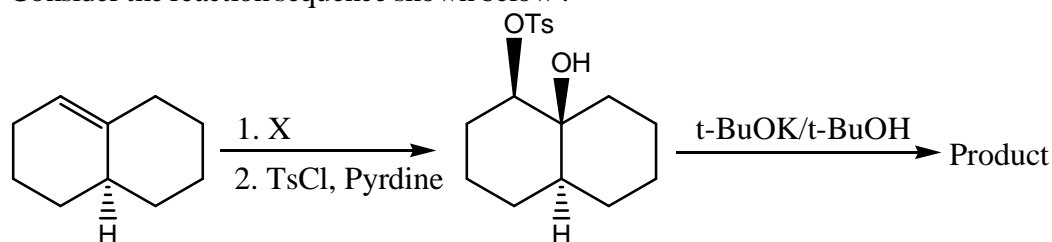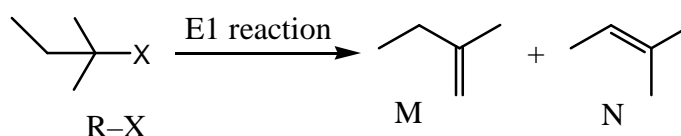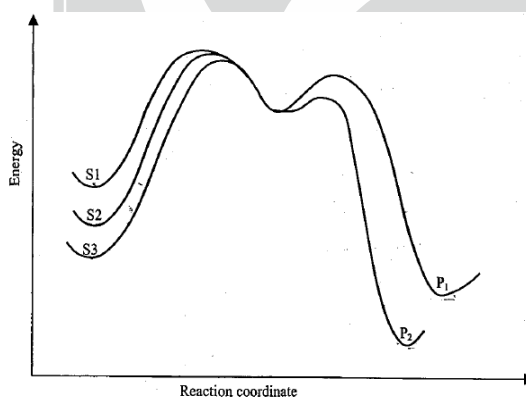

TsCl = p-toluenesulfonyl chloride

48. The oxidant X used in step 1 is

    (a) CrO_3 (b) OsO_4 (c) $NaIO_4$ (d) m-CPBA followed by NaOH

49. The product is

Common Data for Q. 50 and Q. 51
Consider the E1 reaction of tert-amyl halides from the energy profile give below.

50. In the above reaction, X = Cl, Br or I. Based on the graph, identify the alkyl halides (R-X) as S1 S2 and S3

    (a) S1 = R–Cl, S2 = R–Br and S3 = R–1   (b) S1= R–I, S2 = R–Br and S3 = R–Cl

    (c) S1 = R–Cl, S2 = R–I and S3 = R–Br   (d) SI=R–I, S2 = R–Cl and S3 = R–Br

51. Identify product P_1 and its yield relative to P_2

    (a) P_1 is M and is the major product   (b) P_1 is N and is the minor product

    (c) P_1 is N and is the major product   (c) P_1 is M and is the minor product.

Linked Answer Questions.
Statement for Linked Answer for Q.52 and Q.53
A 20491 cm^{-1} laser line was used to excite oxygen molecules (made of ^{16}O only) to obtain the rotational Raman spectrum. The resulting rotational Raman spectrum of oxygen molecule has the first Stokes line at 20479 cm^{-1}.

52. The rotational constant (usually denoted as B) for the oxygen molecule is

(a) 1.2cm^{-1} (b) 2.0 cm^{-1} (c) 3.0 cm^{-1} (d) 6.0 cm^{-1}

53. The next rotational Stokes line is expected at

(a) 20467 cm^{-1} (b) 20469 cm^{-1} (c) 20471 cm^{-1} (d) 20475 cm^{-1}

Statement for Linked Answer for Q.54 and Q.54
Huckel molecular orbital theory can be applied to the allene radical
$$CH_2 = CH - \dot{C}H_2$$

54. The secular determinant (where α, β and E have their usual meanings) is given by

(a) $\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix}$ (b) $\begin{vmatrix} \alpha - E & 0 & 0 \\ 0 & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix}$

(c) $\begin{vmatrix} \alpha - E & 0 & 0 \\ \beta & \alpha - E & 0 \\ 0 & 0 & \alpha - E \end{vmatrix}$ (d) $\begin{vmatrix} \alpha - E & -\beta & 0 \\ -\beta & \alpha - E & -\beta \\ 0 & -\beta & \alpha - E \end{vmatrix}$

55. The possible values of E are

(a) $\alpha + \sqrt{2}\beta, \alpha, \alpha - \sqrt{2}\beta$ (b) $\alpha + 2\sqrt{2}\beta, \alpha, \alpha - 2\sqrt{2}\beta$
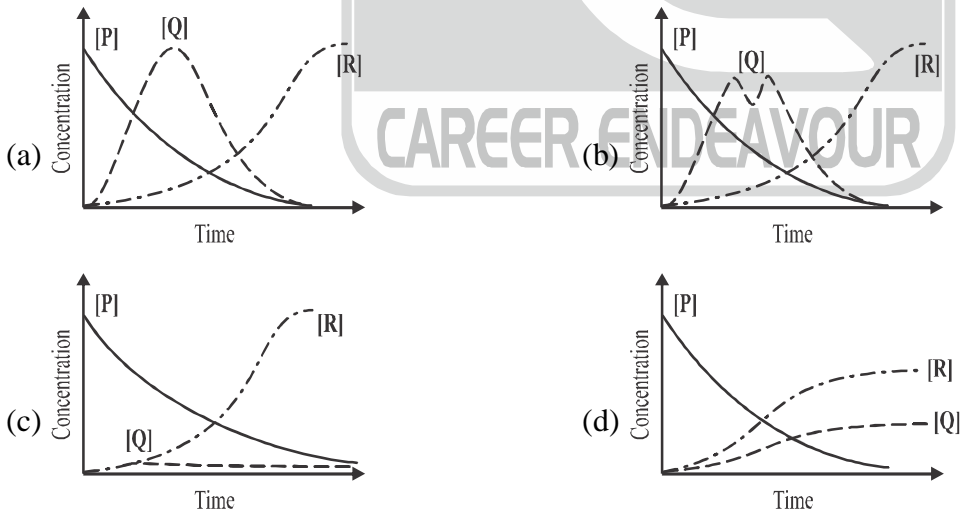
(c) $\alpha + \beta, \alpha, \alpha - \beta$ (d) $\alpha + 2\beta, \alpha, \alpha - 2\beta$

***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.25 : Carry ONE mark each.

1. The point group symmetry of $CH_2 = C = CH_2$ is:
   (a) D_{2h} (b) C_{2h} (c) C_{2v} (d) D_{2d}

2. Two trial wave function $\phi = c_1 x (a - x)$ and $\phi_2 = c_1 x (a - x) + c_2 x^2 (a - x)^2$ give ground state energies E_1 and E_2, respectively, for the microscopic particle in a 1-D box by using the variation method. If the exact ground state energy is E_0, the correct relationship between E_0, E_1 and E_2 is:
   (a) $E_0 = E_1 = E_2$ (b) $E_0 < E_1 < E_2$ (c) $E_0 < E_2 < E_1$ (d) $E_0 > E_2 = E_1$

3. The ground state energies of H atom and H_2 molecule are –13.6 eV and –31.7 eV, respectively. The dissociation energy of H_2 is _____ eV.

4. A 2 L vessel containing 2g of H_2 gas at 27ºC is connected to a 2L vessel containing 176 g of CO_2 gas at 27ºC. Assuming ideal behaviour of H_2 and CO_2, the partial pressure of H_2 at equilibrium is _____ bar.

5. Consider the reaction, $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ at equilibrium,

   The equilibrium can be shifted towards the forward direction by
   (a) Increasing the amount of carbon in the system
   (b) Decreasing the volume of the system.
   (c) Decreasing the pressure of the system.
   (d) Increasing the temperature of the system

6. A sparingly soluble electrolyte M_2X ionizes as $M_2X \rightleftharpoons 2M^+ + X^{2-}$.

   The solubility product (K_{sp}), molal solubility (S) and molal activity coefficient $(\gamma_{\pm})$ are related by

   (a) $K_{SP} = S^2 \gamma_{\pm}^2$ (b) $K_{SP} = S^3 \gamma_{\pm}^3$ (c) $K_{SP} = 4S^3 \gamma_{\pm}^2$ (d) $K_{SP} = 4S^3 \gamma_{\pm}^3$

7. For the first order consecutive reaction, $P \rightarrow Q \rightarrow R$, under steady state approximation to [Q], the variation of [P], [Q] and [R] with time are best reprsented by

8. At 273 K and 10 bar, the langmuir adsorption of a gas on a solid surface gave the fraction of surface coverage as 0.01. The Langmuir adsorption isotherm constant is _____ bar⁻¹.

9. Conversion of boron trifluoride to tetrafluoroborate accompanies
   (a) Increase in symmetry and bond elongation
   (b) Increase in symmetry and bond contraction
   (c) Decrease in symmetry and bond contraction
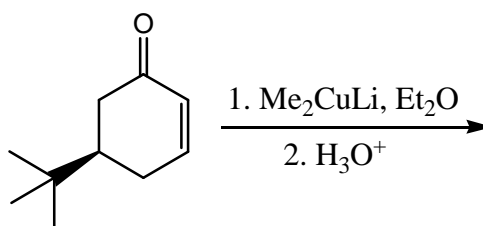   (d) Decrease in symmetry and bond elongation.

10. The correct statement with respect to the bonding of the ligands, Me_3N and Me_3P with the metal ions Be^{2+} and Pd^{2+} is,
    (a) The ligands bind equally strong with both the metal ions as they are dicationic.
    (b) The ligands bind equally strong with both the metal ions as both the ligands are pyramidal.
    (c) The binding is stronger for Me_3N with Be^{2+} and Me_3P with Pd^{2+}.
    (d) The binding is stronger for Me_3N with Pd^{2+} and Me_3P with Be^{2+}.

11. A crystal has the lattice parameters $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$. The crystal system is
    (a) Tetragonal   (b) Monoclinic   (c) Cubic   (d) Orthorhombic

12. The by-product formed in the characteristic reaction of $(CO)_5 Cr = C(OMe)(Me)$ with $MeNH_2$ is
    (a) CO   (b) MeOH   (c) MeCHO   (d) $MeCONH_2$.

13. The catalyst and co-catalyst used in Wacker process, respectively, are
    (a) $PdCl_2$ and Cu   (b) $CuCl_2$ and $[PdCl_4]^{2-}$
    (c) Pd and CuCl   (d) $[PdCl_4]^{2-}$ and $CuCl_2$.

14. Oxymyoglobin $Mb(O_2)$ and oxhyhemoglobin $Hb(O_2)_4$, respectively, are
    (a) Paramagnetic and paramagnetic   (b) Diamagnetic and diamagnetic
    (c) Paramagnetic and diamagnetic   (d) Diamagnetic and paramagnetic.

15. Hapticity of cycloheptatriene in $Mo(C_7H_8)(CO_3)$ is _____

16. The number of oxygen molecule(s) that a molecule of hemerythrin can transport is _____

17. The maximum number of stereoisomers possible for the compound given below is _____
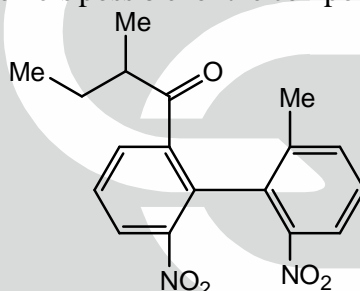
18. The correct sequence of the amino acids present in the tripeptide given below is
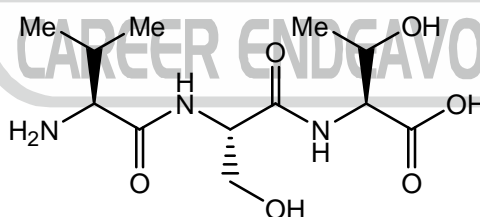
    (a) Val-Ser-Thr   (b) Val-Thr-Ser   (c) Leu-Ser-Thr   (d) Leu-Thr-Ser

19. Among the compounds given in the options (a)–(d), the one that can be used as a formyl anion equivalent (in the presence of a strong base) is:
    (a) ethylene   (b) nitroethane   (c) 1, 3-dithiane   (d) 1, 4-dithiane

20. The major product formed in the reaction given below is:

(a) [structure: cyclohexene ring with HO and Me at top, tert-butyl at bottom]

(b) [structure: cyclohexene ring with Me and OH at top, tert-butyl at bottom]

(c) [structure: cyclohexanone ring with tert-butyl and Me substituents]

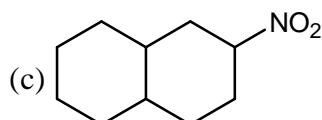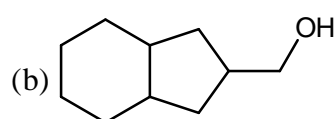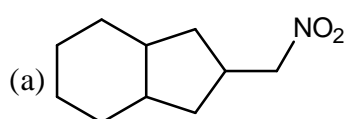(d) [structure: cyclohexanone ring with tert-butyl and Me substituents]

21. The major product formed in the reaction given below is

[structure: phthalimide] $\xrightarrow[\text{2. H}_3\text{O}^+]{\text{1. NaOH, Br}_2}$

(a) [structure: benzene with NH$_2$ and COOH]

(b) [structure: benzene with Br and CONH$_2$]

(c) [structure: benzene with COOH and CONH$_2$]

(d) [structure: phthalic anhydride]

22. The pericyclic reaction given below is an example of

[structure: starting material with OH] $\xrightarrow{\Delta}$ [structure: product with HO]
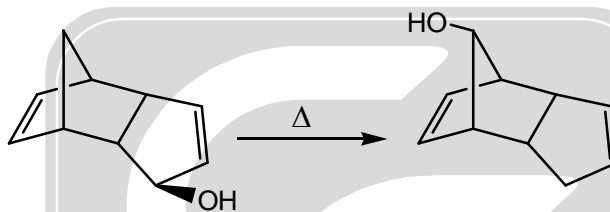
(a) [1, 3]-sigmatropic shift   (b) [1, 5]-sigmatropic shift
(c) [3, 5]-sigmatropic shift   (d) [3, 3]-sigmatropic shift.

23. The major product formed in the reaction of quinoline with potassium amide (KNH$_2$) in liquid ammonia is:

(a) [structure: tetrahydroquinoline with NH]

(b) [structure: quinoline with NH$_2$ at 2-position]

(c) [structure: dihydroquinoline]

(d) [structure: quinoline with H$_2$N at 6-position]
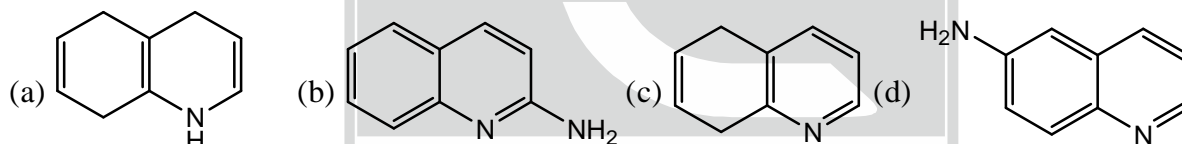
24. The number of signals that appear in the proton decoupled ^{13}C NMR spectrum of benzonitrile (C$_7$H$_5$N) is _____

25. Among the compounds given in the option (a) to (d), the one that exhibits a sharp band at around 3300 cm^{-1} in the IR spectrum is:

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

Q.26 – Q.55 : Carry TWO marks each.

26. In the metathesis reaction given below, 4.32 g of the compound X was treated with 822 mg of the catalyst Y to yield 2.63 g of the product Z. The mol% of the catalyst Y used in this reaction is _____
[Atomic weights of Ru = 101; P = 31; Cl = 35.5]

[structure X: MeO-substituted aromatic with two alkenyl chains]

+

[structure Y: Ru complex with PR$_3$, Cl, Cl, =CHPh]

$\longrightarrow$

[structure Z: MeO-substituted bicyclic product]

X   **Y**   **Z**

(R=cyclohexyl)
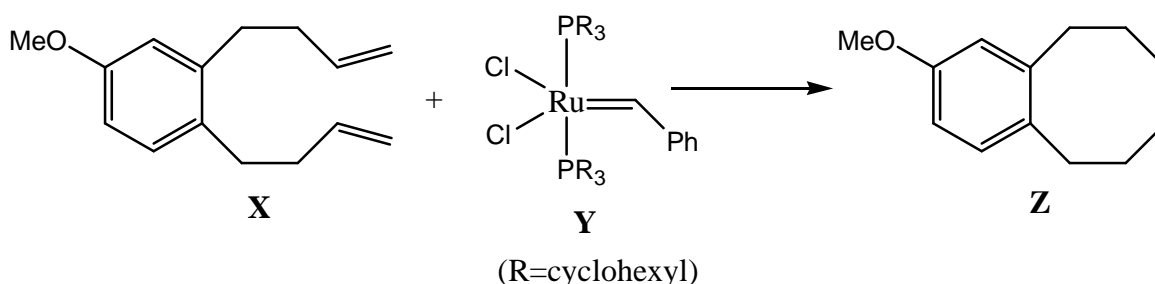
27. An organic compound **Q** exhibited the following spectral data:

    IR: 1760 cm^{-1}

    ^{1}H NMR : δ (ppm) : 7.2 (1H, d, J = 16.0 Hz), 5.1 (1H, m), 2.1 (3H, s), 1.8 (3H, d, J = 7.0 Hz)

    ^{13}C NMR : δ (ppm); 170 (carbonyl carbon),

    Compound **Q** is

(a)   (b)   (c)   (d)
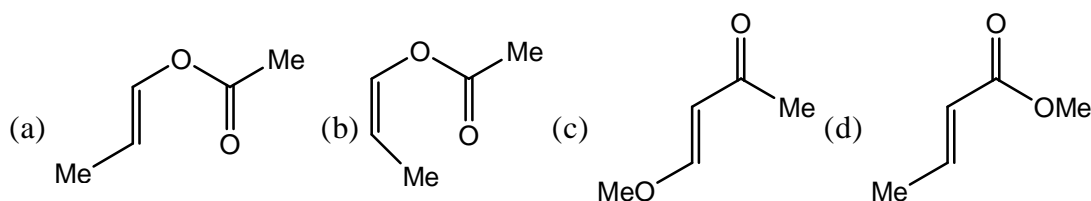
28. The major product formed in the Beckmann rearrangement of the compound given below is:
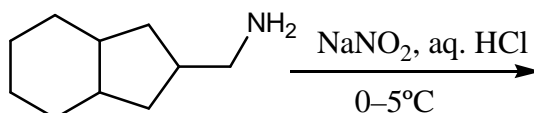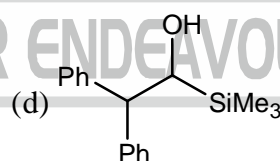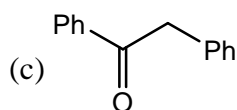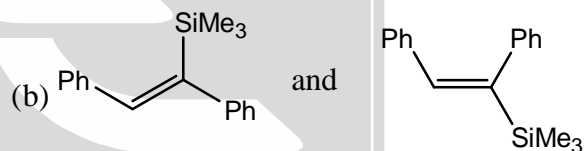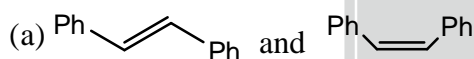

    1. TsCl pyridine
    2. H_3O^+

(a)   (b)   (c)   (d)
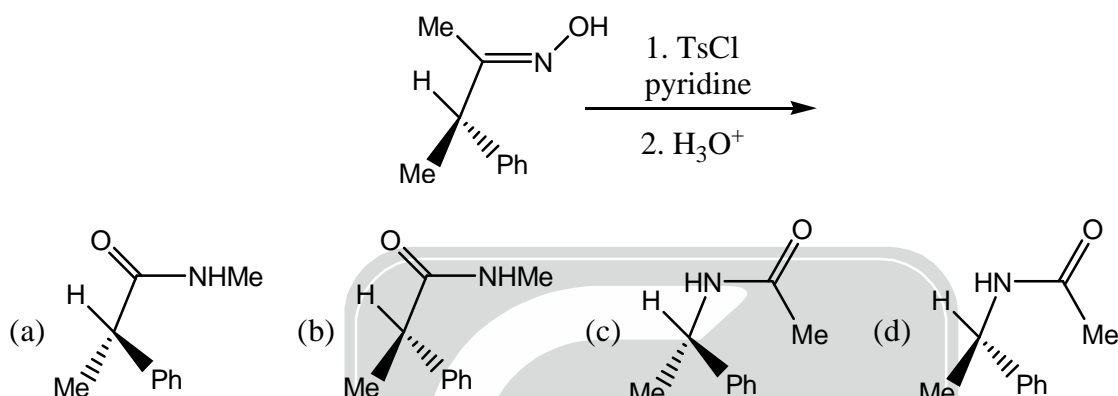
29. The major product formed in the reaction given below is

    conc. H_2SO_4

(a)   (b)

(c)

(d)
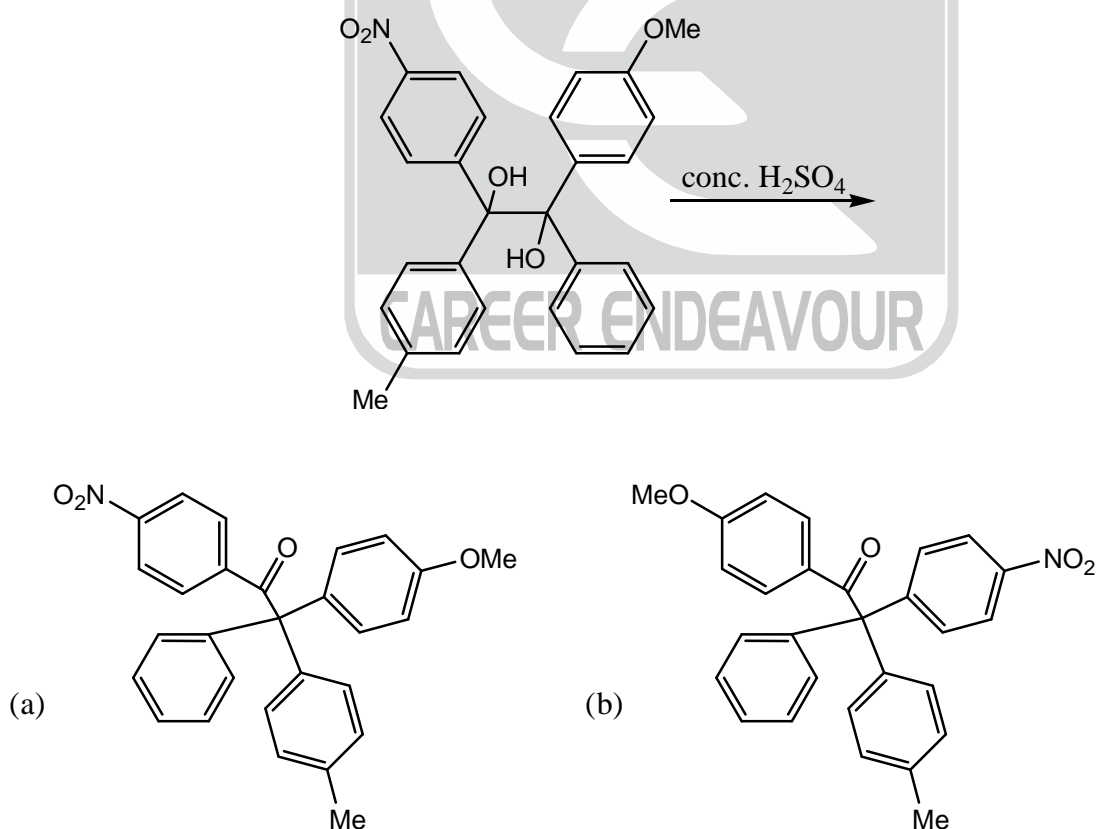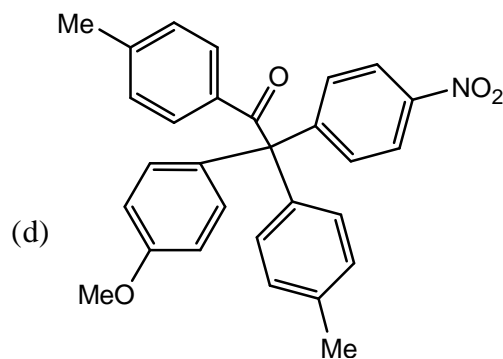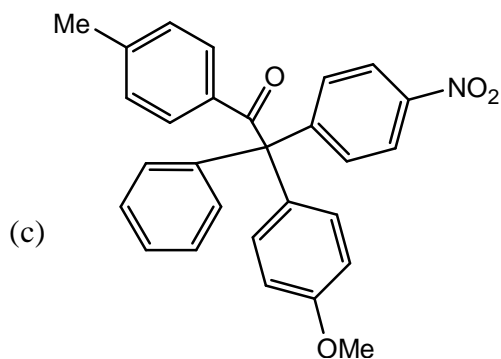
30. The major product formed in the reaction given below is

(a)

(b)

(c)

(d)

31. The major product(s) fromed in the reaction sequence given below is/are

1. Mg, dry Et$_2$O

2. PhCHO

3. aq. H$_2$SO$_4$

(a) Ph   Ph and Ph   Ph

(b)

SiMe$_3$

Ph   Ph   and   Ph   Ph

SiMe$_3$

(c) Ph   Ph

(d)

OH

Ph   SiMe$_3$

Ph
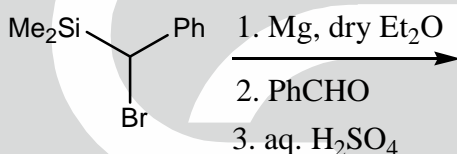
32. Match the compounds in the **Column-I** with photochemical reactions that they can undergo given in the **Column-II:**

Column-I   Column-II

(i)

(p) oxa-di-π-methane rearrangement

(ii)
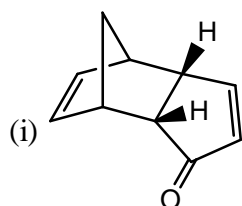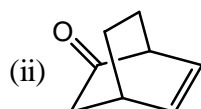
(q) Paterno-Buchi reaction
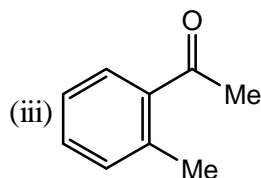
(iii) 　　　　(r) intramolecular [2+2]-cycloaddition.

(a) (i)-(q); (ii)-(s); (iii)-(p)　　　　(b) (i)-(r); (ii)-(p); (iii)-(s)
(c) (i)-(p); (ii)-(r); (iii)-(q)　　　　(d) (i)-(r); (ii)-(q); (iii)-(s)

33. e^{-2x^2} is an eigen function of the operator $\left(\dfrac{d^2}{dx^2} - 16x^2\right)$. The corresponding eigen value is

(a) +4　　　　(b) –4　　　　(c) +2　　　　(d) –2

34. The infrared spectrum of HCl gas shows an absorption band centered at 2885 cm^{-1}. The zero point energy of HCl molecule under hamonic oscillator approximation is:
(a) 2.8665×10^{-22} J　　　　(b) 2.8665×10^{-20} J
(c) 5.7330×10^{-22} J　　　　(d) 5.7330×10^{-20} J

35. For the reaction $X_2O_4(\ell) \rightarrow 2XO_2(g)$ at 298K, given the values,

given the values, $\Delta U = 9kJ$ and $\Delta S = 84\ J\ K^{-1}$, ΔG is
(a) –11.08 kJ　　　　(b) +11.08 kJ　　　　(c) –13.55 kJ　　　　(d) +13.55 kJ

36. The change in enthalpy when 3 mol of liquid benzene transforms to the vapour state at its boiling temperature (80°C) and at 1 bar pressure is _____ kJ.

37. The moment of inertia of a homonuclear diatomic molecule is 7.5×10^{-45} kg m^2. Its rotational partition function at 500 K is _____

38. For a reaction of the type $X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Y$, the correct rate expression is ($[X]_0$ and $[X]$ corresponds to the concentration of X at time t = 0 and t = t, respectively)

(a) $-\dfrac{d[X]}{dt} = k_1[X]_0 - (k_1 + k_2)[X]$　　　　(b) $-\dfrac{d[X]}{dt} = (k_1 + k_2)[X] - k_2[X]_0$

(c) $-\dfrac{d[X]}{dt} = (k_1 + k_2)[X]_0 - k_1[X]$　　　　(d) $-\dfrac{d[X]}{dt} = (k_1 + k_2)[X] - k_1[X]_0$

39. The temperature dependence of partition are as follows:

$q_{translation} \propto T^{3/2}$　　　　　　　　$q_{vibration} \propto T^0$

$q_{rotation} \propto T\ (linear\ molecule)$　　　$q_{rotation} \propto T^{3/2}\ (non-linear\ molecule)$

According to the Conventional Transition State Theory (CTST), the temperature dependence of the Arrhenius pre-exponential factor for a reaction of the type given below is

linear molecule + linear molecule $\rightleftharpoons$ non-liner linear transition state $\longrightarrow$ products.

(a) T^{-1}　　　　(b) T^0　　　　(c) T^1　　　　(d) T^2.

40. Decarbonylation reaction of $[cis\text{-}(CH_3CO)Mn(^{13}CO)(CO)_4]$ yields X, Y and Z, where
$X = [(CH_3)Mn(CO)_5]$; $Y = [cis\text{-}(CH_3)Mn(^{13}CO)CO_4]$; $[Z = trans\text{-}(CH_3)Mn(^{13}CO)(CO)_4]$
The molar ratio of the products (X : Y : Z) in this reaction is
(a) 1 : 1 : 1　　　　(b) 1 : 2 : 1　　　　(c) 1 : 1 : 2　　　　(d) 2 : 1 : 1

41. According to polyhedral electron count rule, the structure of $Rh_6(CO)_{16}$ is:
    (a) closo   (b) nido   (c) arachno   (d) hypho

42. The increasing order of melting points of the halides NaCl, CuCl and NaF is:
    (a) CuCl < NaCl < NaF   (b) NaF < NaCl < CuCl
    (c) NaF < CuCl < NaCl   (d) CuCl < NaF < NaCl

43. The correct electronic configuration and spin only magnetic moment of Gd^{3+} (atomic number 64) are
    (a) $[Xe]4f^7$ and 7.9 BM   (b) $[Xe]4f^7$ and 8.9 BM
    (c) $[Xe]4f^6 5d^1$ and 7.9 BM   (d) $[Rn]5f^7$ and 7.9 BM

44. Among the following octahedral complexes, the one that has the highest enthalpy of hydration is
    (a) $[Ca(H_2O)_6]^{2+}$ (b) $[Mn(H_2O)_6]^{2+}$ (c) $[V(H_2O)_6]^{2+}$ (d) $[Cr(H_2O)_6]^{2+}$

45. A metal crystallizes in the face-centered cubic lattice parameter of 4.20Å. The shortest atom to atom contact distance in the lattice is
    (a) 4.20 Å   (b) 2.97Å   (c) 2.42Å   (d) 2.10Å

46. Polarographic method of analysis to obtain individual amounts of Cu^{2+} and Cd^{2+} in a given mixture of the two ions (Cu^{2+} and Cd^{2+}) is achieved by measuring their
    (a) half-wave potentials   (b) migration currents
    (c) decomposition potentials   (d) diffusion currents

47. The ground state term $[Ni(H_2O)_6]^{2+}$ is:
    (a) $^3T_{1g}$ (b) $^3T_{2g}$ (c) $^3A_{2g}$ (d) $^4T_{1g}$

Commond Data Questions:
Commond data for Q.48 and Q.49:
N, N-Dimethylformamide (DMF) gives different patterns of signals for the methyl protons when its ^1H NMR spectrum is recorded at different temperatures.

48. Match the patterns of the NMR signals given in the **Column-I** with temperatures given in the **Column-II**.

Column-I	Column-II
(i) Two singlets, for three protons each, at δ 2.87 and 2.97 ppm	(x) 25°C
(ii) One sharp singlet for six protons at δ 2.92 ppm	(y) 120°C
(iii) One broad signal for six protons	(z) 150°C

   (a) (i)-(x); (ii)-(y); (iii)-(z)   (b) (i)-(x); (ii)-(z); (iii)-(y)
   (c) (i)-(z); (ii)-(x); (iii)-(y)   (d) (i)-(z); (ii)-(y); (iii)-(x)

49. Based on the above data, the calculated difference in the frequencies of the two methyl singlets, if the spectrum is recorded on a 300 MHz spectrometer, is _____Hz.

Common data for Q.50 and Q.51:
Heating a mixture of ammonium chloride and sodium tetrahydridoborate gives one liquid product (X), along with other products under ambient conditions.

50. Compound X is:
    (a) $NH_4[BH_4]$ (b) $[(NH_3)_2BH_2][BH_4]$
    (c) $N_3B_3H_6$ (d) $N_3B_3H_{12}$

51. Compound X is an example of
    (a) Ionic liquid   (b) saturated heterocycle
    (c) molecular cage   (d) unsaturated heterocycle.

Linked Answer Q.52 and Q.53:

52. The major product X formed in the reaction given below is
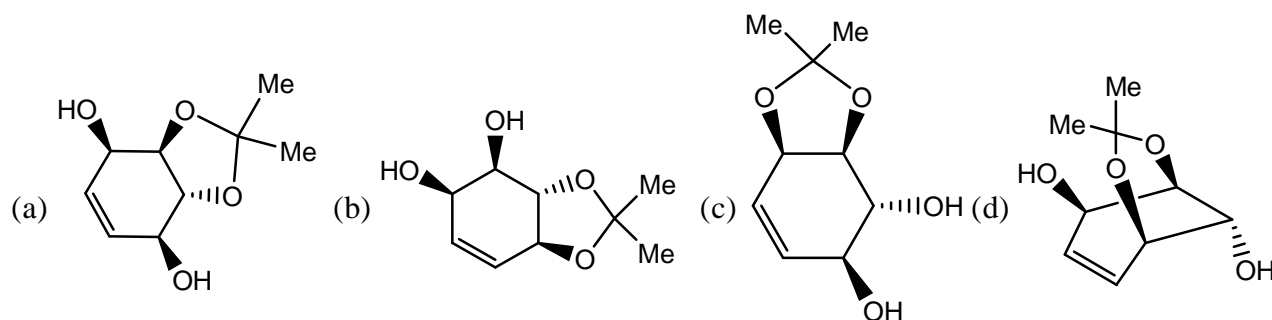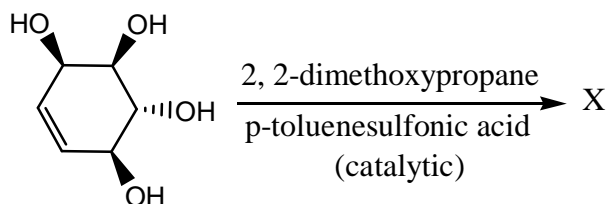
53. Oxidation of the product X, obtained in the above reaction, with active manganse dioxide, followed by acidic hydrolysis gives
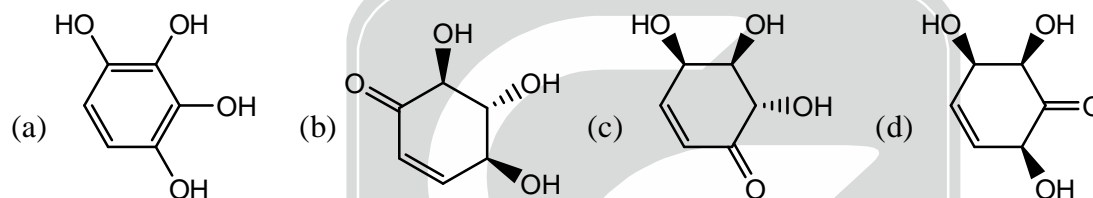
Statement for Linked Answer Q.54 and Q.55:

The standard half-cell reduction potential of Fe^{3+} (aq)|Fe is – 0.036 V and that of OH^- (aq) |$Fe(OH)_3$(s)|Fe is – 0.786 V

54. For the determination of solubility product (K_{SP}) of $Fe(OH)_3$, the appropriate cell representation and its emfare, respectively.

(a) $\left\langle Fe \mid Fe(OH)_3(s) \mid OH^-(aq)\, Fe^{3+}(aq) \mid Fe \right\rangle$,   –0.750V

(b) $\left\langle Fe \mid Fe^{3+}(aq)\, OH^-(aq) \mid Fe(OH)_3(s) \mid Fe \right\rangle$,   –0.750V

(c) $\left\langle Fe \mid Fe(OH)_3(s) \mid OH^-(aq)\, Fe^{3+}(aq) \mid Fe \right\rangle$,   +0.750V

(d) $\left\langle Fe \mid Fe^{3+}(aq)\, OH^-(aq) \mid Fe(OH)_3(s) \mid Fe \right\rangle$,   –0.822V

55. The value of $\log_e(K_{SP})$ for $Fe(OH)_3$ at 298 K is
(a) –38.2   (b) +87.6   (c) –96.0   (d) –87.6

***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.25 : Carry ONE mark each.

1. The maximum non-PV work that a system can perform at constant P is
   (a) ΔH (b) ΔG (c) ΔS (d) ΔA

2. Consider the reaction :

   $$A + B \rightleftharpoons C$$

   The unit of the thermodynamic equilibrium constant for the reaction is
   (a) $mol\, L^{-1}$ (b) $L\, mol^{-1}$ (c) $mol^2\, L^{-2}$ (d) dimensionless

3. The number of IR active vibrational normal modes of CO_2 is _____

4. The number of C_2 axes in CCl_4 is _____

5. The value of the magnetic quantum number of a p_x orbital is
   (a) –1   (b) 0   (c) +1   (d) undefined.

6. The molecular partition function for a system in which the energy levels are equispaced by ε, is

   (a) $\dfrac{1}{1+e^{\beta\varepsilon}}$ (b) $\dfrac{1}{1-e^{\beta\varepsilon}}$ (c) $\dfrac{1}{1+e^{-\beta\varepsilon}}$ (d) $\dfrac{1}{1-e^{-\beta\varepsilon}}$

7. A monoatomic gas, X, adsobred on a surface, Langmuir adsorption isotherm. A plot of the fraction of surface coverage, θ against the concentration of the gas [X], for very low concentration of the gas, is described by the equation

   (a) $\theta = K[X]$ (b) $1-\theta = \dfrac{1}{K[X]}$ (c) $\theta = K^{1/2}[X]^{1/2}$ (d) $\theta = \dfrac{K[X]}{1-K[X]}$

8. At a given temperature and pressure, the ratio of the average speed of hydrogen gas to that of helium gas is approximately _____

9. An example of nido-borane from the following is
   (a) B_4H_{10} (b) B_6H_{10} (c) B_6H_{12} (d) B_8H_{14}

10. The geometries of $Ni(CO)_4$ and $[NiCl_4]^{2-}$, respectively, are
    (a) tetrahedral and square planar   (b) square planar and tetrahedral
    (c) tetrahedral and tetrahedral   (d) square planar and square planar

11. The number of S–S bonds in $H_2S_5O_6$ is _____

12. In atomic absorption spectroscopy, the atomization process utilizes
    (a) flame   (b) electric field   (c) magnetic field   (d) electron beam

13. At room temperature, the number of singlet resonances observed in the ^1H NMR spectrum of $Me_3CC(O)NMe_2$ (N N–dimethyl pivalamide) is _____

14. Amongst the following, the metal that does NOT form homoleptic polynuclear carbonyl is
    (a) Mn   (b) Fe   (c) Cr   (d) Co

15. The reaction of $[Cp_2TaMe_2]I$ $(Cp = C_5H_5^-)$ with NaOMe yields.
    (a) $[Cp_2Ta(OMe)_2]I$ (b) $[Cp_2Ta(Me)OMe]I$
    (c) $Cp_2Ta(Me) = CH_2$ (d) $Cp_2Ta(OMe) = CH_2$

16. The complexes $[Co(H_2O)_4Cl_2]NO_2$ and $[Co(H_2O)_4Cl(NO_2)]Cl$ are
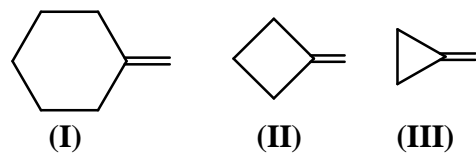   (a) linkage isomers   (b) positional isomers   (c) ionization isomers   (d) optical isomers

17. The major product of the following reaction is

$$\xrightarrow[\text{2. HCl, H}_2\text{O}]{\text{1. Me}_2\text{SO}_4,\ \text{NaOH}}$$

(a)

(b)

(c)

(d)
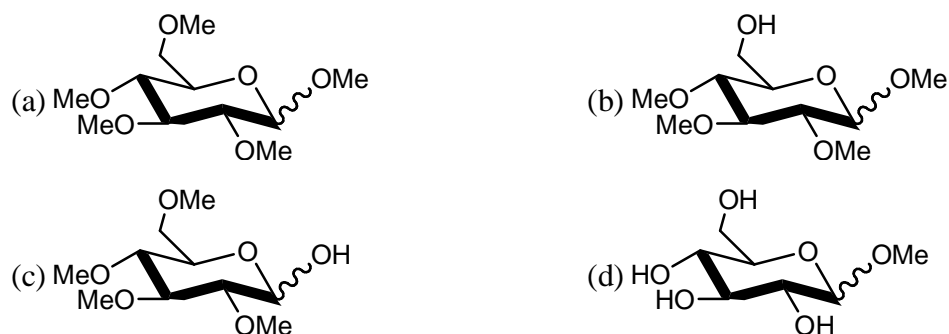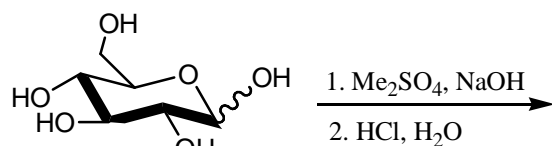
18. Amongst the following, the structure of guanosine is

(a)

(b)

(c)

(d)
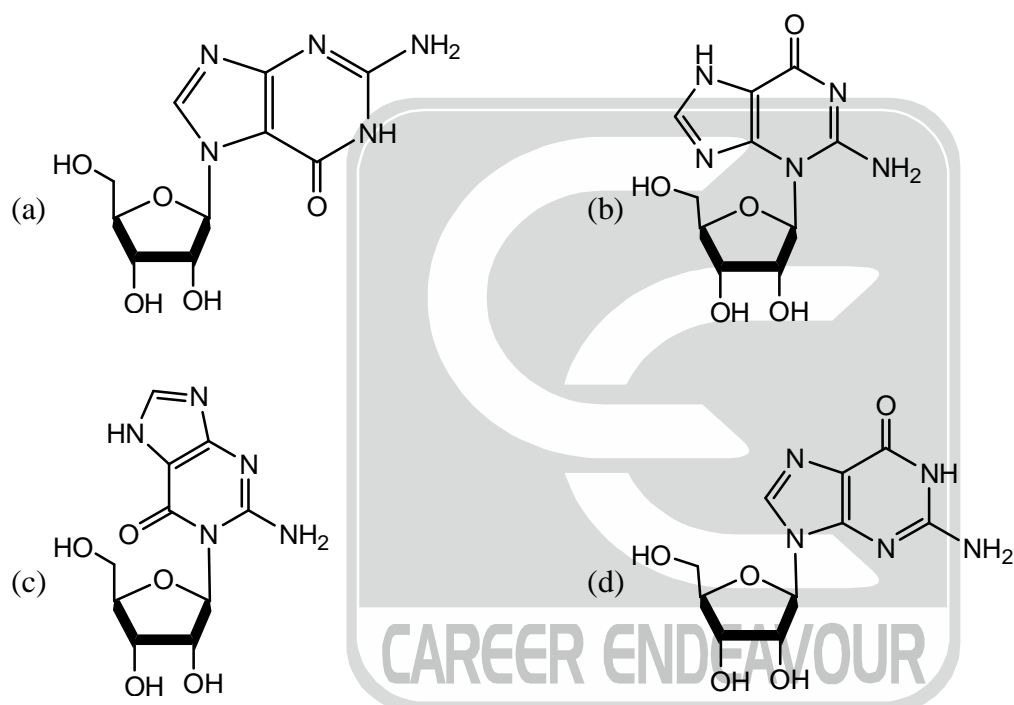
19. The correct order of IR stretching frequency of the $C=C$ in the following olefins is
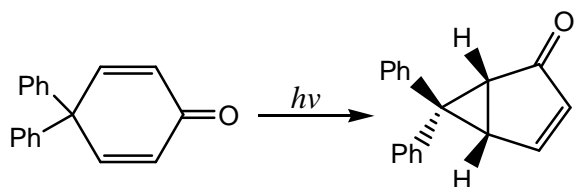

    (I)   **(II)**   **(III)**

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

20. The correct order of the solvolysis for the following chlorides in acetic acid is
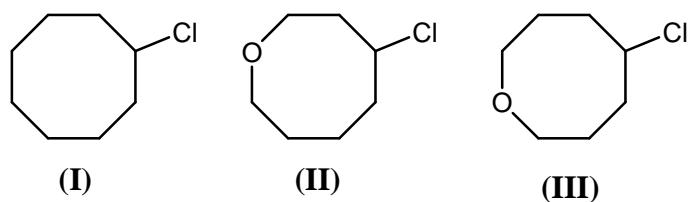
    (I)   **(II)**   **(III)**

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

21. Formation of the product in the following photochemical reaction involves

    (a) di-π-methane rearrangement   (b) Paterno-Buchi reaction
    (c) [2, 3]-sigmatropic rearrangement   (d) Norrish type I reaction

22. The correct order of stability for the following conformations of cyclohexane is
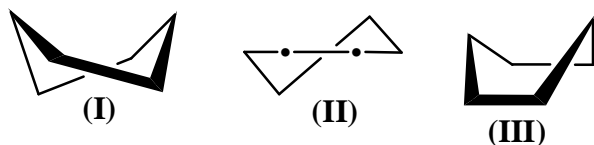
    (I)   **(II)**   **(III)**

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

23. The major product formed in the following reaction is

    (a)   (b)   (c)   (d)
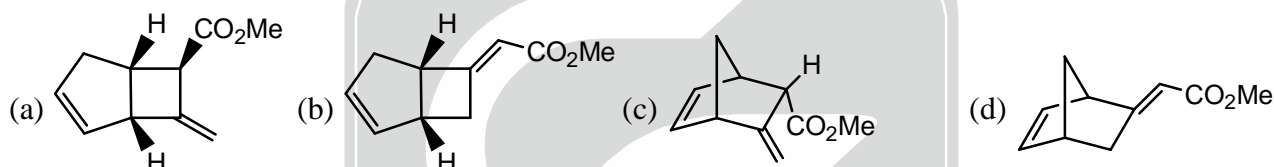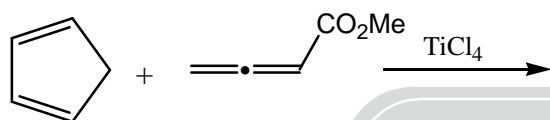
24. The overall yield (in %) for the following reaction sequence is _____

    $Ph-CHO \xrightarrow[90\%]{MeMgBr}$ (OH) $Ph\ Me \xrightarrow[80\%]{Jone's\ reagent}$ (O) $Ph\ Me \xrightarrow[80\%]{Ph-CHO\ aq.\ NaOH}$ (O) $Ph\ \ Ph$
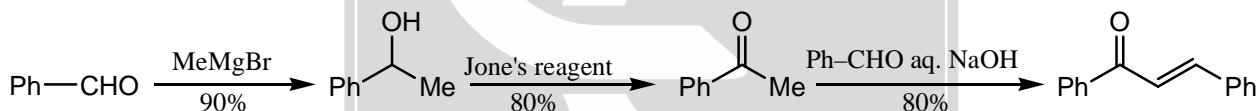
25. The most suitable reagent combination to effect the following conversion is
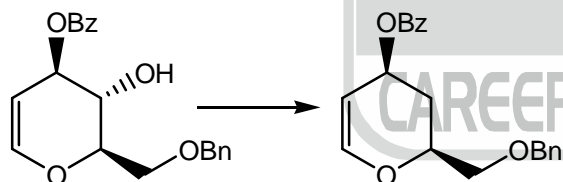
    (a) (i) NaH, CS_2, then MeI; (ii) Bu_3SnH, AIBN, C_6H_6, Reflux.
    (b) (i) I_2, PPh_3, imidazole; (ii) H_2, 10% Pd-C, AcOH, high pressure
    (c) (i) Me_3SiCl, pyridine, DMAP; (ii) Bu_3SnH, AIBN, C_6H_6, reflux
    (d) (i) MsCl, pyridine, DMAP; (ii) $LiAlH_4$, THF, reflux,

    Q.26 – Q.55 : Carry TWO marks each.

26. $\psi = N\,r\left(6 - Z\,r\right)e^{-Zr/3}\cos\theta$, is a proposed hydrogenic wavefunction, where Z = atomic number, r = radial

    distance from the nucleus, θ = azimuthal angle, N is a constant. The **INCORRECT** statement about ψ is

    (a) $\psi = 0$ in the xy-plane
    (b) two radial nodes are presenet in ψ
    (c) one angular node is present in ψ
   (d) the size of the orbital decreases with increase in atomic number

27. The van der waals constant a and b of CO_2 are 3.64 L^2 bar mol^{-2} and 0.04 L mol^{-1}, respectively. The value of R is 0.083 bar dm^3 $mol^{-1}K^{-1}$. If one mole of CO_2 is confined to a volume of 0.15L at 300K, then the pressure (in bar) exerted by the gas, is _____

28. A plot of osmotic pressure against concentration (gL^{-1}) of a polymer is constructed. The slope of the plot
    (a) increases with increase in temperature
    (b) increases with increase in molar mass of the polymer
    (c) decreases with decrease in concentration of the polymer
    (d) decreases with increase in temperature.

29. A platinum electrode is immersed in a solution containing 0.1 M Fe^{2+} and 0.1 M Fe^{3+}. Its potential is found to be 0.77V against SHE. Under standard conditions and considering activity coefficients to be equal to unity, the potential of the electrode, when the concentration of Fe^{3+} is increased to 1 M, is _____

30. Molybdenum crystallizes in a bcc structure with unit cell dimensions of 0.314 nm. Considering the atomic mass of molybdenum to be 96, its density (in kg m^{-3}) is _____

31. The ratio of molecules distributed between two states is 9.22×10^6 at 300K. The difference in energy (in kJ mol^{-1}) of the two states is _____

32. A Carnot engine operates at 55% efficiency. If the temperature of reject steam is 105°C, then the absolute temperature of input steam is _____

33. Of the following plots, the correct representation of chemical potential (μ) against absolute temperature (T) for a pure substance is (S, L and g denote solid, liquid and gas phases, respectively)

34. The enthalpy of fusion of ice at 273K is 6.01 kJ mol^{-1} and the enthalpy of vaporization of water at 273K is 44.83 kJ mol^{-1}. The enthalpy of sublimation (in kJ mol^{-1}) of ice at 273K, is _____

35. Suppose ψ_1 and ψ_2, are two hybrid orbitals:

    $\psi_1 = 0.12\,\psi_{3s} + 0.63\psi_{3p_x} + 0.77\psi_{3p_y}$ and $\psi_2 = 0.12\,\psi_{3s} - 0.63\psi_{3p_x} - 0.77\psi_{3p_y}$

    The angle (in degrees) between them is _____

36. BCl_3 and NH_4Cl were heated at 140°C to give compound X, which when treated with $NaBH_4$ gave another compound Y. Compounds X and Y are
    (a) X = $B_3N_3H_3Cl_3$ and Y = $B_3N_3H_6$ (b) X = $B_3N_3H_9Cl_3$ and Y = $B_3N_3H_6$
    (c) X = $B_3N_3H_3Cl_3$ and Y = $B_3N_3H_{12}$ (d) X = $B_3N_3Cl_6$ and Y = $B_3N_3H_6$

37. The number of microstates in term ^1G is _____

38. The set of protons (underlined) in $CH_3CH_2CH_2OCH_3$ that would exhibit different splitting patterns in high (500 MHz) and low (60 MHz) field ^1H NMR, is
    (a) C<u>H</u>$_3$CH$_2$CH$_2$OCH$_3$ (b) CH$_3$C<u>H</u>$_2$CH$_2$OCH$_3$
    (c) CH$_3$CH$_2$C<u>H</u>$_2$OCH$_3$ (d) CH$_3$CH$_2$CH$_2$OC<u>H</u>$_3$

39. Amongst the following, the complex ion that would show strong Jahn-Teller distortion is
    (a) $[Cr(H_2O)_6]^+$ (b) $[Ti(H_2O)_6]^{3+}$ (c) $[Co(H_2O)_6]^{2+}$ (d) $[Fe(H_2O)_6]^{2+}$

40. Amonst the following, the metal carbonyl species having the highest ν_{CO} stretching freqency is
    (a) $[Mn(CO)_6]^+$ (b) $Cr(CO)_6$ (c) $[V(CO)_6]^-$ (d) $[Fe(CO)_4]^{2-}$

41. The correct order of thermal stability for the given compounds is
    (a) $TiMe_4 > Ti(CH_2CMe_3)_4 > TiEt_4$ (b) $TiEt_4 > Ti(CH_2CMe_3)_4 > TiMe_4$
    (c) $TiMe_4 > TiEt_4 > Ti(CH_2CMe_3)_4$ (d) $Ti(CH_2CMe_3)_4 > TiMe_4 > TiEt_4$

42. Amongst the following, the complex ion that is expected to the highest magnetic moment at room temperature is
    (a) $[Ni(CN)_4]^{2-}$ (b) $[Fe(CN)_6]^{3-}$ (c) $[Cu(H_2O)_6]^{2+}$ (d) $[Co(CN)_6]^{3-}$

43. $MnCr_2O_4$ is
    (a) normal spinel with total CFSE of –15.5 Dq
    (b) inverse spinel with total CFSE of –15.5 Dq
    (c) normal spinel with total CFSE of –24 Dq
    (d) inverse spinel with total CFSE of –24 Dq

44. Mg^{2+} is preferred in photosynthesis by chlorphyll because
    (a) it has strong spin-orbit coupling   (b) it has weak spin-orbit coupling
    (c) it is a heavy metal   (d) it binds strongly with chlorophyll

45. In Monsanto acetic acid process shown below, the role of HI is

    $$CH_3OH + CO \xrightarrow[180°C,\ 30\ bar]{Rh(\ell)\ catalyst/HI} CH_3CO_2H$$
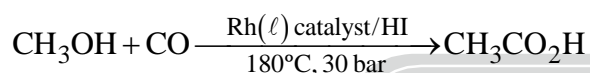
    (a) to convert CH_3OH to a stronger nucleophile (CH_3O^-)
    (b) to reduce the Rh(I) catalyst to a Rh(0) species
    (c) to reduce a Rh(III) active species to a Rh(I) species in the catalytic cycle
    (d) to convert CH_3OH to CH_3I

46. Formation of the ketone H from the diazoketone I involves
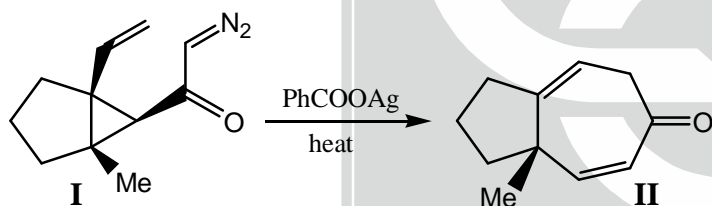
    (a) generation of carbene and a [2, 3]-sigmatropic rearrangement
    (b) generation of carbene and an electrocyclic ring closing reaction
    (c) generation of ketene and a [2+2] cycloaddition
    (d) generation of ketene and a [3, 3] sigmatropic rearrangement

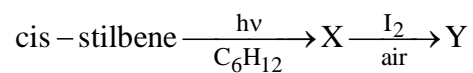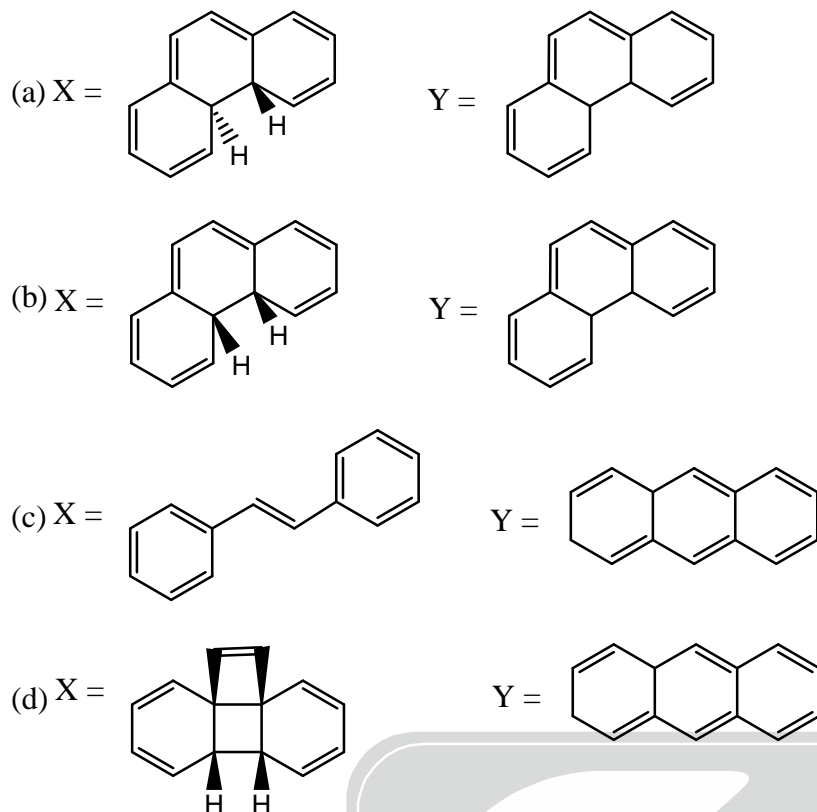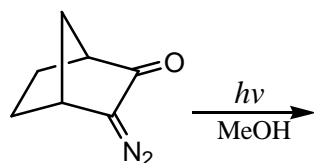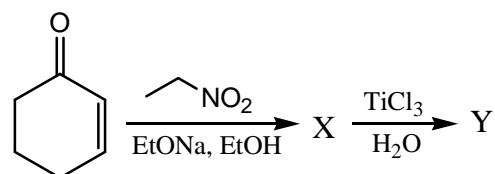47. The major products X and Y formed in the following reaction sequence are

(b) X =   Y =

(c) X =   Y =

(d) X =   Y =
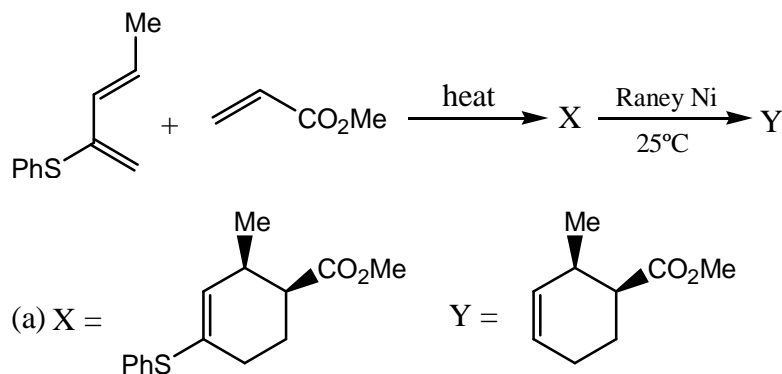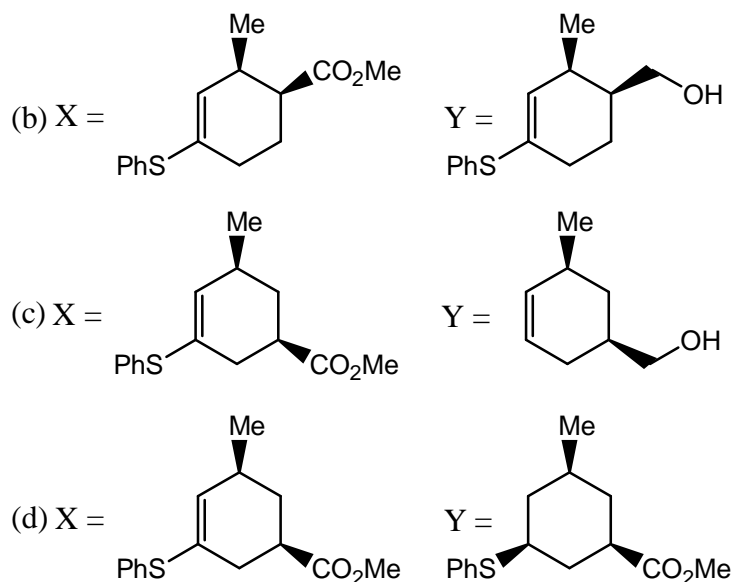
48. The major products X and Y formed in the following reactions are

(a) X =   Y =

(b) X =   Y =

(c) X =   Y =

(d) X =   Y =
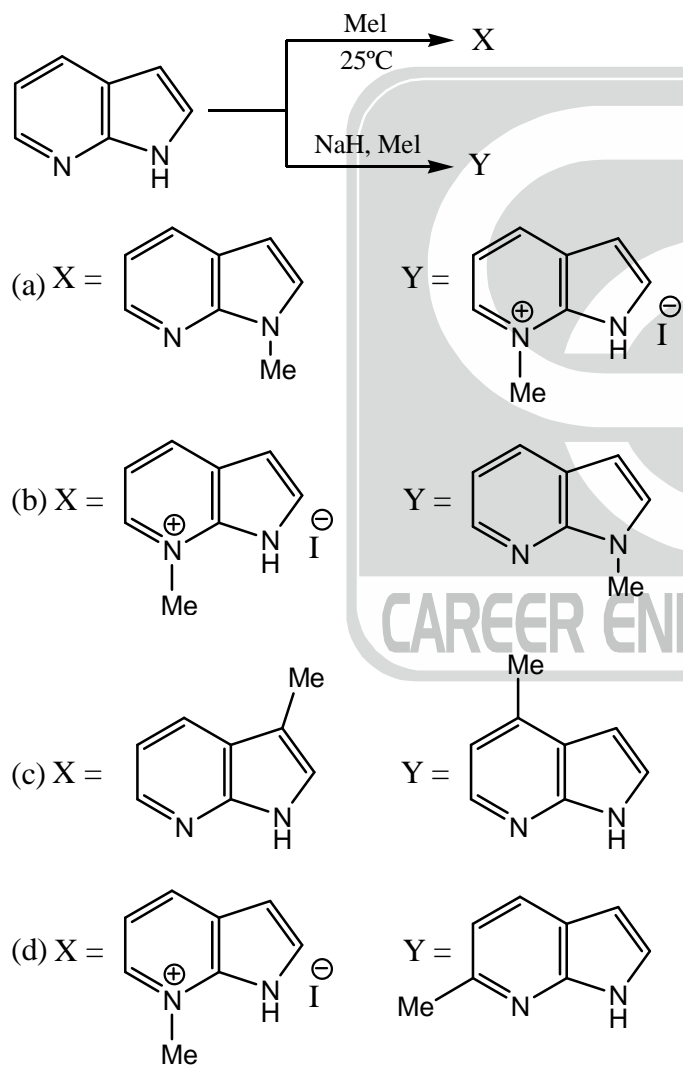
49. The major product X and Y formed in the following reaction sequence are

$$\text{cis} - \text{stilbene} \xrightarrow[\text{C}_6\text{H}_{12}]{h\nu} X \xrightarrow[\text{air}]{\text{I}_2} Y$$

(a) X =   Y =

(b) X =   Y =

(c) X =   Y =

(d) X =   Y =

50. The product of the following reaction gave 6 line ^{13}C NMR spectrum with peaks at δ 175, 52, 50, 46, 37, 33 ppm. The structure of the product is
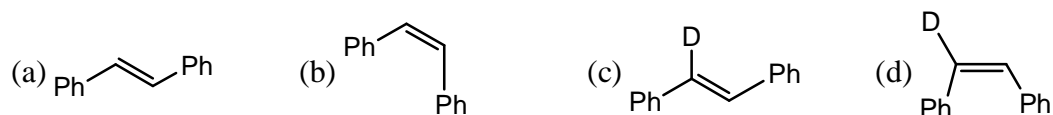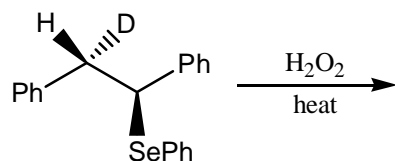
$$\xrightarrow[\text{MeOH}]{h\nu}$$

(a)   (b)   (c)   (d)

51. The major product formed in the following reaction is

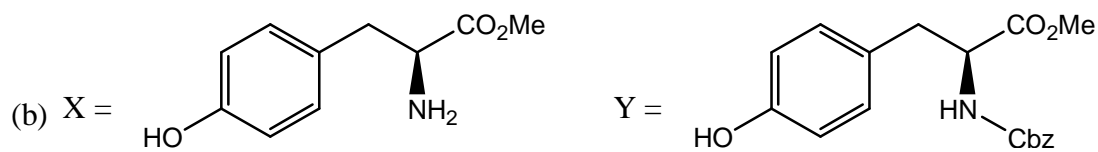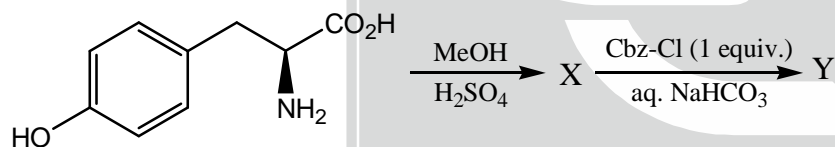$$\xrightarrow[\text{heat}]{H_2O_2}$$

(a)   (b)   (c)   (d)

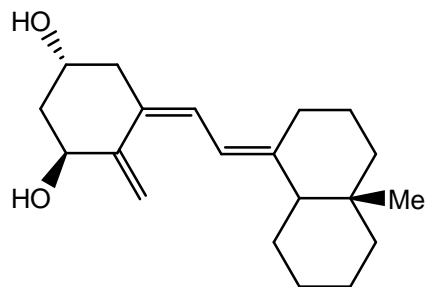52. The major products X and Y formed in the following reaction sequence are

$$\xrightarrow[\text{EtONa, EtOH}]{\diagup\!\!\!\diagdown NO_2} X \xrightarrow[\text{H}_2\text{O}]{\text{TiCl}_3} Y$$

(a) X =   Y =

(b) X =   Y =

(c) X =   Y =

(d) X =   Y =

53. The major products X and Y formed in the following reaction sequence are

(a) X =   Y =

(b) X =   Y =

(c) X =   Y =

(d) X =   Y =
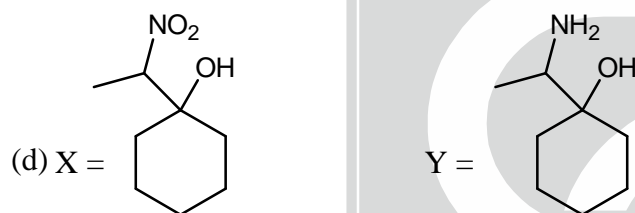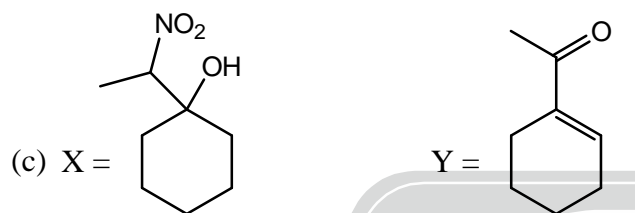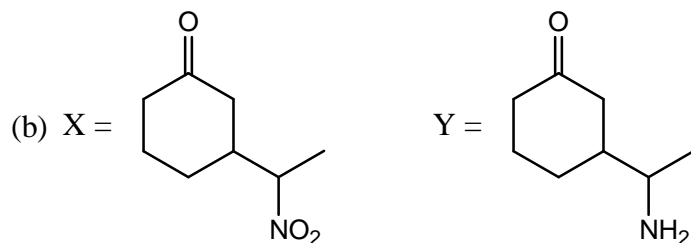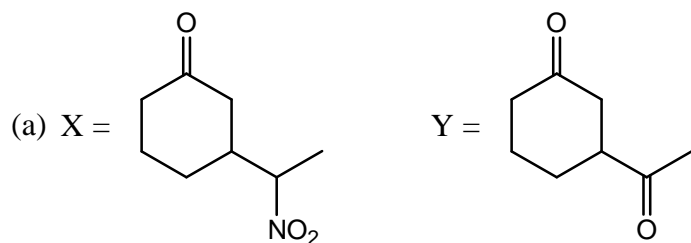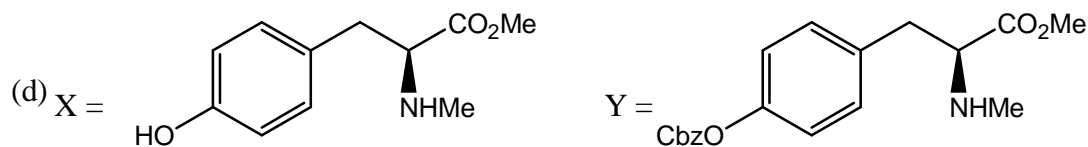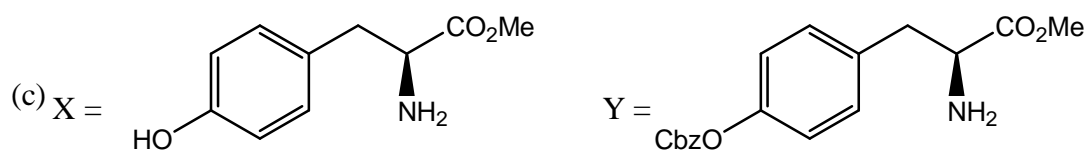
54. Given the fact that 1, 3-butadiene has a UV absorption of 217nm, the absorption wavelength (in nm) for the conjugated system shown below is _____

(Use these absorption values for auxochromic groups:
alkyl : +5; exo-cyclic double bond : +5; every additional conjugated $C = C$: + 30)

55. The m/z value of the detectable fragment formed by McLafferty like rearrangement of the following compound in mass spectrometer is _____
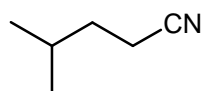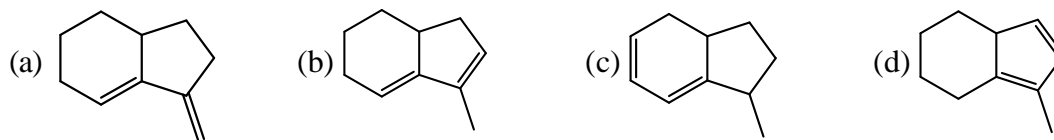
***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.25 : Carry ONE mark each.

1. Amongst the following the compound that **DOES NOT** act as a diene in Diels-Alder reaction is

(a)   (b)   (c)   (d)

2. An efficient catalyst for hydrogenation of alkenes is $\left[\text{Rh}\left(\text{PPh}_3\right)_3\text{Cl}\right]$. However, $\left[\text{Ir}\left(\text{PPh}_3\right)_3\text{Cl}\right]$ does not catalyze this reaction, because
(a) PPh_3 binds stronger to Ir than to Rh   (b) Cl binds stronger to Ir than to Rh
(c) PPh_3 binds stronger to Rh than to Ir   (d) Cl binds stronger to Rh than to Ir

3. Which of the following properties are characteristics of an ideal solution?

(i) $\left(\Delta_{mix}G\right)_{T,P}$ is negative   (ii) $\left(\Delta_{mix}S\right)_{T,P}$ is postiive

(iii) $\left(\Delta_{mix}V\right)_{T,P}$ is positive   (iv) $\left(\Delta_{mix}H\right)_{T,P}$ is negative.

(a) (i) and (iv)   (b) (i) and (ii)   (c) (i) and (iii)   (d) (iii) and (iv)

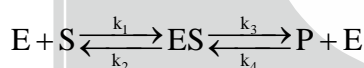4. Among the following compounds, the one that is non-aromatic, is

(a)   (b)   (c)   (d)

5. Given the E_0 values for the following reaction sequence,

$$\text{Mn}^{6+} \xrightarrow{1.28\text{V}} \text{Mn}^{5+} \xrightarrow{2.9\text{V}} \text{Mn}^{4+} \xrightarrow{0.96\text{V}} \text{Mn}^{3+} \xrightarrow{1.5\text{V}} \text{Mn}^{2+}$$

the computed value of E^0 for $\text{Mn}^{6+} \to \text{Mn}^{2+}$ (in volts) is _____

6. The expression for the equilibrium constant $\left(\text{K}_{eq}\right)$ for the enzyme catalyzed reaction given below, is

$$\text{E} + \text{S} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{ES} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{P} + \text{E}$$
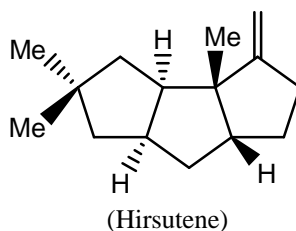
(a) $\dfrac{k_1 k_3}{k_2 k_4}$ (b) $\dfrac{k_1 k_2}{k_3 k_4}$ (c) $\dfrac{k_2 k_3}{k_1 k_4}$ (d) $\dfrac{k_1 k_4}{k_2 k_3}$

7. The absorption spectrum of $\left[\text{Ti}\left(\text{H}_2\text{O}\right)_6\right]^{3+}$ in solution comprises of a maximum with a shoulder. The reason for the shoulder is
(a) ligand-to-metal charge transfer (LMCT)   (b) metal-to-ligand charge transfer (MLCT)
(a) Jahn-Teller distortion   (d) nephelauxetic effect.

8. The compound given below is a


(Hirsutene)

(a) sesterterpene   (b) monoterpene   (c) sesquiterpene   (d) triterpene

9. The electrical conductivity of a metal
   (a) increases with increasing temperature
   (b) decreases with increasing temperature
   (c) is independent of temperature
   (d) shows oscillatory behaviour with temperature

10. Which one of the following statements is **INCORRECT**?
    (a) Frenkel defect is a cation vacancy and a cation interstitial
    (b) Frenkel defect is an anion vacancy and a cation interstitial
    (c) Density of a solid remains unchanged in case of Frenkel defects.
    (d) Density of a solid decreases in case of Schottky defects.

11. Among the given pH values, the O_2 binding efficiency of hemoglobin is maximum at
    (a) 6.8   (b) 7.0   (c) 7.2   (d) 7.4

12. When the operator, $-\hbar^2 d^2/dx^2$, operates on the function e^{-ikx}, the result is
    (a) $k^2\hbar^2 e^{-ikx}$ (b) $ik^2\hbar^2 e^{-ikx}$ (c) $i\hbar^2 e^{-ikx}$ (d) $\hbar^2 e^{-ikx}$

13.
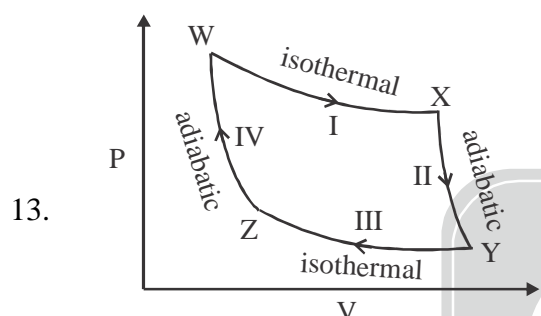
    From the above Carnot cycle undergone by an ideal gas, identify the processes in which the change in internal energy is **NON-ZERO.**
    (a) I and II   (b) II and IV   (c) II and III   (d) I and IV

14. Which one of the following defines the absolute temperature of a system?

    (a) $\left(\dfrac{\partial U}{\partial S}\right)_V$ (b) $\left(\dfrac{\partial A}{\partial S}\right)_V$ (c) $\left(\dfrac{\partial H}{\partial S}\right)_V$ (d) $\left(\dfrac{\partial G}{\partial S}\right)_V$

15. The following conversion is an example of
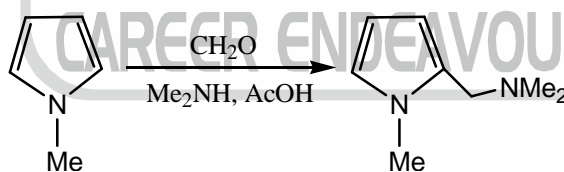
    (a) Arndt-Eistert homologation   (b) Mannich reaction
    (c) Michael addition   (d) Chichibabin amination reaction

16. The compound with planar geometry is
    (a) $N(t-Bu)_3$ (b) NPh_3 (c) NF_3 (d) $N(SiH_3)_3$

17. Reaction of benzaldehyde and p-methylbenzaldehyde under McMurry coupling conditions ($TiCl_3$ and $LiAlH_4$) gives a mixture of alkenes. The number of alkenes formed is _____

18. The correct order of reactivity of p-halonitrobenzenes in the following reaction is

    (X = F, Cl, Br, I)
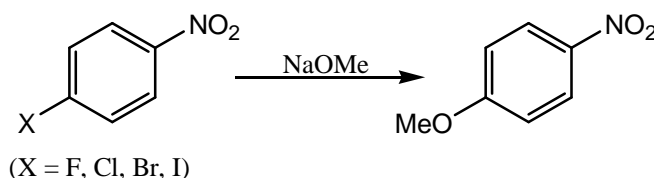
(a) p-chloronitrobenzene > p-iodonitrobenzene > p-fluoronitrobenzene > p-bromonitrobenzene

(b) p-fluoronitrobenzene > p-chloronitrobenzene > p-bromonitrobenzene > p-iodonitrobenzene

(c) p-iodonitrobenzene > p-bromonitrobenzene > p-chloronitrobenzene > p-fluoronitrobenzene

(d) p-bromonitrobenzene > p-fluoronitrobenzene > p-iodonitrobenzene > p-chloronitrobenzene

19. The absolute configuration of C2 and C3 in the following compound is
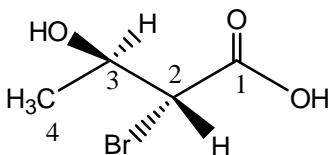
  (a) 2R, 3S   (b) 2S, 3R   (c) 2S, 3S   (d) 2R, 3R

20. For an ideal gas with molar mass M, the molar translational entropy at a given temperature is proportional to

  (a) $M^{3/2}$ (b) $M^{1/2}$ (c) e^{M} (d) $\ln(M)$

21. Tollen's test is **NEGATIVE** for

  (a) mannose   (b) maltose   (c) glucose   (d) sucrose

22. The intense red color of $\left[Fe(bpy)_3 \right]^{2+}$ (bpy = 2, 2'-bipyridine) is due to

  (a) metal-to-ligand charge transfer (MLCT)   (b) ligand-to-metal charge transfer (LMCT)

  (c) d-d transition   (d) inter-valence charge transfer (IVCT)

23. The ease of formation of the adduct, $NH_3 \cdot BX_3$ (where X = F, Cl, Br) follows the order

  (a) $BBr_3 < BCl_3 < BF_3$ (b) $BCl_3 < BF_3 < BBr_3$

  (c) $BF_3 < BCl_3 < BBr_3$ (d) $BBr_3 < BF_3 < BCl_3$

24. Which one of the following plots represents an acceptable wavefunction?


25. The mass spectrum of a dihalo compound shows peaks with relative intensities of 1 : 2 : 1 corresponding to M, M + 2 and M + 4 (M is the mass of the molecular ion), respectively. The compound is
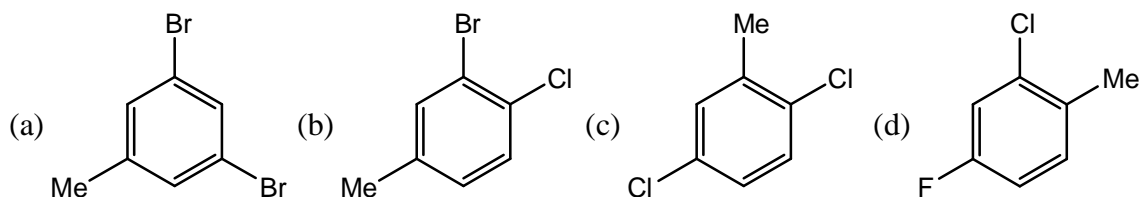
Q.26 – Q.55 : Carry TWO marks each.

26. The value of 'g' and the number of signals observed for the reference standard, diphenylpicrylhydrazyl (DPPH), in the solid state ESR spectrum are, respectively

    (a) 2.0036 and 1   (b) 2.0036 and 3   (c) 2.2416 and 1   (d) 2.2416 and 3

27. Solvolysis of the optically active compound X gives, mainly

(a) (optically active)

(b) (optically active)

(c) racemic (optically inactive)

(d) racemic (optically inactive)
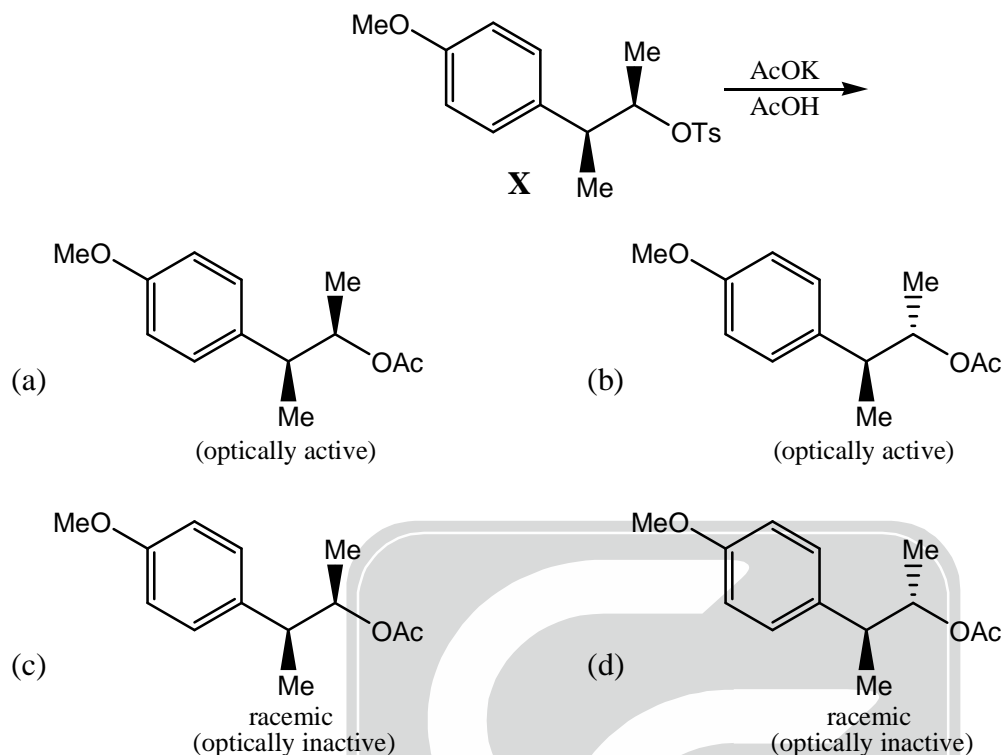
28. The complexes $K_2[NiF_6]$ and $K_3[CoF_6]$ are

    (a) both paramagnetic
    (b) both diamagnetic
    (c) paramagnetic and diamagnetic, respectively
    (d) diamagnetic and paramagnetic, respectively

29. The tetrapeptide, Ala-Val-Phe-Met, on reaction with Sanger's reagent, followed by hydrolysis gives
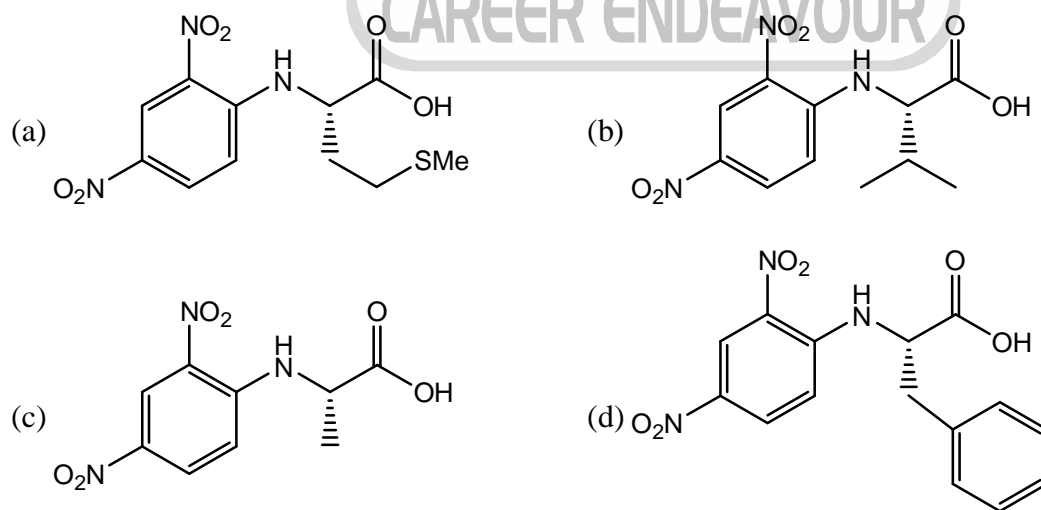
30. For a gas phase unimolecular reaction at temperature 298K, with a pre-exponential factor of $2.17 \times 10^{13}\, s^{-1}$, the entropy of activation ($JK^{-1}\, mol^{-1}$) is _____

31. The process given below follows the Langmuir adsorption isotherm

$$A_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A_{ads}$$
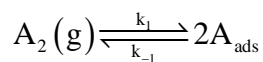
If θ denotes the surface coverage and P denotes the pressure, the slope of the plot of $1/\theta$ versus $1/\sqrt{P}$ is

(a) $1/\left(K_{eq}\right)^2$ (b) $1/K_{eq}$ (c) $-1/K_{eq}$ (d) $1/\left(K_{eq}\right)^{1/2}$

32. The major product formed in the following reaction is
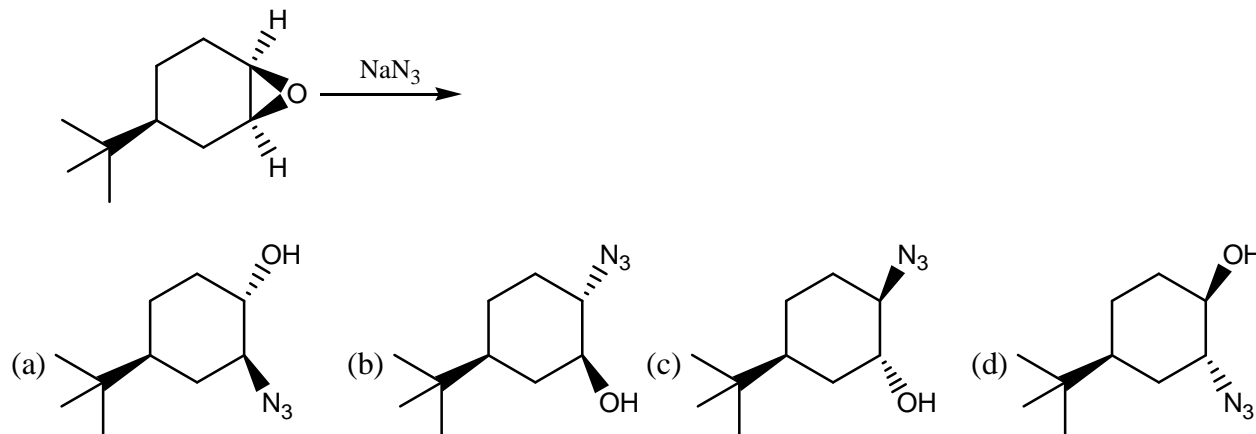
33. A liquid has vapor pressure of $2.02 \times 10^3 \, N \, m^{-2}$ at 293 K and heat of vaporization of 41 kJ mol⁻¹. The boiling point of the liquid (in Kelvin) is _____

34. The difference in the ground state energies (kJ/mol) of an electron in one-dimensional boxes of lengths 0.2 nm and 2 nm is _____

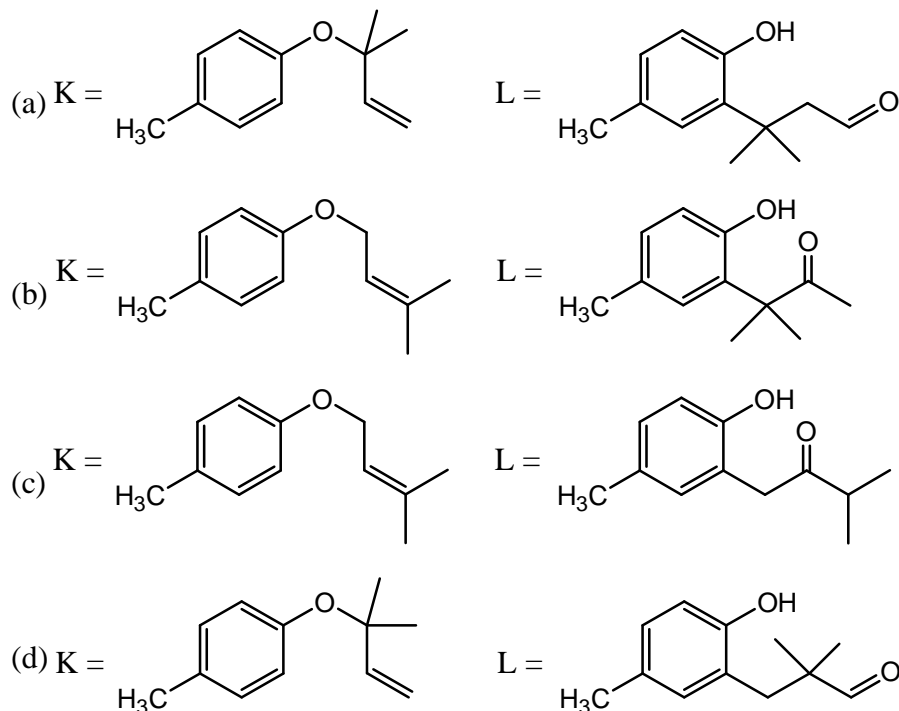35. The major product formed in the following reaction is
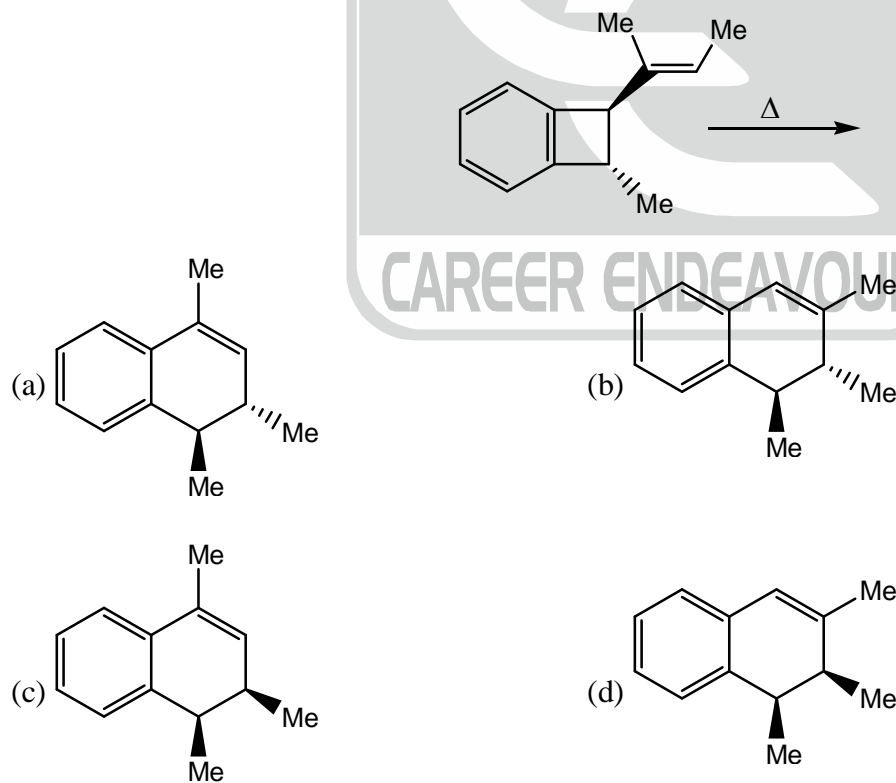
36. The internal energy of an ideal gas follows the equation $U = 3.5\ PV + k$, where k is a constant. The gas expands from an initial volume of $0.25\ m^3$ to a final volume of $0.86\ m^3$. If the initial pressure is $5\ N\ m^{-2}$, the change in internal energy (in joules) is (given $PV^{1.3} = $ constant) _____

37. One mole of a substance is heated from 300K to 400K at contant pressure. The C_P of the substance is given by, $C_P\left(JK^{-1}mol^{-1}\right) = 5 + 0.1T$. The change in entropy, in $JK^{-1}\ mol^{-1}$, of the sustance is _____

38. The solubility product of AgBr(s) is 5×10^{-13} at 298K. If the standard reduction potential of the half-cell, $E^0_{Ag|AgBr(s)|Br^-}$ is 0.07V, the standard reduction potential, $E^0_{Ag^+|Ag}$ (in volts) is _____

39. The most suitable reagent (s) to effect the following transformed is
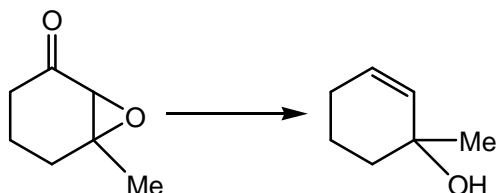
   (a) N_2H_4, KOH heat   (b) $TsNHNH_2$, CF_3COOH
   (c) $LiAlH_4$ (d) Na, liq. NH_3

40. Ammonolysis of S_2Cl_2 in an inert solvent gives
   (a) S_2N_2 (b) S_2N_2Cl (c) $S_2N_2H_4$ (d) S_4N_4

41. The mean ionic activity coefficient of 0.001 molal $ZnSO_4$ (aq) at 298K according to the Debye-Huckel limiting law is (Debye-Huckel constant is $0.509\ molal^{-\frac{1}{2}}$) _____

42. Identify the function of hemocyanin and the metal responsible for it
   (a) O_2 transport and Fe   (b) O_2 transport and Cu
   (c) electron transport and Fe   (d) electron transport and Cu

43. The point group of IF_7 is
   (a) D_{6h} (b) D_{5h} (c) C_{6v} (d) C_{5v}

44. The limiting current (in μA) from the reduction of $3 \times 10^{-4}\ M\ Pb^{2+}$, using a dropping mercury electrode (DMF) with characteristics, $m = 3.0\ mg\ s^{-1}$ and $t = 3s$, is (diffusion coefficient of $Pb^{2+} = 1.2 \times 10^{-5}\ cm^2s^{-1}$) _____

45. Identify X in the reaction, $\left[Pt\left(NH_3\right)_4\right]^{2+} + 2HCl \rightarrow X$

   (a) $cis-\left[PtCl_2\left(NH_3\right)_2\right]$ (b) $trans-\left[PtCl_2\left(NH_3\right)_2\right]$

   (c) $\left[PtCl\left(NH_3\right)_3\right]^+$ (d) $\left[PtCl_3\left(NH_3\right)\right]^-$

46. The major products, K and L formed in the following reactions are

(a) K =   L =

(b) K =   L =

(c) K =   L =

(d) K =   L =

47. The major product formed in the following reaction is


(a)   (b)   (c)   (d)
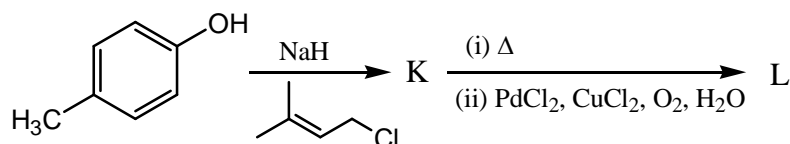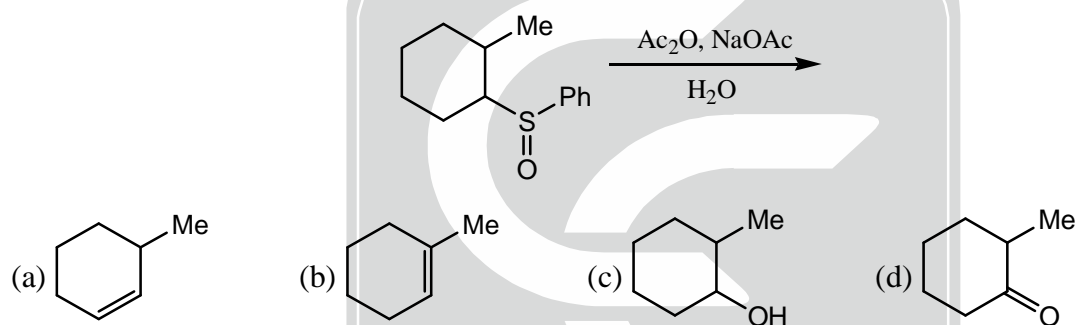
48. The percent transmittance of 8×10^{-5} M solution of $KMnO_4$ is 39.8 when measured at 510 nm in a cell of path length of 1 cm. The absorbance and the molar extinction coefficient (in $M^{-1}\ cm^{-1}$) of this solution are, respectively

(a) 0.30 and 4500   (b) 0.35 and 4800   (c) 0.4 and 5000   (d) 0.48 and 5200

49. The rotational partition function of a diatomic molecule with energy levels corresponding to J = 0, 1, is (where , ε is a constant)

(a) $1 + e^{-2\varepsilon}$ (b) $1 + 3e^{-2\varepsilon}$ (c) $1 + e^{-3\varepsilon}$ (d) $1 + 3e^{-3\varepsilon}$

50. When one CO group is replaced by PPh_3 in $[Cr(CO)_6]$, which one of the following statement is TRUE?
(a) The Cr-C bond length increases and CO bond length decreases
(b) The Cr-C bond length decreases and CO bond length decreases
(c) The Cr-C bond length decreases and CO bond length increases
(d) The Cr-C bond length increases and CO bond length increases

51. The number of possible stereoisomers obtained in the following reaction is _____

52. The major product formed in the following reaction is

(i) NBS, H_2O
(ii) K_2CO_3
(iii) $BF_3 \cdot OEt_2$

(a)   (b)   (c)   (d)
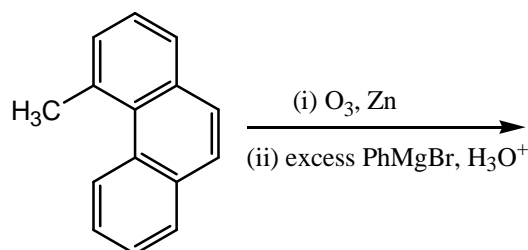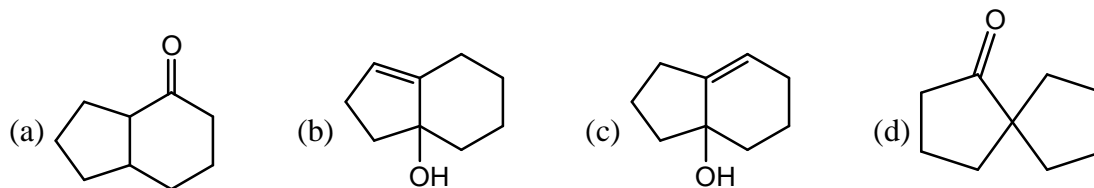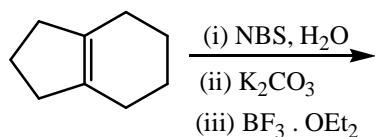
53. The Beckmann rearrangement of a bromoacetophenone oxime (C_8H_8BrNO) gives a major product having the following ^{1}H NMR (δ, ppm) : 9.89 (s, 1H), 7.88(s, 1H), 7.45 (d, 1H, J = 7.2 Hz), 7.17 (m, 1H), 7.12 (d, 1H, J = 7.0 Hz), 2.06 (s, 3H). The structure of the product is

(a) $NHCOCH_3$ (b) $CONHCH_3$

(c) $NHCOCH_3$ (d) $CONHCH_3$
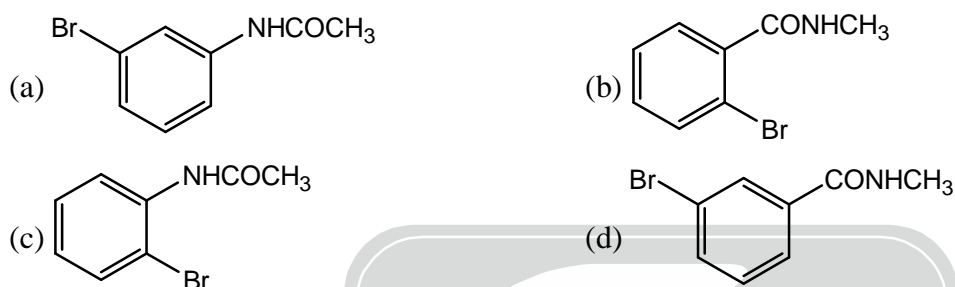
54. The distance between two successive (110) planes in a simple cubic lattice with lattice parameter 'a' is

(a) $\sqrt{2}\, a$ (b) $\sqrt{3}\, a$ (c) $2\sqrt{2}\, a$ (d) $\dfrac{a}{\sqrt{2}}$

55. The potential energy (PE) versus reaction coordinate diagrams for electron transfer reactions with rate constants k_1, k_2 and k_3, are given below. The inreasing order of the rate constants is
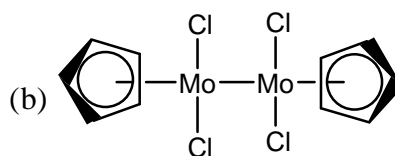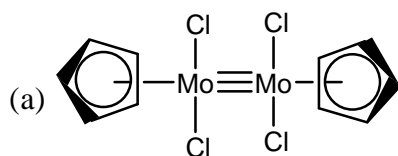
k_1 k_2 k_3

Reaction coordinate
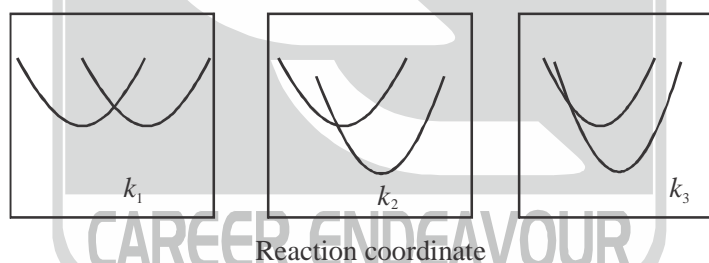
(a) $k_2 < k_3 < k_1$ (b) $k_2 < k_1 < k_3$ (c) $k_3 < k_2 < k_1$ (d) $k_3 < k_1 < k_2$

***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.25 : Carry ONE mark each.

1. $[CpMoCl_2]_2$ obeys the 18 electron rule. The correct structure of this compound is (atomic number of Mo = 42)
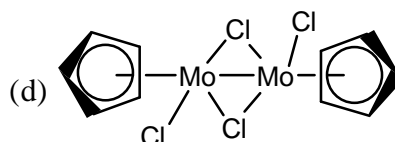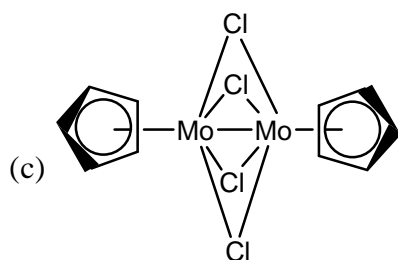
2. During oxygen transport by hemerythrin, oxygen is bound as
   (a) O_2^- to one Fe(III) only
   (b) HO_2^- to one Fe(III) only
   (c) O_2^{2-} to one Fe(II) and one Fe(III)
   (d) O_2^{2-} to two Fe(II)

3. Among the following, the most stable isotope to radioactive decay is
   (a) $^{206}_{82}Pb$
   (b) $^{210}_{82}Pb$
   (c) $^{212}_{82}Pb$
   (d) $^{214}_{82}Pb$

4. At pH 7.2 and 10 Torr oxygen partial pressure, the extent of O_2 binding is
   (a) high for both haemoglobin and myoglobin
   (b) high for haemoglobin and low for myoglobin
   (c) high for myoglobin and low for haemoglobin
   (d) low for both haemoglobin and myoglobin

5. In the first row high-spin transition metal complexes $[M(H_2O)_6]Cl_2$ with d^5 and d^7 metal ions, the d-d transitions are
   (a) spin-forbidden for both
   (b) spin-allowed for both
   (c) spin-forbidden for d^5 and spin-allowed for d^7
   (d) spin-allowed for d^5 and spin-forbidden for d^7

6. Among the given boranes and heteroboranes, the example which belongs to 'closo' type is
   (a) $B_5H_8^-$
   (b) $[C_2B_9H_{11}]^{2-}$
   (c) $GeC_2B_9H_{11}$
   (d) B_6H_{10}

7. The reaction of P_2O_5 with HNO_3 and $HClO_4$, respectively, gives
   (a) NO_2 and ClO_2
   (b) N_2O_5 and Cl_2O_6
   (c) N_2O_3 and Cl_2O_7
   (d) N_2O_5 and Cl_2O_7

8. When crystals of sodium chloride are heated in the presence of sodium vapor, they turn yellow. This is due to the formation of
   (a) Schottky defects
   (b) Frenkel defects
   (c) F-centres
   (d) H-centres

9. One mole of an ideal gas is compressed from 5L to 2L at constant temperature. The change in entropy, in $J\ K^{-1}$, of the gas is _____. ($R = 8.314\ JK^{-1}\ mol^{-1}$)

10. The linear momentum of a particle described by the wavefunction e^{-ikx} is

(a) kh　　　　(b) $-kh$　　　　(c) $k\hbar$　　　　(d) $-k\hbar$

11. For an elementary bimolecular gas phase reaction, activation energy is 5.5 kJ mol^{-1}. Enthalpy of activation, in kJ mol^{-1}, at 300K is _____. (R = 8.314 J K^{-1} mol^{-1})

12. The titration of a strong acid with a strong base is represented by the plot

(a)

ΔpH/ΔV

Volume (V)

(b)

ΔpH/ΔV

Volume (V)

(c)

ΔpH/ΔV

Volume (V)

(d)

ΔpH/ΔV

Volume (V)
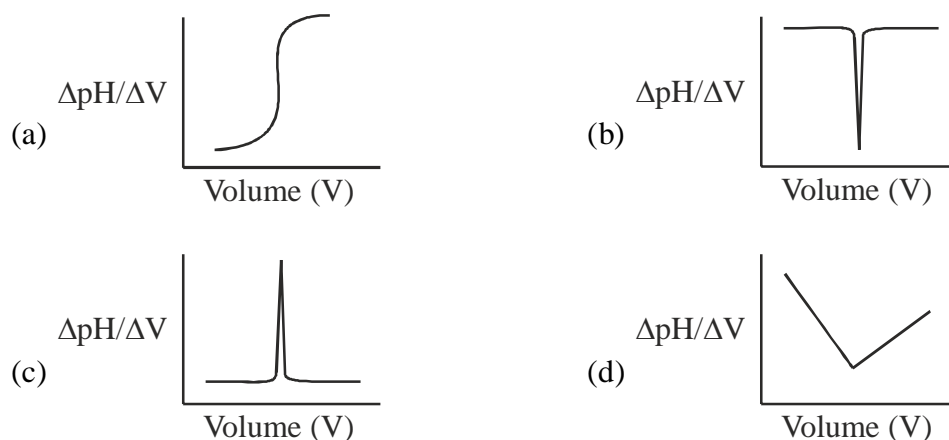
13. Of the following inequalities, the criteria for spontaneity of a chemical reaction is/are

(i) $(\Delta G)_{T,P} < 0$　　　　(ii) $(\Delta U)_{S,V} > 0$　　　　(iii) $(\Delta S)_{U,V} > 0$

(a) (i) only　　　　(b) (ii) only　　　　(c) (i) and (ii)　　　　(d) (i) and (iii)

14. A protein sample consists of an equimolar mixture of ribonuclease (molar mass = 13.7 kg mol^{-1}), hemoglobin (molar mass = 15.5 kg mol^{-1}), and myoglobin (molar mass = 17.2 kg mol^{-1}). The statement that is true about the weight-average molar mass $(\bar{M}_w)$, the number-average molar mass $(\bar{M}_n)$, and the polydispersity index (PDI) for this sample is

(a) $\bar{M}_w > \bar{M}_n = 15.5\ kg\ mol^{-1}$ and $PDI > 1$　　　(b) $\bar{M}_w > \bar{M}_n = 15.5\ kg\ mol^{-1}$ and $PDI < 1$

(c) $\bar{M}_w = 15.5\ kg\ mol^{-1} > \bar{M}_n$ and $PDI > 1$　　　(d) $\bar{M}_w = 15.5\ kg\ mol^{-1} < \bar{M}_n$ and $PDI < 1$

15. The band structure given below represent a

Conduction Band

Energy

Valence Band
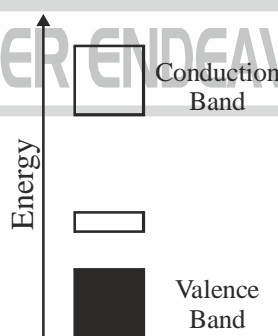
(a) n-type semiconductor formed by doping Si with B
(b) n-type semiconductor formed by doping Si with P
(c) p-type semiconductor formed by doping Si with P
(d) p-type semiconductor formed by doping Si with B

16. The experimental ionization energies of hydrogen and helium atoms in their ground states are, respectively, 13.6 eV and 24.6 eV. The ground state energy of helium atom, in eV, is

(a) $-\frac{1}{2}(13.6) - 24.6$　　(b) $-4(13.6) - 24.6$　　(c) $-\frac{1}{4}(13.6) - 24.6$　　(d) $-2(13.6) - 24.6$

17. Ring flipping of the compound in the following conformation leads to

(a)   (b)   (c)   (d)
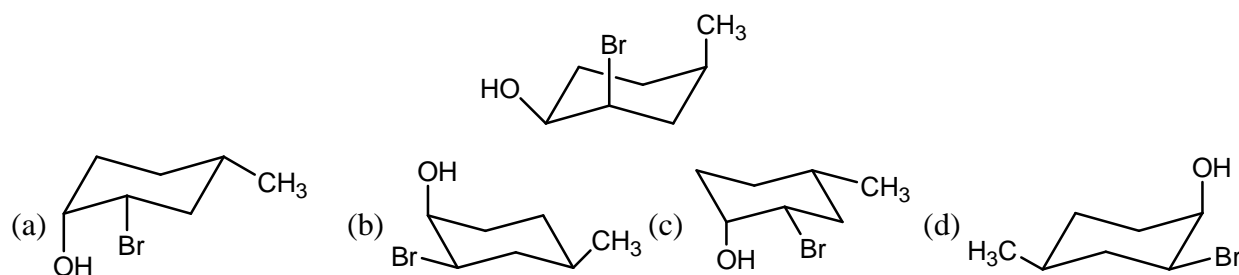
18. The total number of lines expected (due to spin-spin coupling of proton with fluorine and deuterium nuclei) in the ^1H NMR spectrum of the following compound is _____.
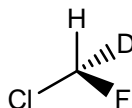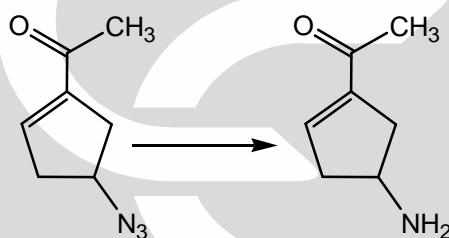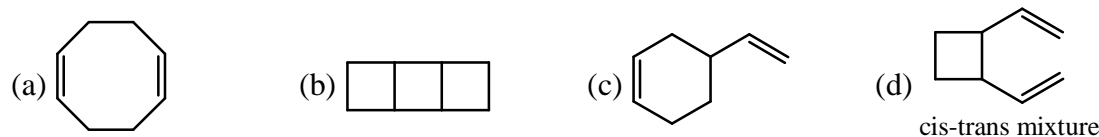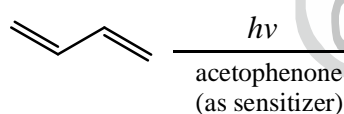
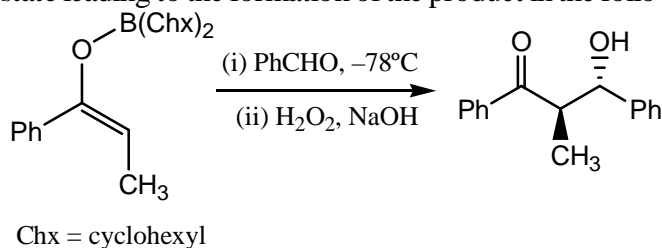19. The compound in 'R' configuration is   **[GATE 2016]**

(a)   (b)

(c)   (d)

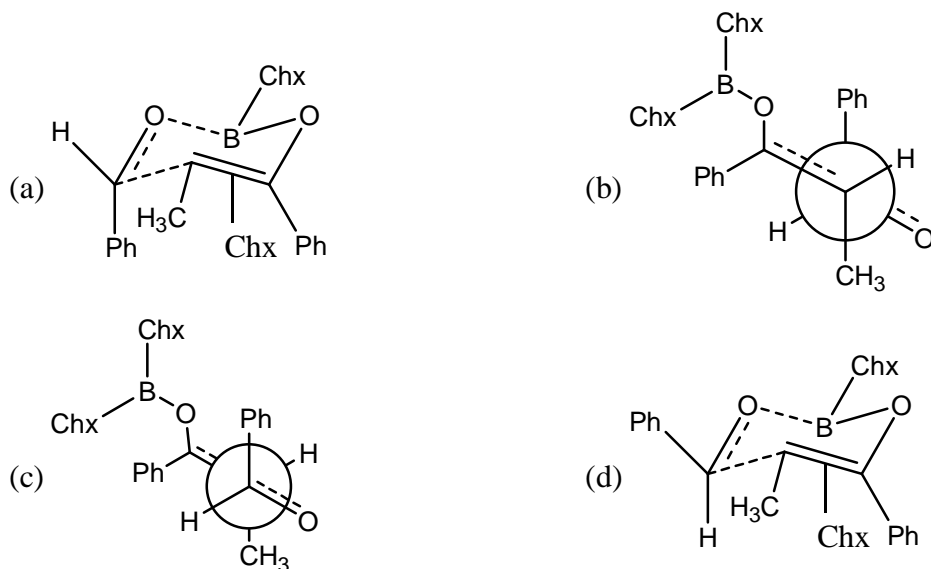20. The most suitable reagent for performing the following transformation, is

(a) $LiAlH_4$ (b) H_2, Pd/C   (c) PPh_3, H_2O (d) Li, Liq. NH_3

21. The major product obtained in the following reaction, is

$\xrightarrow[\substack{\text{acetophenone} \\ \text{(as sensitizer)}}]{hv}$

(a)   (b)   (c)   (d)

cis-trans mixture

22. The Favourable transition state leading to the formation of the product in the following reaction, is

(i) PhCHO, –78ºC

(ii) H_2O_2, NaOH

Chx = cyclohexyl

(a)

(b)

(c)

(d)

23.   The major product of the following reaction is,

$$\xrightarrow[\text{BF}_3.\text{Et}_2\text{O, 0}^\circ\text{C}]{(\text{CH}_3\text{CO})_2\text{O}}$$

(a)   (b)   (c)   (d)

24.   The major product obtained in the following reaction, is

$$\text{H—C}\equiv\text{C—CH}_2\text{OH} \xrightarrow[\text{(ii) C}_2\text{H}_5\text{Br(1 equiv.)}]{\text{(i) LiNH}_2 \text{ (2equiv.)/liq. NH}_3}$$

(ii) H$_3$O$^+$

(a) H$_3$CH$_2$C—C$\equiv$C—CH$_2$OH   (b) H—C$\equiv$C—CH$_2$OCH$_2$CH$_3$

(c) H$_3$CH$_2$C—C$\equiv$C—CH$_2$NH$_2$ (d) H—C$\equiv$C—CH$_2$NH—CH$_2$CH$_3$

25.   The major product formed in the following reaction, is

$$\xrightarrow[\text{(ii) NaHCO}_3/\text{MeOH, warm}]{\text{(i) CH}_3\text{I}}$$

(a)   (b)

(c)   (d)
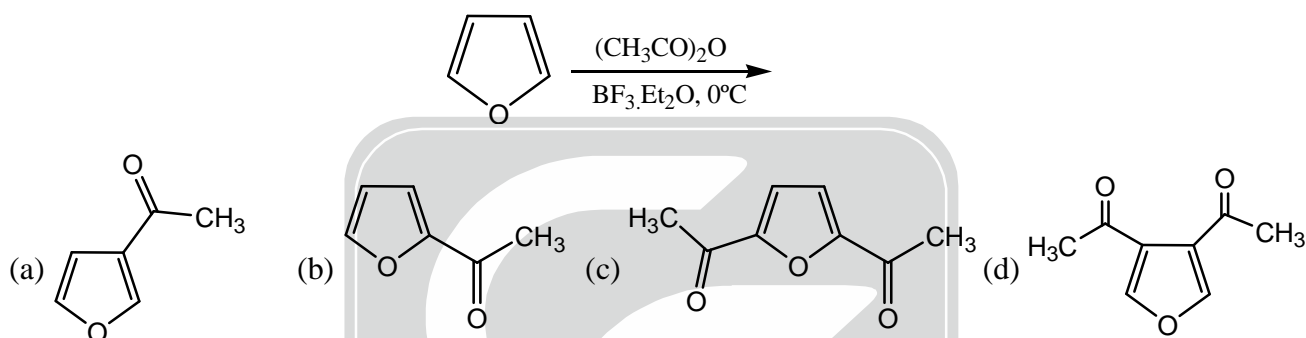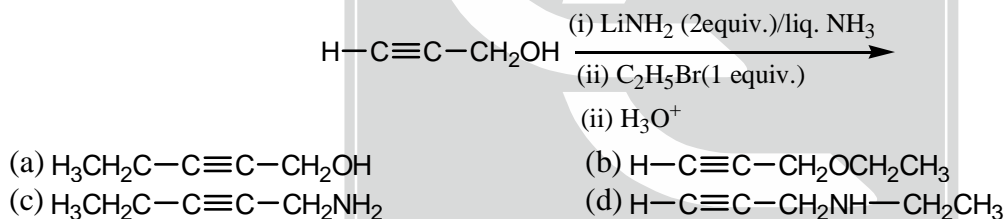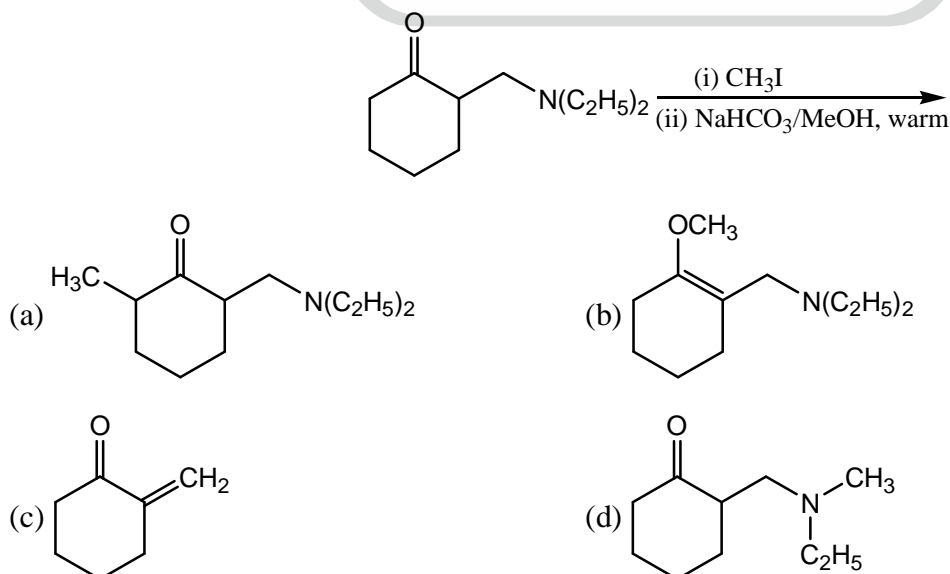
Q.26 – Q.55 : Carry TWO marks each.

26. The Larmor frequency of ^{1}H at 1 Tesla (T) is 42.57 MHz. If the magnetogyric ratios for ^{1}H and ^{13}C are 26.75 $\times 10^7$ rad T^{-1} s^{-1} and 6.72×10^7 rad T^{-1} s^{-1}, respectively, the Larmor frequency of ^{13}C, in MHz, at 1 Tesla will be _____

27. At 1 bar and 298K, for the process $A(s) \rightarrow A(\ell)$, the ΔG is 200 J mol^{-1} and ΔV_m is -2×10^{-6} m^3 mol^{-1}. The minimum pressure, in bar, at which the process becomes spontaneous at 298K is _____. (1 bar $= 10^5$ Pa).

28. The reaction, $A \rightleftharpoons B$, is first order in both the directions. The forward and reverse rate constants are 4.2×10^{-4} s^{-1} and 1.04×10^{-3} s^{-1}, respectively. The relaxation time for this reaction, in seconds, in a temperature jump experiment is _____

29. Adsorption of CO on charcoal at 273K follows Langmuir isotherm. A plot of P(kPa)/V(cm^3) versus P (kPa) is linear with a slope of 0.01 y-intercept of 0.5. The equilibrium constant, K (kPa^{-1}), for the adsorption is _____.

30. For the following reaction,

$$A + B \underset{k_{-1}=10^4 s^{-1}}{\overset{k_1=10^5 \text{ L mol}^{-1}s^{-1}}{\rightleftharpoons}} I \xrightarrow{k_2=10s^{-1}} P$$
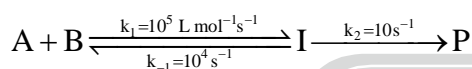
if steady state approximation can be applied on [I], the observed rate constant of product formation, in L mol^{-1} s^{-1}, will be _____

31. The correct set of infra-red spectral bands (in cm^{-1}) for the ν_{CO} stretching mode of the given carbonyl complex is
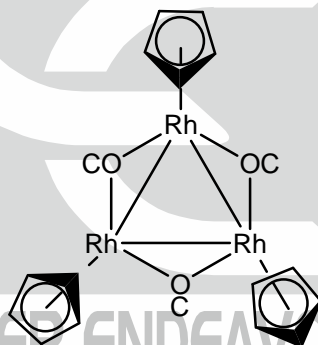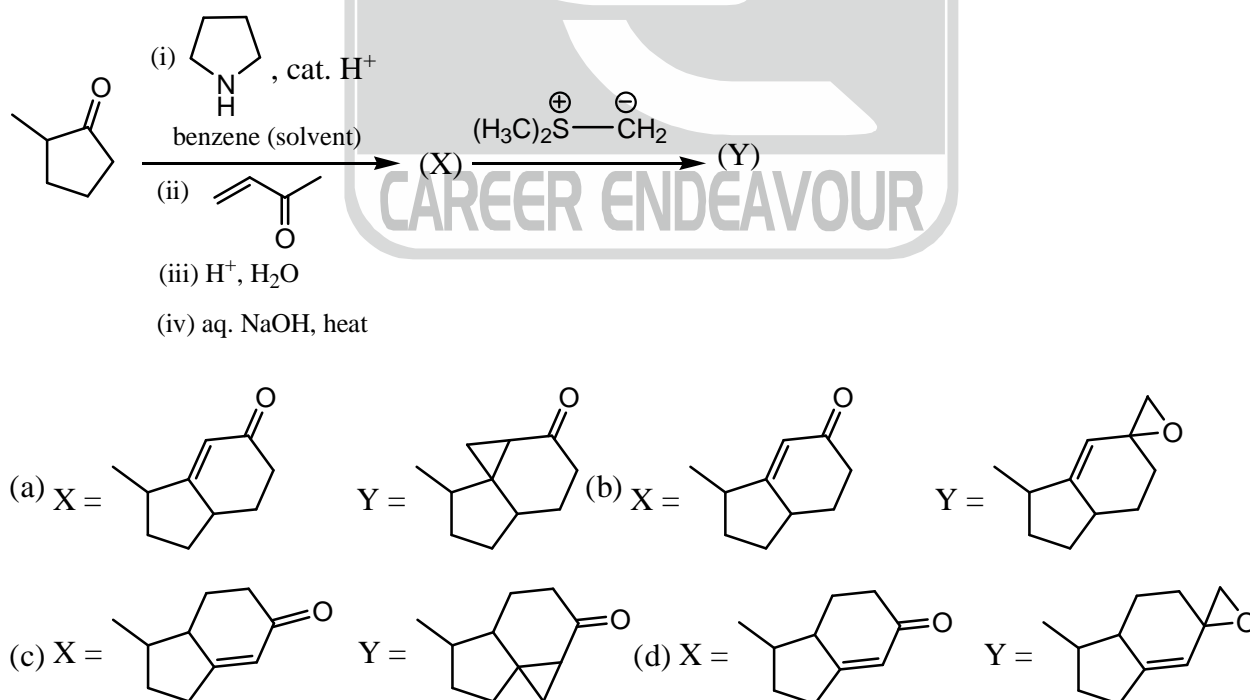

   (a) 1827, 1783, 1766
   (b) 1973, 1827, 1794
   (c) 1833, 1775, 1650
   (d) 1960, 1918

32. The ^{19}F NMR spectrum of ClF$_3$ when measured at $-60°$C will be observed as a
   (a) singlet
   (b) doublet
   (c) doublet and triplet
   (d) doublet of doublet and a doublet of triplet

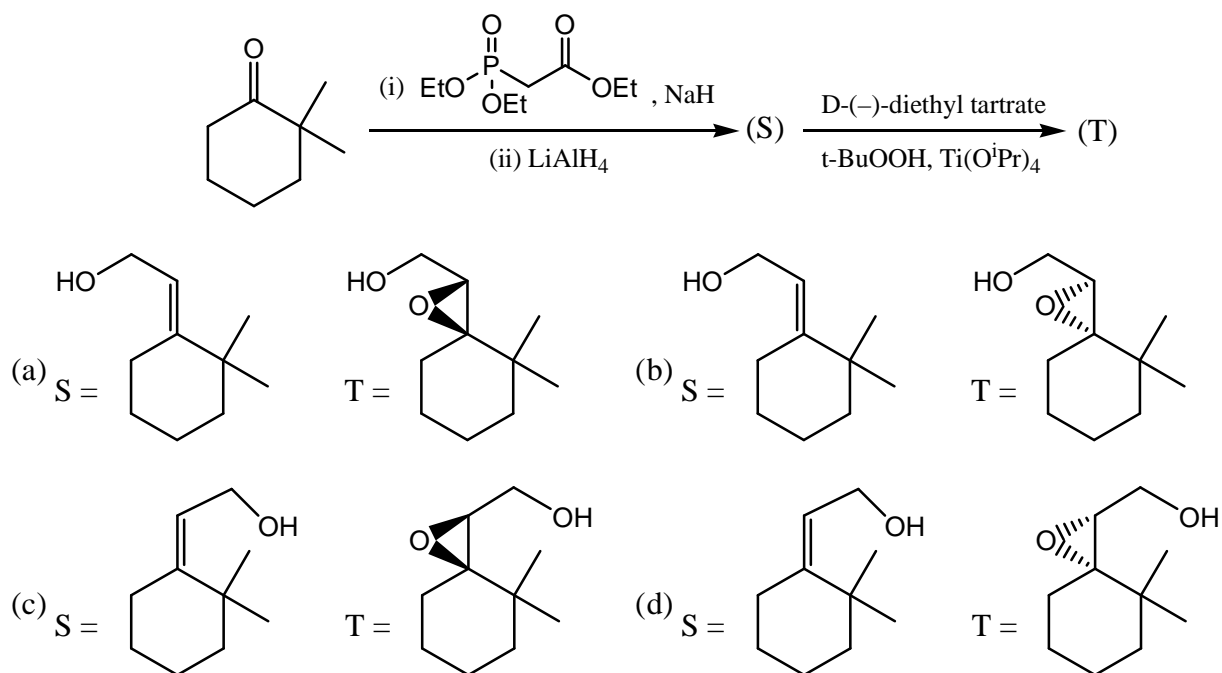33. Among the given platinum(II) complexes, the one that is thermally the most unstable is
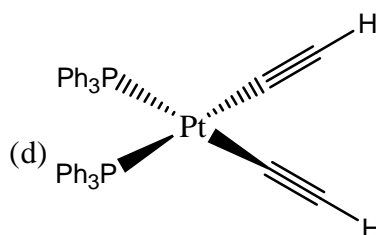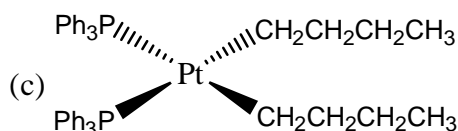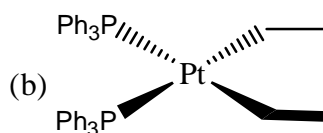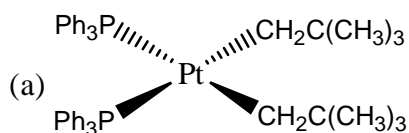
34. The shapes of XeF_5^+ and XeF_5^-, respectively, are
    (a) pentagonal planar and square pyramidal
    (b) pentagonal planar and trigonal bipyramidal
    (c) square pyramidal and pentagonal bipyramidal
    (d) square pyramidal and pentagonal planar

35. Sodium salt of pseudohalogens, X, Y and Z form colorless solutions in water. Solution of X decolorizes I_3^- solution with brisk effervescence. Solution of Y gives an intense red colour on reaction with Fe^{3+} solution. Solution of Z gives an intese blue color on reaction with a solution containing Fe^{3+} and Fe^{2+} ions. The pseudohalogens X, Y and Z respectivley are

    (a) CN^-, N_3^- and CNS^- (b) N_3^-, CNS^- and CN^-

    (c) $N_3^-, CN^-,$ and CNS^- (d) $N_3^-, CNS^-,$ and CNO^-

36. On reacting 1.55g of a diol with an excess of methylmagnesium iodide, 1.12L (corrected to STP) of methane gas is liberated. The molecular mass $(g\ mol^-)$ of the diol is _____

37. The structure of the compound having the following characteristics spectral data, is IR : $1690\ cm^{-1}$.
    ^{1}H-NMR : 1.30 (3H, t, J = 7.2 Hz); 2.41 (2H, q, J = 7.2 Hz); 2.32 (3H, s); 7.44 (1H, t, J = 7.0 Hz); 7.57 (1H, dt, J = 7.0, 3.0 Hz); 7.77 (1H, t, J = 3.0 Hz); 7.90 (1H, dt, J = 7.0, 3.0 Hz); EI mass : m/z 119 (100%); 57 (80%)
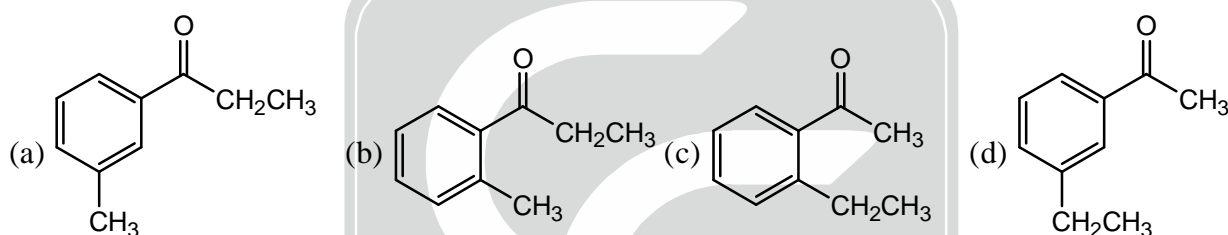
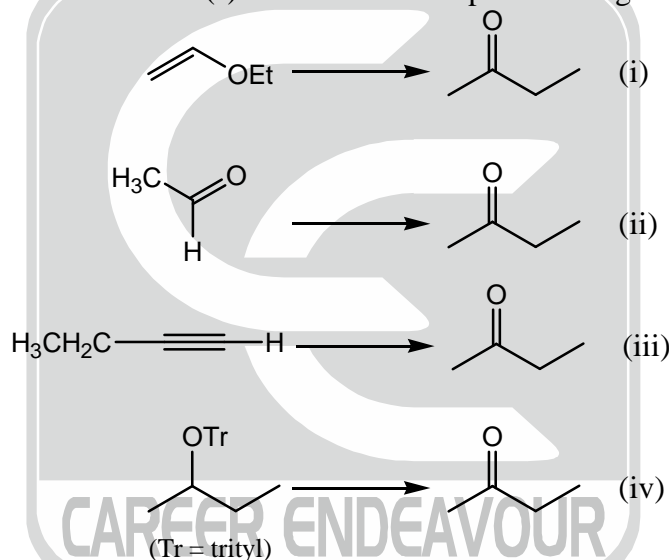38. The major products X and Y formed in the following formed in the following synthetic scheme, are

39. The major product S and T formed in the following synthetic schemem, are

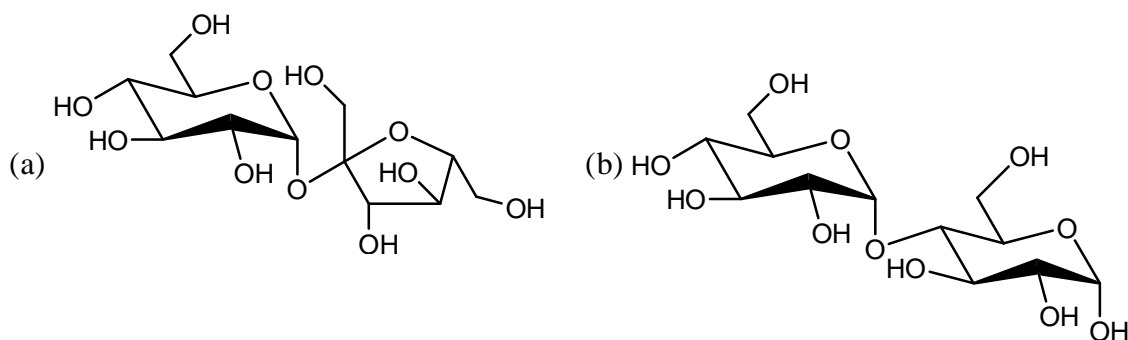(a) S = [structure] T = [structure]

(b) S = [structure] T = [structure]

(c) S = [structure] T = [structure]

(d) S = [structure] T = [structure]

40. Among the following, the transformation(s) that can be accomplished using umpolung concept is(are)


(i)

(ii)

(iii)

(iv)

(Tr = trityl)

(a) (i) and (iii)　　(b) (ii) and (iv)　　(c) (ii) only　　(d) (i) and (ii)

41. A disaccharide does NOT give a positive test for Tollen's reagent. Upon acidic hydrolysis, it gives an equimolar mixture of two different monosaccharides, both of which can be oxidized by bromine water. This disaccharide is

(a) [structure]

(b) [structure]

(c)

(d)

42. The major products M and N in the following reaction sequence are

(a) M =   N =

(b) M =   N =

(c) M =   N =

(d) M =   N =

43. The major products P and Q in the following reaction sequence, are

(a) P =   Q =

(b) P =   Q =

(c) P =   Q =

(d) P =   Q =

44. The major product formed in the following reaction, is

PhBr(1 equiv.)
Cat. Pd(PPh$_3$)$_4$
KOAc, DMF

(a)   (b)   (c)   (d)
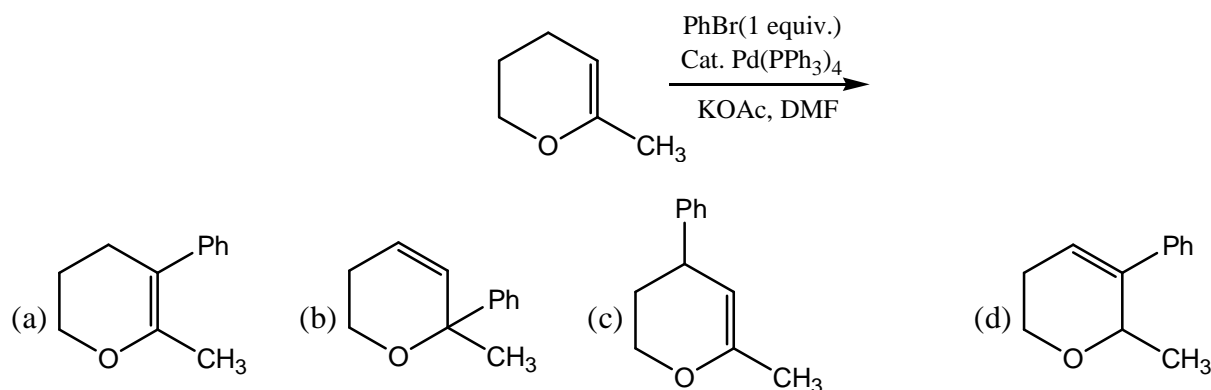
45. The following synthetic transformation can be achieved using
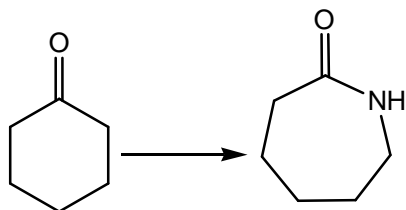
Reagents:
(p) (i) NH_2OH/H^+, (ii) H_2SO_4
(q) NH_3/H^+
(r) (i) NH_2OH/H^+, (ii) NaOH
(a) p only   (b) p and q   (c) q and r   (d) r only

46. Consider a two-state system at thermal equilibrium with equal degeneracy where the excited state is higher in energy than the ground state by 0.1 eV. The ratio of the population of the excited state to that of the ground state, at a temperature for which $k_BT = 0.05$ eV, is _____

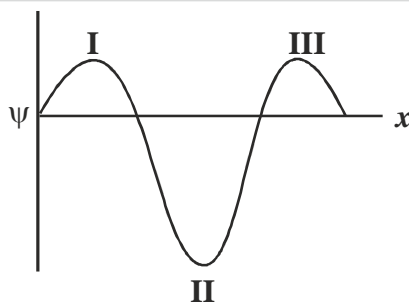47. Of the vibrational modes given below, the IR active mode(s) is(are)

(i) $O=C=O$ (ii) $O=C=O$ (iii) $O=C=O$
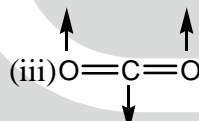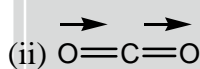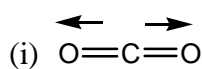
(a) (ii) only   (b) (iii) only   (c) (i) and (ii)   (d) (ii) and (iii)

48. A system is described by the following real wavefunction.

The probability (P) of finding the particle in a region dx around points I, II and III in the figure obeys the trend
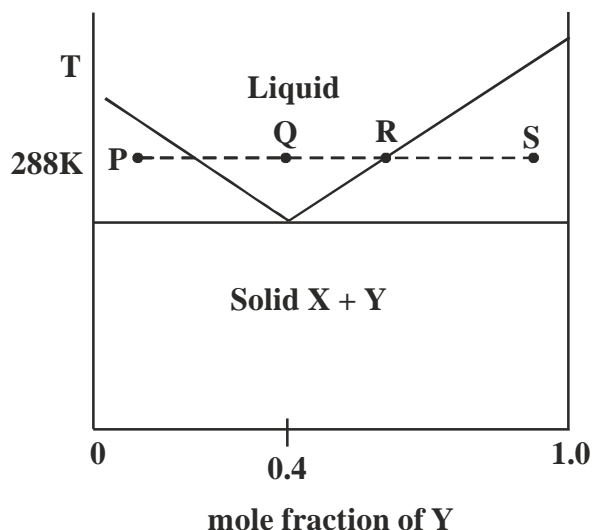(a) $P(I) > P(II) > P(III)$ (b) $P(II) > P(III) > P(I)$
(c) $P(II) > P(I) > P(III)$ (d) $P(III) > P(I) > P(II)$

49. The temperature-composition (T-x) phase diagram of the two-component system made of X and Y is given below. At a temperature of 288K and starting at the point P, Y is added until the composition reaches S. Which of the following statements is NOTR TRUE?

mole fraction of Y

(a) At P, the solid and liquid are present in almost equal proportions
(b) At Q, the system is all liquid
(c) At S, the system has more solid than liquid
(d) At R, the liquid is pure X

50. For a system subjected to only P-V work, entropy is given by

(I) $-\left(\dfrac{\partial G}{\partial T}\right)_P$　　　(II) $\left(\dfrac{\partial G}{\partial P}\right)_T$　　　(III) $-\left(\dfrac{\partial A}{\partial V}\right)_T$　　　(IV) $-\left(\dfrac{\partial A}{\partial T}\right)_V$

(a) I and II　　　(b) I and IV　　　(c) I only　　　(d) II only

51. According to Irving-Williams series, the number of d electrons for the first row transition metal (M) ion having the highest overall stability cosntant $(\log\beta)$ for $[M(EDTA)]^{2-}$ is _____

52. The magnitude of the difference in the crystal field stabilization energies, in Δ_0 (irnoring pairing energy), of $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ is _____

53. The calculated and observed magnetic moments differ considerably for an aqua complex of a Lanthanide (III) ion as a result of low lying states of high J. The ion, among the follwing, is
(a) Ce^{3+}　　　(b) Pr^{3+}　　　(c) Eu^{3+}　　　(d) Yb^{3+}

54. In the electronic spectra of $\left[CrF_6\right]^{3-}$, absorption bands observed at 670, 440 and 290 nm are, respectively, due to the transitions.

(a) $^4A_{2g} \to {}^4T_{1g}(P)$, $^4A_{2g} \to {}^4T_{1g}(F)$ and $^4A_{2g} \to {}^4T_{2g}$

(b) $^4A_{2g} \to {}^4T_{1g}(P)$, $^4A_{2g} \to {}^4T_{2g}$ and $^4A_{2g} \to {}^4T_{1g}(F)$

(c) $^4A_{2g} \to {}^4T_{1g}(F)$, $^4A_{2g} \to {}^4T_{1g}(P)$ and $^4A_{2g} \to {}^4T_{2g}$

(d) $^4A_{2g} \to {}^4T_{2g}$, $^4A_{2g} \to {}^4T_{1g}(F)$ and $^4A_{2g} \to {}^4T_{1g}(P)$

55. Amongst the following, the group that is bound to the metal ion in coenzyme B_{12} is

(a) methyl　　　(b) cyanide　　　(c) adenosyl　　　(d) hydroxyl

***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.25 : Carry ONE mark each.

1. Consider N particles at temperature T, pressure P, volume V and chemical potential μ having energy E. The parameters that are kept constant for a canonical ensemble are
   (a) N, V, T   (b) N, V, E   (c) N, P, T   (d) μ, V, T

2. For *ortho*-hydrogen, the nuclear wavefunction and the rotational quantum number, respectively, are
   (a) antisymmetric and even   (b) symmetric and odd
   (c) symmetric and even   (d) antisymmetric and odd

3. m_1 and m_2 are the slopes (dP/dT) of the solid-liquid equilibrium lines in the *P-T* phase diagrams of H_2O and CO_2, respectively. For $P < 10$ atm, the values of m_1 and m_2 are
   (a) $m_1 > 0$ and $m_2 > 0$ (b) $m_1 > 0$ and $m_2 < 0$ (c) $m_1 < 0$ and $m_2 < 0$ (d) $m_1 < 0$ and $m_2 > 0$

4. The rate constant of a reaction is 1.25×10^{-4} mol L^{-1} s^{-1}. If the initial concentration of the reactant is 0.250 mol L^{-1}, the total time (in seconds) required for complete conversion is _____

5. Consider an ideal gas of volume V at temperature T and pressure P. If the entropy of the gas is S, the partial derivative $(\partial P / \partial S)_V$ is equal to
   (a) $(\partial T / \partial P)_S$ (b) $(\partial T / \partial V)_P$ (c) $-(\partial T / \partial V)_S$ (d) $(\partial T / \partial S)_P$

6. The wavelength associated with a particle in one-dimensional box of length *L* is (*n* refers to the quantum number)
   (a) $2L/n$ (b) L/n (c) nL (d) $L/2n$

7. The dependence of rate constant k on temperature T(in K) of a reaction is given by the expression
   $$\ln k = [(-5000 \text{ K})/T] + 10$$
   The activation energy of the reaction (in kJ mol^{-1}) is _____ (up to two decimal places)

8. The lowest energy of a quantum mechanical one-dimensional simple harmonic oscillator is 300 cm^{-1}. The energy (in cm^{-1}) of the next higher level is _____

9. The electronic ground state term for the chromium ion in $[Cr(CN)_6]^{4-}$ is
   (a) ^3F (b) ^3H (c) ^3G (d) ^5D

10. The VO_4^{3-}, CrO_4^{2-} and MnO_4^- ions exhibit intense ligand to metal charge transfer transition. The wavelengths of this transition follow the order
    (a) $CrO_4^{2-} < VO_4^{3-} < MnO_4^-$ (b) $MnO_4^- < VO_4^{3-} < CrO_4^{2-}$
    (c) $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$ (d) $CrO_4^{2-} < MnO_4^- < VO_4^{3-}$

11. The lanthanide ion the exhibits color in aqueous solution is
    (a) La(III)   (b) Eu(III)   (c) Gd(III)   (d) Lu(III)

12. The hapticity of cycloheptatriene, (C_7H_8), in $Mo(C_7H_8)(CO)_3$ is _____

13. The v_{O-O} resonance Raman stretching frequency (in cm^{-1}) of the O_2 coordinated to iron centre in oxy-hemoglobin is nearly
    (a) 1100   (b) 850   (c) 1550   (d) 1950

14. The energy band diagram for magnesium is

(The hatched and unhatched regions in the figure correspond to filled and unfilled regions of the band, respectively.)

(a) Energy
p-band
s-band

(b) Energy
p-band
s-band

(c) Energy
p-band
s-band

(d) Energy
p-band
s-band
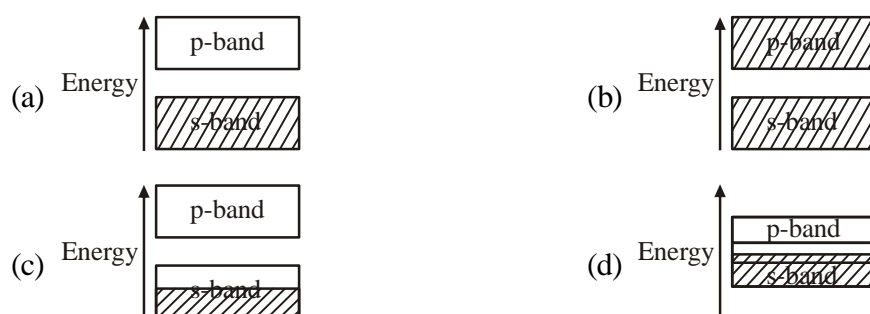
15. P, F and I represent primitive, face-centered and body-centered lattices, respectively. The lattice types of NaCl and CsCl, respectively, are
(a) F and I (b) F and P (c) I and P (d) P and I

16. The characteristic feature of an electron spin resonance (ESR) spectrum of frozen aqueous solution of $CuSO_4 \cdot 5H_2O$ at 77 K is

(a) $g_{\parallel} > g_{\perp}$ (b) $g_{\parallel} < g_{\perp}$ (c) $g_{\parallel} = g_{\perp}$ (d) $g_x \neq g_y \neq g_z$

17. The most suitable reagent for the following transformation is
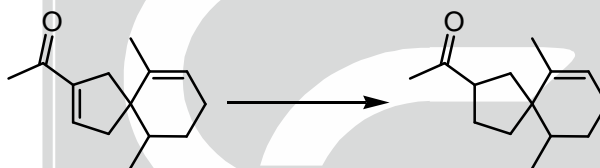
(a) $Li / Liq. NH_3$ (b) PtO_2 / H_2 (c) $LiAlH_4$ (d) B_2H_6

18. The major products M and N formed in the following reactions are

$$N \xleftarrow{CH_2N_2} \quad \xrightarrow{CH_3I/NaOH} M$$

(a) M = , N =
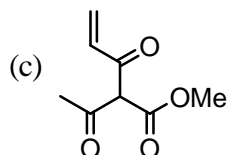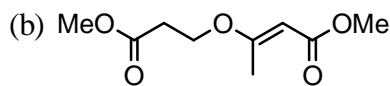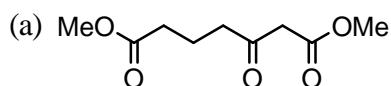
(b) M = , N =

(c) M = , N =

(d) M = , N =
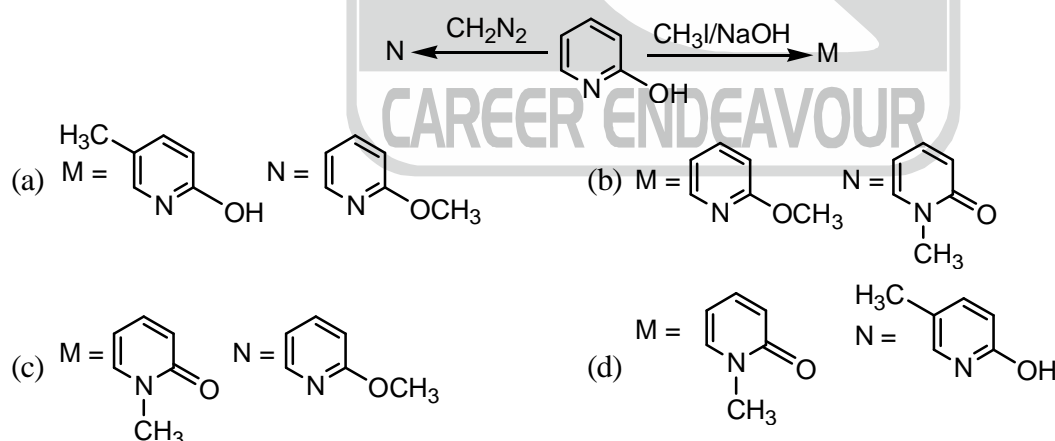
19. The ^{13}C NMR spectrum of acetone-d_6 has a signal at 30 ppm as a septet in the intensity ratio
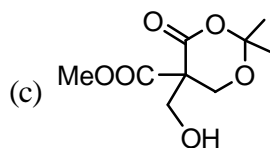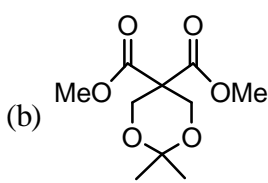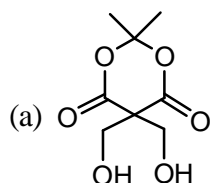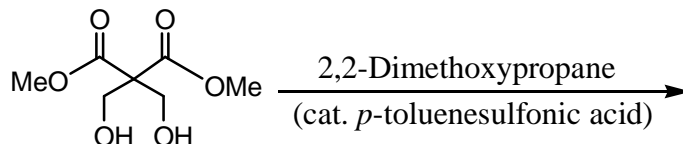(a) 1 : 6 : 15 : 20 : 15 : 6 : 1
(b) 1 : 3 : 6 : 7 : 6 : 3 : 1
(c) 1 : 2 : 3 : 5 : 3 : 2 : 1
(d) 1 : 3 : 7 : 10 : 7 : 3 : 1

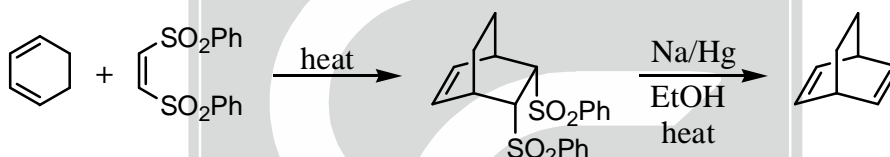20. The major product formed in the following reaction is

$$\text{(OMe ester)} + \text{(OMe acrylate)} \xrightarrow[\text{MeOH}]{\text{MeONa}}$$

(a) MeO—C(=O)—CH2—CH2—C(=O)—CH2—C(=O)—OMe

(b) MeO—C(=O)—CH2—CH2—O—C(=CH3)=CH—C(=O)—OMe

(c) vinyl ketone structure with OMe ester

(d) structure with two OMe esters and a ketone

21.   The major product obtained in the following reaction is

MeO—C(=O)—C(CH2OH)2—C(=O)—OMe → 2,2-Dimethoxypropane / (cat. *p*-toluenesulfonic acid)

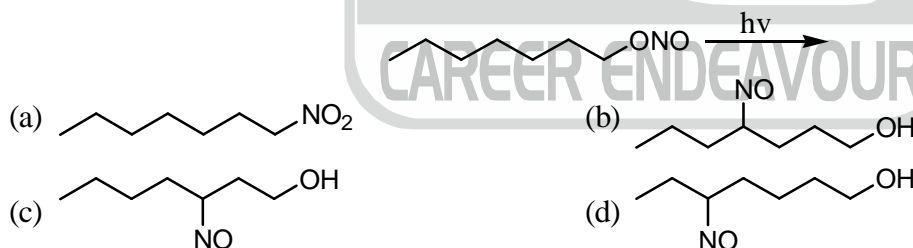(a)   structure   (b)   structure   (c)   MeOOC structure   (d)   structure
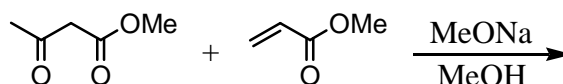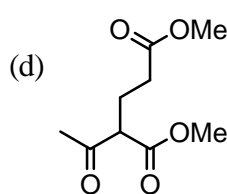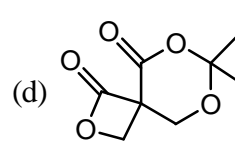
22.   In the two step reaction sequence given below, the starting bis-sulfone acts as

cyclohexadiene + *cis*-bis(phenylsulfonyl)ethylene →(heat)→ bicyclic SO2Ph SO2Ph →(Na/Hg, EtOH, heat)→ bicyclic diene
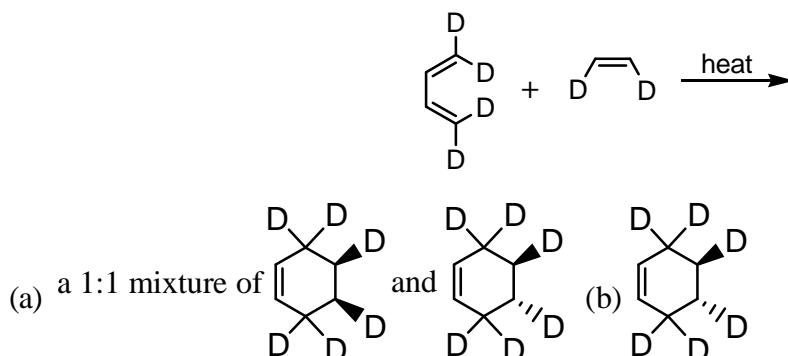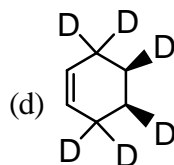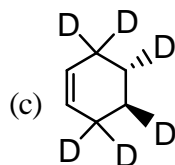
   (a) a dienophile and synthetic equivalent of acetylene
   (b) a dienophile and synthetic equivalent of ethylene
   (c) a dipolarophile and synthetic equivalent of acetylene
   (d) a dipolarophile and synthetic equivalent of ethylene

23.   The major product formed in the following photochemical reaction is

chain—ONO —(hv)→

(a)   chain—NO2

(b)   structure with NO and OH

(c)   structure with OH and NO

(d)   structure with OH and NO

24.   The product formed in the following reaction is

deuterated cyclohexadiene + deuterated ethylene —(heat)→

(a) a 1:1 mixture of   two deuterated bicyclic structures   (b)   deuterated bicyclic structure
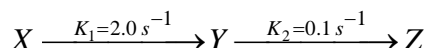
(c) [structure]   (d) [structure]

25. The number of possible stereoisomers for cyclononene is _____

Q.26 – Q.55 : Carry TWO marks each.

26. The mobility of a univalent ion in aqueous solution is 6.00×10^{-8} m^2 s^{-1} V^{-1} at 300 K. Its diffusion coefficient at 300 K is $X \times 10^{-9}$ m^2 s^{-1}. The value of X is _____ (up to two decimal places)

27. For the following consecutive first order reactions

$$X \xrightarrow{K_1 = 2.0\ s^{-1}} Y \xrightarrow{K_2 = 0.1\ s^{-1}} Z$$

the time (in seconds) required for Y to reach its maximum concentration (assuming only X is present at time $t = 0$) is _____ (up to two decimal places)

28. Under physiological conditions, the conversion of CO_2 to bicarbonate ion by carbonic anhydrase enzyme (MW = 30,000 g mol^{-1}) has a turnover number of 4.00×10^5 s^{-1}. The minimum amount of enzyme (in μg) required to convert 0.44 g of CO_2 to bicarbonate ions in 100 seconds is _____ (up to two decimal places)

29. Assume 1,3,5-hexatriene to be a linear molecule and model the π electrons as particles in a one-dimensional box of length 0.70 nm. The wavelength (in nm) corresponding to the transition from the ground-state to the first excited-state is _____

30. The standard Gibbs free energy change of the reaction shown below is –2.7 kJ mol^{-1}.

$$Sn(s) + Pb^{2+} = Sn^{2+} + Pb(s)$$
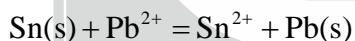
Given that $E^0(Pb^{2+}/Pb)$ is –0.126 V, the value of $E^0(Sn^{2+}/Sn)$ in V is _____ (up to two decimal places)

31. The dissociative chemisorption of $X_2(g)$ on a metal surface follows langmuir adsorption isotherm. The ratio of the rate constants of the adsorption and desorption processes is 4.0 atm^{-1}. The fractional surface coverage of X(adsorbed) at 1.0 atm pressure is _____ (up to two decimal places)

32. The ionic activity coefficients of Ca^{2+} and F^- are 0.72 and 0.28, respectively. The mean activity coefficient of CaF_2 is _____ (up to two decimal places)

33. The angle of orientation (in degrees) of the angular momentum vector with respect to z-axis for $I = 2$ and $m_\ell = +2$ state of H-atom is _____ (up to two decimal places).

34. The Gibbs free energy of mixing is denoted as ΔG_{mix}. 1.0 mole of He, 3.0 moles of Ne and 2.0 moles of Ar are mixed at the same pressure and temperature. Assuming ideal gas behavior, the value of $\Delta G_{mix}/RT$ is _____. (up to two decimal places)

35. $\Psi = \left[c\phi_1 - \left(1/\sqrt{3}\right)\phi_2 \right]$ represents a normalized molecular orbital constructed from two different atomic orbitals ϕ_1 and ϕ_2 that form an orthonormal set. The value of |c| is _____. (up to two decimal places)

36. In cyclophosphazenes, $(NPX_2)_3$ (X = F, Cl, Br and Me), the strength of P–N π-bond varies with X in the order

(a) $F > Cl > Br > Me$　(b) $Me > F > Cl > Br$　(c) $Br > Cl > F > Me$　(d) $Me > Br > Cl > F$

37. The structure type and shape of the polyhedral (skeletal) framework of the carborane $Me_2C_2B_{10}H_{10}$, respectively, are

(a) *nido* and *dodecahedron*　　　　　　　　(b) *closo* and *icosahedron*
(c) *nido* and *icosahedron*　　　　　　　　(d) *closo* and *dodecahedron*

38. If Δ_o is the octahedral splitting energy and P is the electron pairing energy, then the crystal-field stabilization energy (CFSE) of $[Co(NH_3)_6]^{2+}$ is

(a) $-0.8\Delta_o + 2\,P$　　　(b) $-0.8\Delta_o + 1\,P$　　　(c) $-0.8\Delta_o$　　　(d) $-1.8\Delta_o + 3\,P$

39. The rates of substitution for the following reaction vary with L in the order

$L = CH_3^-, Cl^-, Ph^-$ and H^-
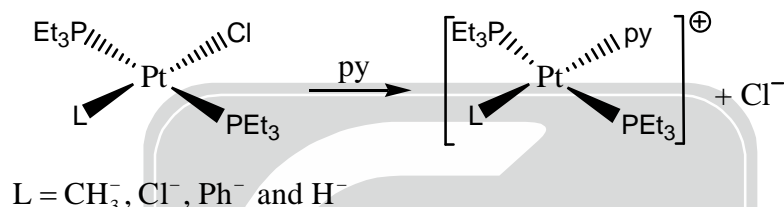
(a) $CH_3^- > Cl^- > Ph^- > H^-$　　　　　　(b) $Cl^- > Ph^- > H^- > CH_3^-$

(c) $Ph^- > CH_3^- > H^- > Cl^-$　　　　　　(d) $H^- > CH_3^- > Ph^- > Cl^-$

40. The product formed in the reaction of $MeMn(CO)_5$ with ^{13}CO is

(a) $(Me^{13}CO)Mn(CO)_5$　　　　　　　　(b) $(MeCO)Mn(CO)_5$

(c) $(MeCO)Mn(CO)_4(^{13}CO)$　　　　　　(d) $(Me^{13}CO)Mn(CO)_4(^{13}CO)$

41. For the following three alkenes, 1, 2 and 3, the rates of hydrogenation using Wilkinson's catalyst at 25ºC vary in the order
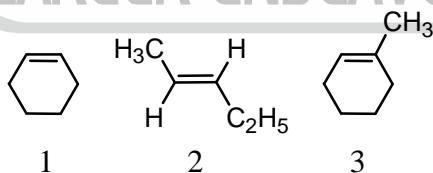

(a) $1 > 3 > 2$　　　(b) $1 > 2 > 3$　　　(c) $2 > 1 > 3$　　　(d) $2 > 3 > 1$

42. ^{210}Bi undergoes β^- decay to 1/8 of its initial amount in 15 days. The time required for its decay to 1/4 of its initial amount is _____ days (up to two decimal places).

43. The metal ion and the macrocyclic skeleton present in the green pigment of plants, respectively, are
(a) Mg(II) and chlorin　(b) Mg(II) and corrin　(c) Mn(II) and chlorin　(d) Mg(II) and porphine

44. The spinel structure of $MgAl_2O_4$ has cubic close packed arrangement of oxide ions. The fractions of the octahedral and tetrahedral sites occupied by cations, respectively, are

(a) 1/8 and 1/2　　　(b) 1/4 and 1/2　　　(c) 1/2 and 1/4　　　(d) 1/2 and 1/8

45. The diffusion limiting current (I_d) at a dropping mercury electrode for an aqueous Mg(II) solution of concentration 'c' (mol L^{-1}) is 300 μA. If 'c' is increased by 0.1 mol L^{-1}, I_d increases to 900 μA. The value of 'c' (in mol L^{-1}) is _____ (up to two decimal places)
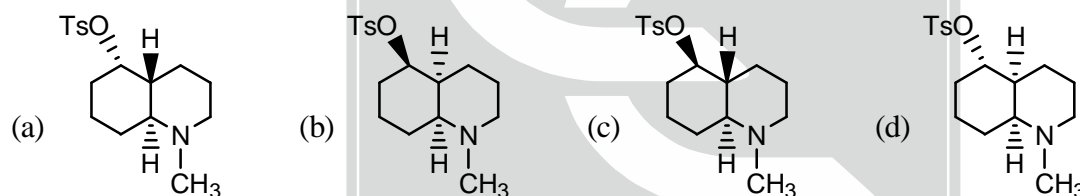
46. The major product formed in the following reaction is

(a)   (b) OHC—=—CHO   (c)   (d) OHC—=—OH
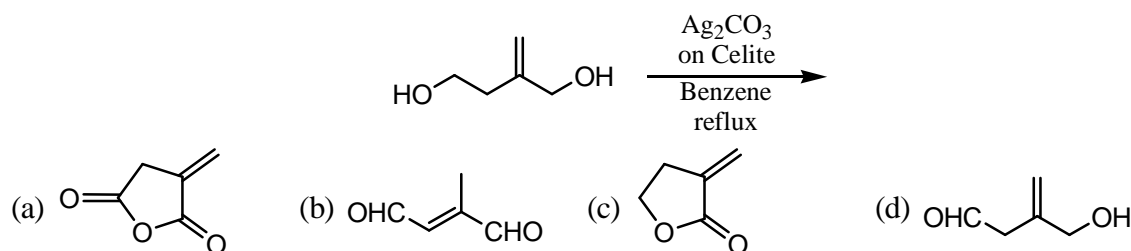
47. The product formed in the following photochemical reaction is

(a)   (b)   (c)   (d)
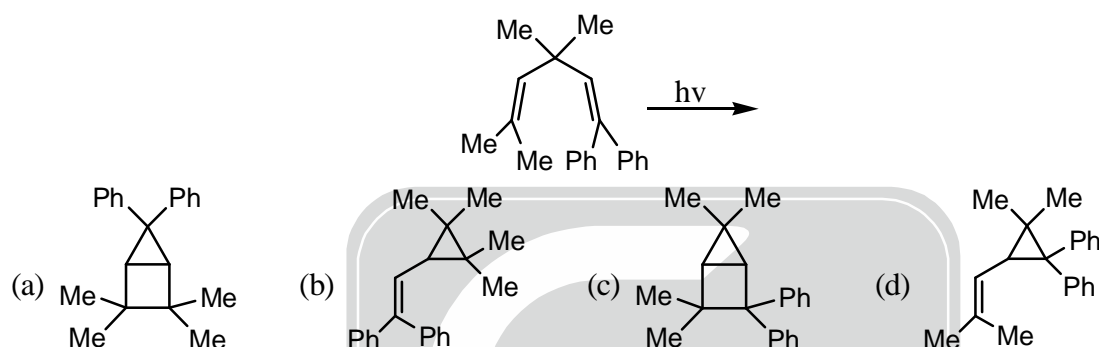
48. Among the following decahydroquinoline toluenesulfonates (Ts), the one that yields 9-methylamino-E-non-5-enal as a major product upon aqueous solvolysis is

(a)   (b)   (c)   (d)

49. The product obtained in the following solvolysis reaction is


Enantiomerically pure compound
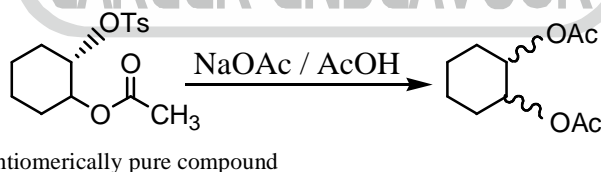
(a) a racemic mixture of trans 1,2-diacetoxycyclohexane
(b) enantiomerically pure trans 1,2-diacetoxycyclohexane
(c) racemic cis 1,2-diacetoxycyclohexane
(d) a mixture of cis and trans 1,2-diacetoxycyclohexane

50. The spectroscopic data for an organic compound with molecular formula $C_{10}H_{12}O_2$ are given below. IR band around 1750 cm^{-1}. ^1H NMR δ 7.3 (m, 5H), 5.85 (q, 1H, J = 7.2 Hz), 2.05 (s, 3H), 1.5 (d, 3H, J = 7.2 Hz) ppm. the compound is

(a) methyl 2-phenylpropionate   (b) 1-(phenylethyl) acetate
(c) 2-(phenylethyl) acetate   (d) methyl 3-phenylpropionate

51. The structures of the intermediate [P] and major product Q formed in the following reaction sequence are
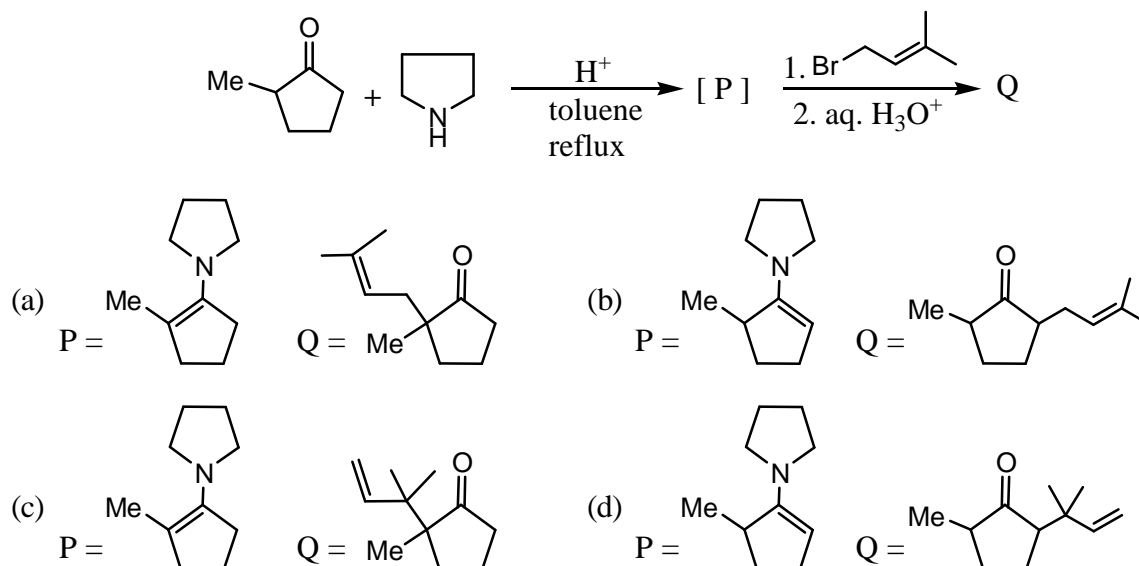

52. Hydration of fumaric acid gives malic acid as shown below. Assume that addition of water takes place specifically from A face or B face. The correct statement pertaining to stereochemistry of malic acid formed is
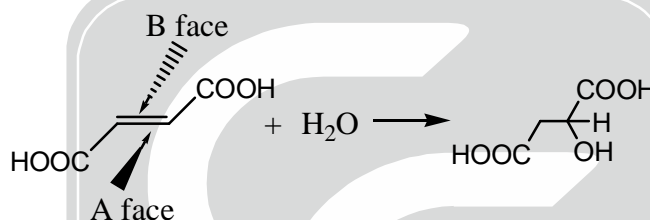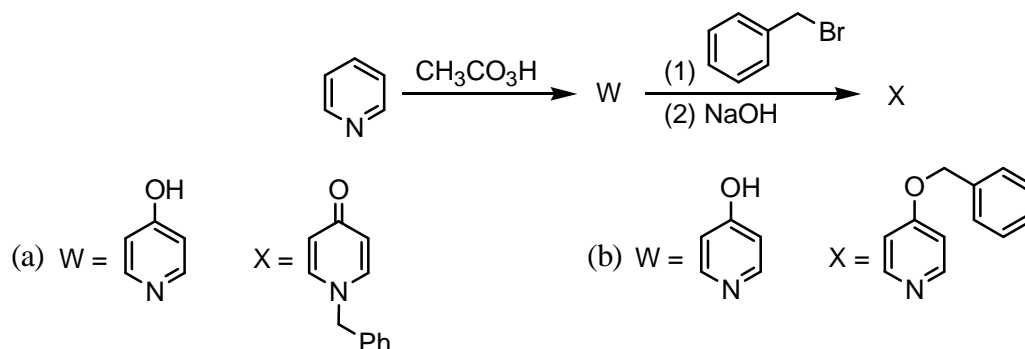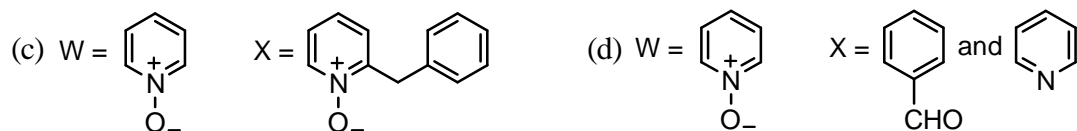

(a) addition specifically from A face gives S isomer of malic acid
(b) addition specifically from B face gives S isomer of malic acid
(c) addition specifically from A face gives R isomer of malic acid
(d) addition specifically from B face gives a racemic mixture of malic acid

53. Hydroboration of 2-butyne with $(C_6H_{11})_2BH$ yields the intermediate U, which on treatment with I_2 and NaOMe at -78ºC, gives product V. The structures of U and V are
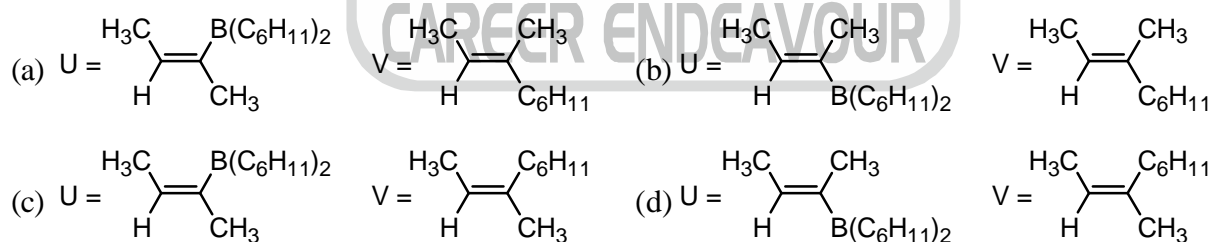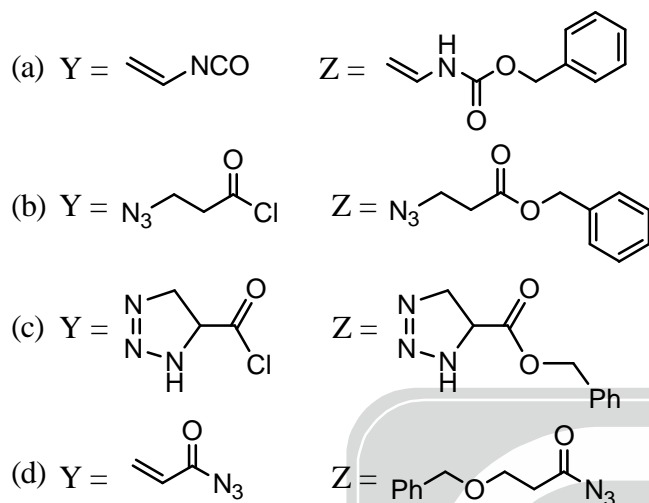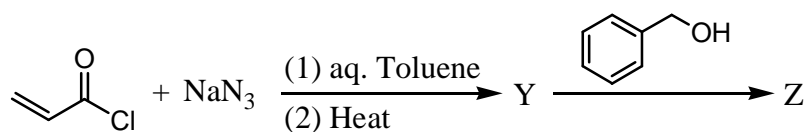

54. The structures of the major products W and X in the following synthetic scheme are

(c) W = [pyridine N-oxide structure] X = [2-benzyl pyridine N-oxide structure]   (d) W = [pyridine N-oxide structure] X = [benzaldehyde structure] and [pyridine structure]

55. The major products Y and Z in the following reaction sequence are

[acryloyl chloride structure] + NaN$_3$ $\xrightarrow[\text{(2) Heat}]{\text{(1) aq. Toluene}}$ Y $\xrightarrow{\text{[benzyl alcohol structure] OH}}$ Z

(a) Y = [vinyl isocyanate structure] NCO   Z = [vinyl carbamate benzyl ester structure]

(b) Y = N$_3$ [3-azidopropanoyl chloride structure] Cl   Z = N$_3$ [3-azidopropanoic acid benzyl ester structure]

(c) Y = [triazoline carbonyl chloride structure] Cl   Z = [triazoline carbonyl benzyl ester structure] Ph

(d) Y = [acryloyl azide structure] N$_3$ Z = Ph [benzyloxy propanoyl azide structure] N$_3$

***** END OF THE QUESTION PAPER *****

CHEMISTRY-CY

Q.1 – Q.25 : Carry ONE mark each.

1. For low partial pressure of ozone (O_3), the adsorption of ozone on graphite surface is the fully dissociative in nature and follows Langmuir isotherm. Under these conditions, if the dependence of the surface coverage of graphite (θ) on partial pressure of ozone (P_{O_3}) is given by $\theta \propto (P_{O_3})^x$, the value of x is _____(Upto two decimal places)

2. According to Eyring state theory for a bimolecular reaction, the activated complex has
   (a) no vibrational degrees of freedom
   (b) vibrational degrees of freedom but they never participate in product formation
   (c) one high frequency vibration that leads to product formation
   (d) one low frequency vibration that leads to product formation

3. The major product formed in the following reaction is
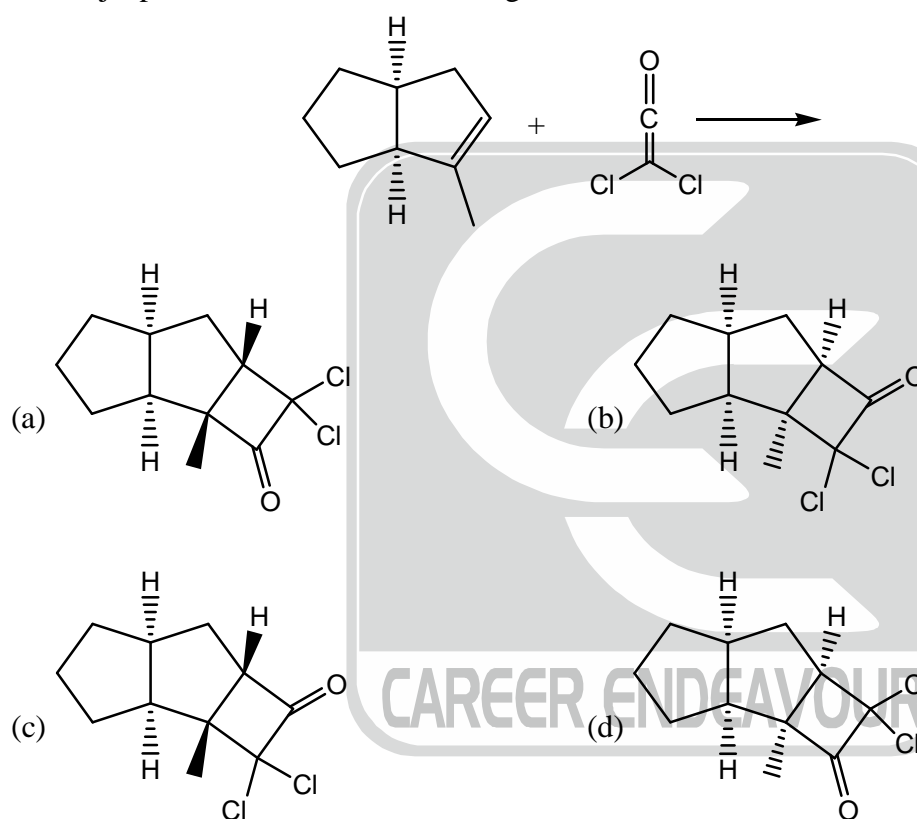
4. The major product of the following intramolecular cycloaddition reaction is
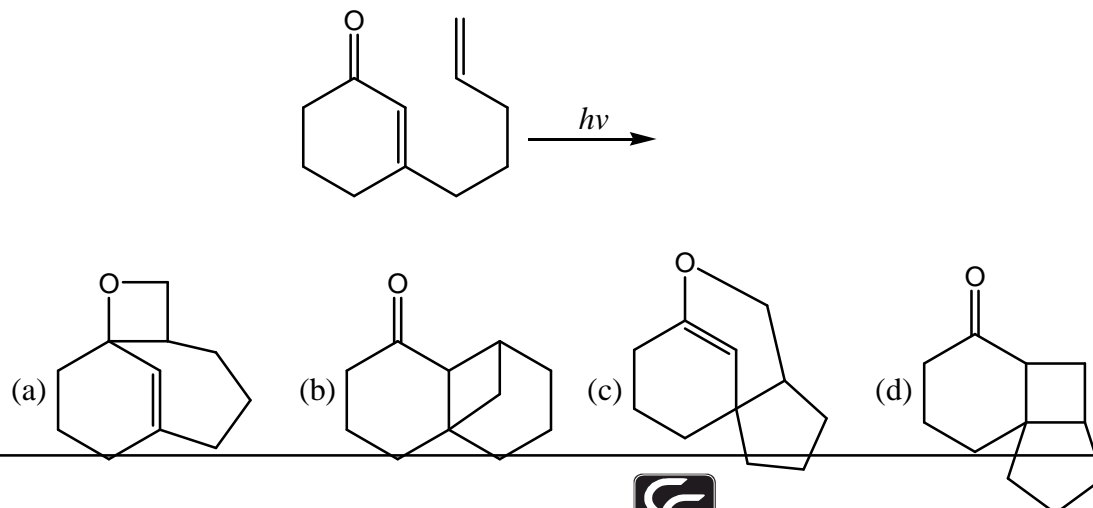
5. The coordination geometries around the copper ion of plastocyanin (a blue-copper protein) in oxidized and reduced form, respectively are
   (a) tetrahedral and square-planar   (b) square-planar and tetrahedral
   (c) distorted tetrahedral for both   (d) ideal tetrahedral for both

6. The major product formed in the following reaction is

(a)   (b)

(c)   (d)
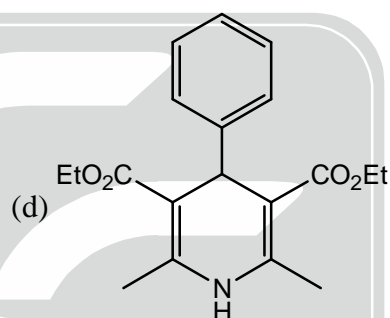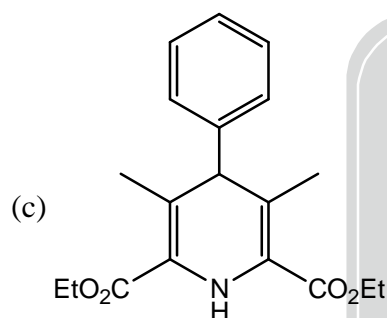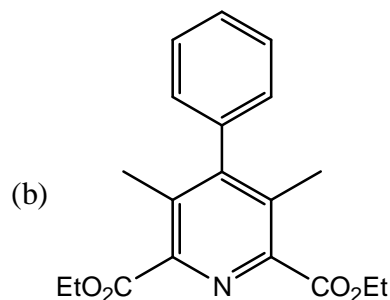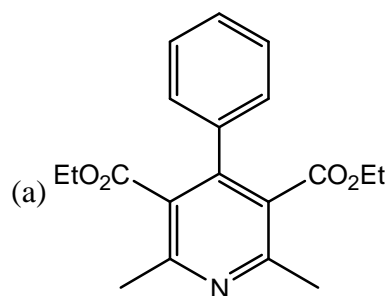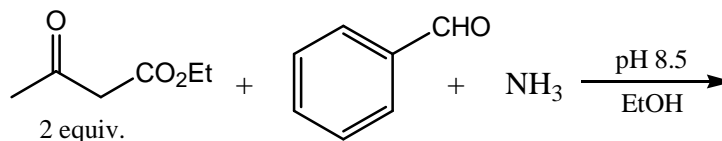
7. The spherical harmonic function $Y_{\ell,m}(\theta, \phi)$, with appropriate values of ℓ and m, is an eigenfunction of $\hat{L}_x^2 + \hat{L}_y^2$ operator. The corresponding eigenvalue is

   (a) $\left(\ell(\ell+1) - m^2\right)\hbar^2$ (b) $\left(\ell(\ell+1) + m^2\right)\hbar^2$

   (c) $\ell(\ell+1)\hbar^2$ (d) $m^2\hbar^2$
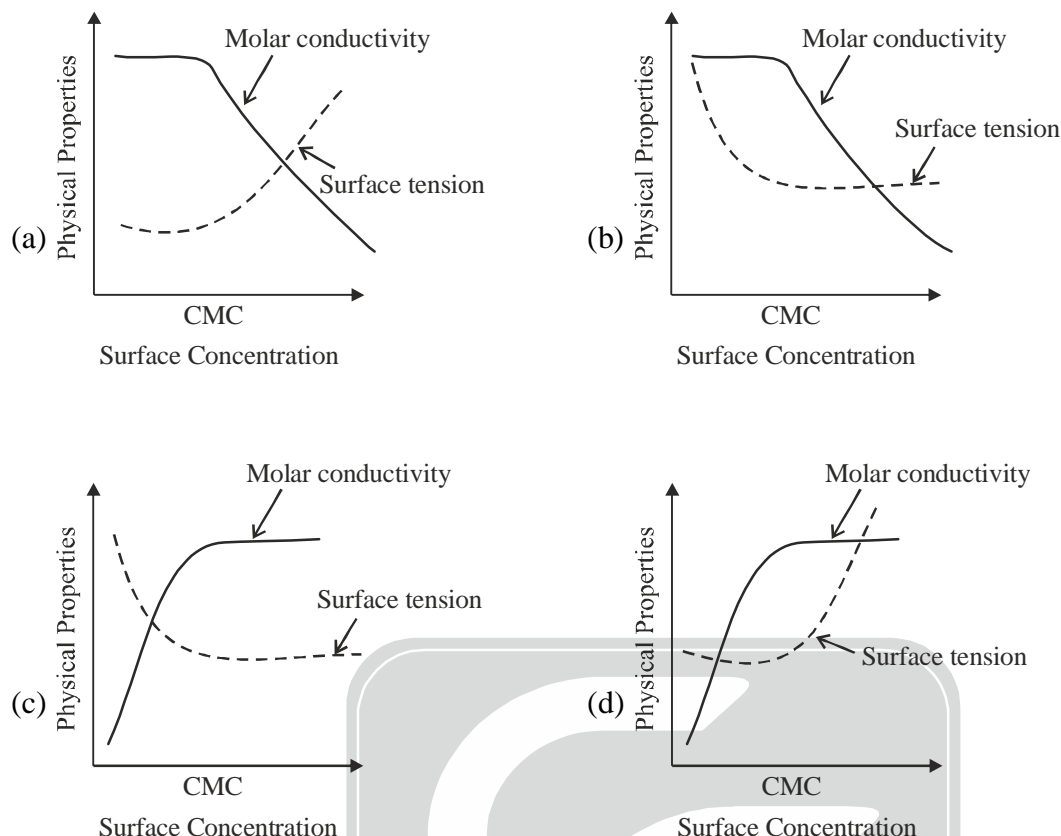
8. The temperature derivative of electrochemical potential E at constant pressure, $\left(\dfrac{\partial E}{\partial T}\right)_P$ is given by

   (a) $-\dfrac{\Delta S}{nF}$ (b) $\dfrac{\Delta S}{nF}$ (c) $\dfrac{\Delta S}{nFT}$ (d) $-\dfrac{\Delta S}{nFT}$

9. The water exchange rates for the complex ions follow the order

   (a) $\left[V(H_2O)_6\right]^{2+} > \left[Co(H_2O)_6\right]^{2+} > \left[Cr(H_2O)_6\right]^{3+}$

   (b) $\left[Cr(H_2O)_6\right]^{3+} > \left[Co(H_2O)_6\right]^{2+} > \left[V(H_2O)_6\right]^{2+}$

   (c) $\left[Co(H_2O)_6\right]^{2+} > \left[Cr(H_2O)_6\right]^{3+} > \left[V(H_2O)_6\right]^{3+}$

   (d) $\left[Co(H_2O)_6\right]^{2+} > \left[V(H_2O)_6\right]^{2+} > \left[Cr(H_2O)_6\right]^{3+}$

10. For an ionic micelle-forming surfactant near its critical micelle concentration (CMC), the dependence of molar conductivity and surface tension on surfactant concentration is best represented by


(a)

(b)

(c)

(d)

11. The major product formed in the following reaction sequence is

(i) LDA, –78ºC
(ii) PhSeCl
(iii) H_2O_2, Δ

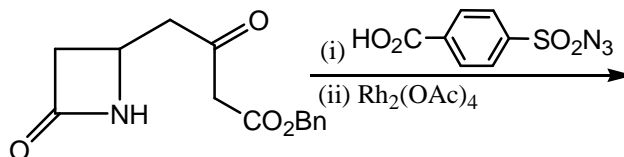(a)   (b)   (c)   (d)
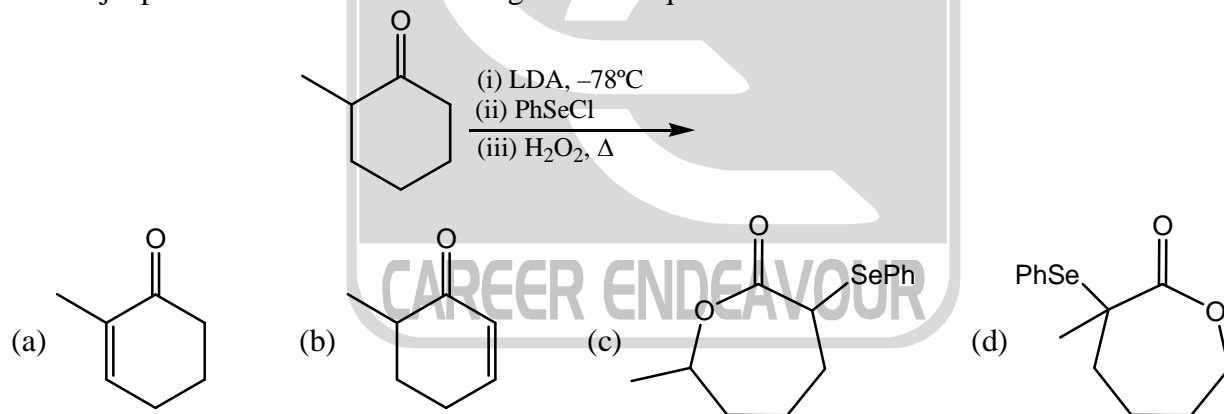
12. Two moles of an ideal gas X and two moles of an ideal gas Y, initially at the same temperature and pressure, are mixed under isothermal-isobaric condition. The entropy change on mixing is _____ JK^{-1}. (Upto one decimal place, Use $R = 8.31 \, JK^{-1} mol^{-1}$)

13. Consider the operators, $\hat{a}_{+} = \dfrac{1}{\sqrt{2}}\left(\hat{x} + i\hat{p}_x\right)$ and $\hat{a}_{-} = \dfrac{1}{\sqrt{2}}\left(\hat{x} - i\hat{p}_x\right)$, where $\hat{x}$ and $\hat{p}_x$ are the position and linear momentum operators, respectively. The commutator, $\left[\hat{a}_{+}, \hat{a}_{-}\right]$ is equal to

(a) $i\hbar$ (b) $-i\hbar$ (c) $\hbar$ (d) $-\hbar$

14. In the ^{1}H NMR spectrum of an organic compound recorded on a 300 MHz instrument, a proton resonates as a quartet at 4.20 ppm. The individual signals of quartet appear at δ 4.17, 4.19, 4.21 and 4.23 ppm . The coupling constant J in Hz is _____

15. The bond angle (Ti–C–C) in the crystal structure of

$$\{(CH_3)_2P(CH_2)_2P(CH_3)_2\}Cl_3Ti\text{—}CH_2$$

with angle $86°$, connecting to CH_2 and H
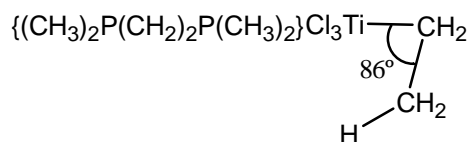
is severely distorted due to
(a) hydrogen-bonding interaction
(b) agostic interaction
(c) steric bulk of the phosphine ligand
(d) higher formal charge on metal.

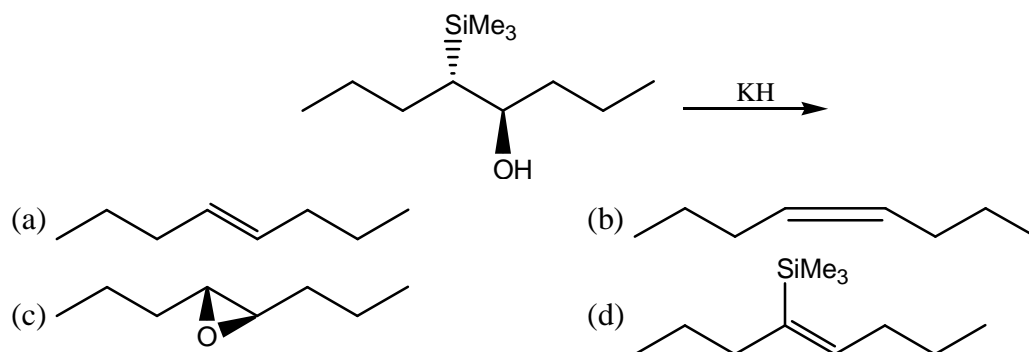16. The major product formed in the following reaction sequence is

$$\xrightarrow[\text{(ii) } Rh_2(OAc)_4]{\text{(i) } HO_2C\text{—}C_6H_4\text{—}SO_2N_3}$$

(a)

(b)

(c)

(d)

17. The lowest energy $d \rightarrow d$ transition of the complexes follow the order

(a) $\left[Cr(H_2O)_6\right]^{3+} < \left[Cr(NH_3)_6\right]^{3+} < \left[Cr(CN)_6\right]^{3-}$

(b) $\left[Cr(CN)_6\right]^{3-} < \left[Cr(NH_3)_6\right]^{3+} < \left[Cr(H_2O)_6\right]^{3+}$

(c) $\left[Cr(CN)_6\right]^{3-} < \left[Cr(H_2O)_6\right]^{3+} < \left[Cr(NH_3)_6\right]^{3+}$

(d) $\left[Cr(NH_3)_6\right]^{3+} < \left[Cr(CN)_6\right]^{3-} < \left[Cr(H_2O)_6\right]^{3+}$

18. The major product of the following reaction is

$$\xrightarrow{KH}$$

(a)

(b)

(c)

(d)

19. The total number of valence electrons in $W\left(\eta^3 - Cp\right)\left(\eta^5 - Cp\right)(CO)_2$ is _____ (Atomic number of $W = 74$)

20. The energy of a hydrogen molecule in its ground state equilibrium configuration is –31.7 eV. Its dissociation energy is _____ eV. (Upto one decimal places)

21. The molar heat capacity of a substance is represented in the temperature range 298K to 400K by the empirical relation $C_{p,m} = 14 + bT \ JK^{-1}mol^{-1}$, where b is a constant. The molar enthalpy change when the substance is heated from 300K to 350K is 2 kJ mol^{-1}. The value of b is _____ J K^{-2} mol^{-1}. (Upto two decimal places)

22. In the electron ionization (EI) mass spectra, methyl hexanoate, methyl heptanoate and methyl octanoate give the same base peak. The m/z value of the base peak is _____

23. For the radioactive isotope ^{131}I, the time required for 50% disintegration is 8 days. The time required for the 99.9% disintegration of 5.5g of ^{131}I is _____ days. (Upto one decimal place)

24. The symmetry label of valence p orbitals of a metal ion in an octahedral ligand field is

    (a) t_{1g} (b) t_{1u} (c) $e_g + a_{1g}$ (d) t_{2g}

25. Based on Wade's rule, the structure-type of $[B_5H_8]^-$ is
    (a) closo   (b) nido   (c) arachno   (d) hypho

    Q.26 – Q.55 : Carry TWO marks each.

26. Spectroscopic ground state term symbols of cobalt ions in $\left[Co(H_2O)_6 \right]^{2+}$ and $\left[CoCl_4 \right]^{2+}$ respectively are

    (a) $^2T_{1g}$ and $^4A_2$ (b) $^4T_{1g}$ and $^4A_2$ (c) $^2T_{2g}$ and $^4T_1$ (d) $^2T_1$ and $^4A_1$

27. The reaction of equimolar quantities of $Fe(CO)_5$ and OH^- gives a complex species X which on further reaction with MnO_2 gives species Y. X and Y, respectively, are

    (a) $\left[Fe(CO)_5(OH) \right]^-$ and $Fe_2(CO)_9$ (b) $\left[Fe(CO)_4 \right]^{2-}$ and $Mn_2(CO)_{10}$

    (c) $\left[HFe(CO)_4 \right]^-$ and Fe_2O_3 (d) $\left[HFe(CO)_4 \right]^-$ and $Fe_3(CO)_{12}$

28. The enantiomeric pair, among the following is
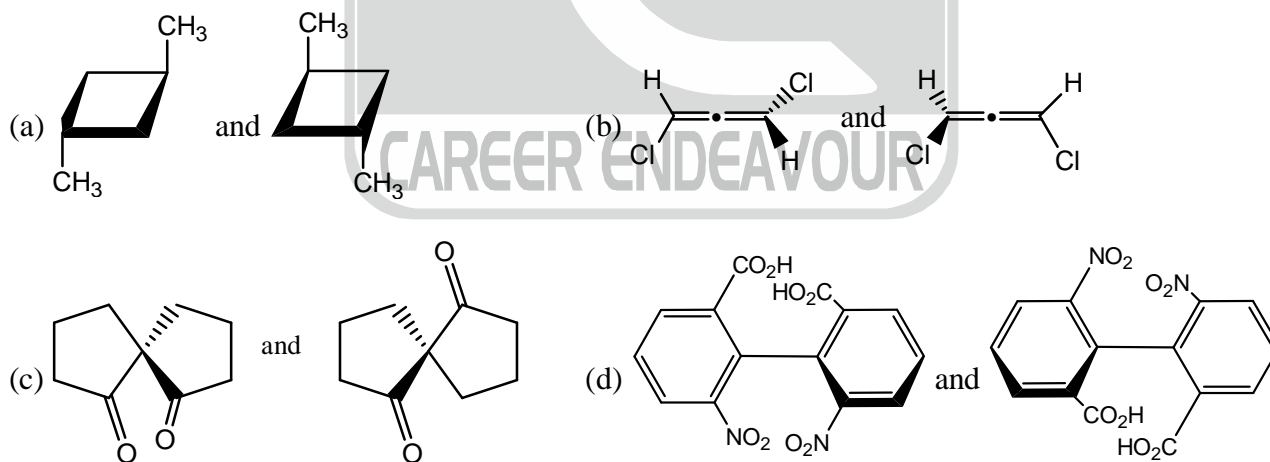
29. In a molecule XY, let ψ_X and ψ_Y denote normalized atomic orbitals of atoms X and Y, respectively. A normalized molecular orbital of XY is given by $\psi_+ = 0.56(\psi_X + \psi_Y)$. The value of the overlap integral of ψ_X and ψ_Y is _____ (Upto two decimal places)

30. The absorption maxima of two dyes X and Y are 520 and 460 nm, respectively. The absorbance data of these measured in a 1cm path length cell are given in the table below.
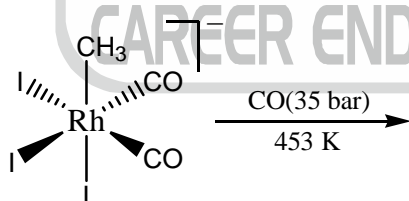
Dye solution	Absorbance at 460 nm	Absorbance at 520 nm
$X\,(9\,mM)$	0.144	0.765
$Y\,(12\,mM)$	0.912	0.168
Mixture of X and Y	0.700	0.680

The concentration of Y in the mixture is _____ mM. (Upto two decimal places)

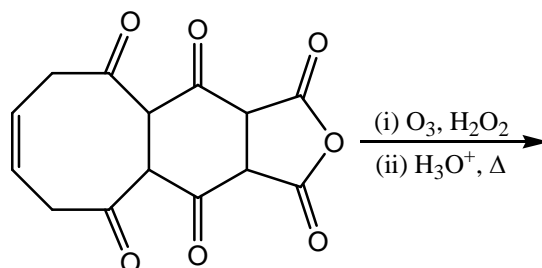31.   The major product in the following reaction sequence is

(i) mCPBA, NaHCO$_3$
(ii) NaOH, H$_2$O
(iii) I$_2$, KI, NaHCO$_3$, H$_2$O

(a)

(b)

(c)

(d)
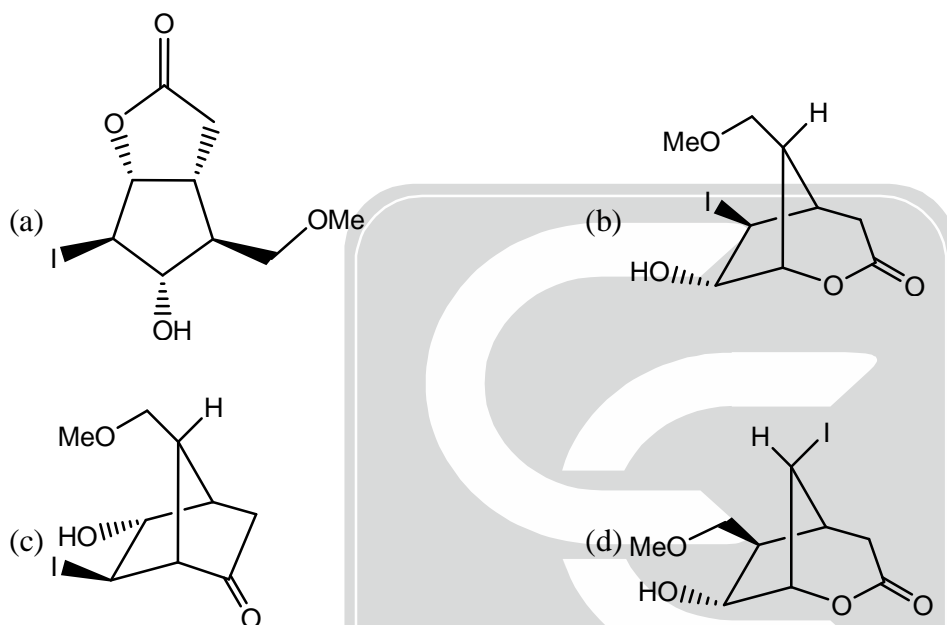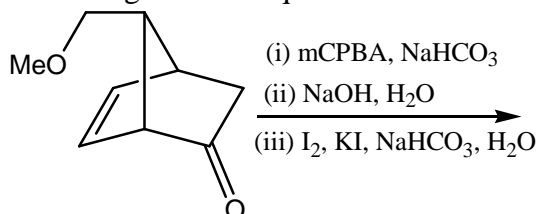
32.   The elimination product of the following reaction is
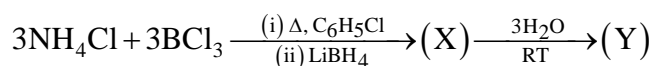

CO(35 bar)
453 K

(a) I$_2$ (b) CH$_3$I   (c) CH$_3$COI   (d) I$_3^-$

33.   Number of carbonyl groups present in the final product of the following reaction sequence is

(i) O$_3$, H$_2$O$_2$
(ii) H$_3$O$^+$, Δ

34. For the following reaction sequence,

$$3NH_4Cl + 3BCl_3 \xrightarrow[\text{(ii) LiBH}_4]{\text{(i) } \Delta, \, C_6H_5Cl} (X) \xrightarrow[\text{RT}]{3H_2O} (Y)$$

X and Y, respectively, are

(a) $\{HB(NH)\}_3$ and $\{H(OH)B(NH_2)\}_3$

(b) $\{HB(NH)\}_3$ and $\{HB(NH_2OH)\}_3$

(c) $(NH_4)\{(H)_2(BH_2)_3\}$ and $\{H(OH)(NH_2OH)\}_3$

(d) $(NH_4)\{(H)_2(BH_2)_3\}$ and $\{HB(NH_2OH)\}_3$

35. The major product of the following reaction sequence is
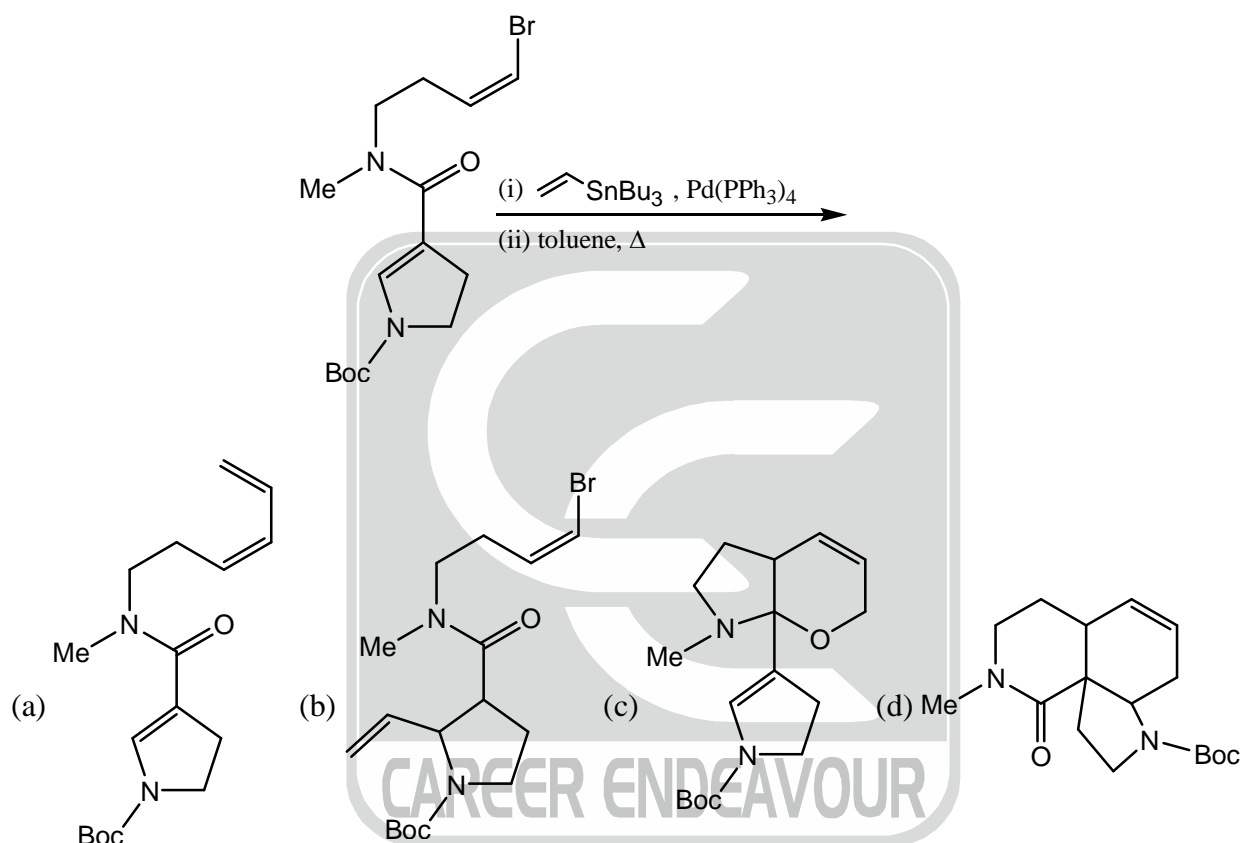
36. For a diatomic vibrating rotor, in vibrational level $v = 3$ and rotational level J, the sum of the rotational and vibrational energies is 11493.6 cm^{-1}. Its equilibrium oscillation frequency is 2998.3 cm^{-1}, anharmonicity constant is 0.0124 and rotational constant under rigid rotor approximation is 9.716 cm^{-1}. The value of J is _____(Upto nearest integer)

37. At temperature T, the canonical partition function of a harmonic oscillator with fundamental frequency (v) is given by

$$q_{vib}(T) = \frac{e^{-hv/2k_BT}}{1 - e^{-hv/k_BT}}$$

For $\dfrac{hv}{k_BT} = 3$, the probability of finding the harmonic oscillation in its ground vibrational state is _____(Upto two decimal places)

38. A one-dimensional anharmonic oscillator is treated by perturbation theory. The harmonic oscillator is used as the unperturbed system and the perturbation is $\frac{1}{6}\gamma x^3$ (γ is a constant). Using only the first order correction, the total ground state energy of the anharmonic oscillator is

    (**Note:** For a one-dimensional harmonic oscillator $\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2}$; $\alpha = \left(\frac{k\mu}{h^2}\right)^{1.2}$

    (a) $\frac{1}{2}\hbar\left(\frac{k}{\mu}\right)^{1/2}$ (b) $\left(\frac{1}{2}+\frac{\gamma}{6}\right)\hbar\left(\frac{k}{\mu}\right)^{1/2}$ (c) $\left(\frac{1}{2}+\frac{\gamma}{3}\right)\hbar\left(\frac{k}{\mu}\right)^{1/2}$ (d) $\left(\frac{1}{2}+\frac{\gamma}{12}\right)\hbar\left(\frac{k}{\mu}\right)^{1/2}$

39. The rate constant of a first order reaction, $X \rightarrow Y$, is 1.6×10^{-1} s-1 at 300K. Given that the activation energy of the reaction is 28 kJ mol^{-1} and assuming Arrhenium behaviour for the temperature dependence, the total time required to obtain 90% of Y at 350 K is _____ s. (Upto to one decimal place, use R = 8.31 JK^{-1} mol^{-1}).

40. The strongest band observed in the IR spectrum of the final product of the following reaction appears, approximately at _____ $\times100$ cm^{-1}(Upto one decimal place)
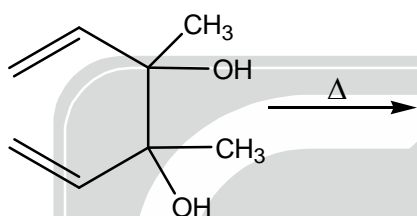
41. The reaction of PCl$_3$ with PhLi in 1 : 3 molar ratio yields X as one of the products, which on further treatment with CH$_3$I gives Y. The reaction of Y with n-BuLi gives product Z. The product X, Y and Z respectively, are

    (a) $[PPh_4]Cl, [Ph_2P=CH_2]$ and $Ph_2P(n\text{-}Bu)$

    (b) $PPh_3, [Ph_3PI](CH_3)$ and $Ph_2P(n\text{-}Bu)_3$

    (c) $PPh_3, [Ph_3P(CH_3)]I$ and $Ph_3P=CH_3$

    (d) $[PPh_4]Cl, [Ph_3P=CH_2]$ and $[Ph_3P(n\text{-}Bu)]Li$

42. The π electrons in benzene can be modelled as particles in a ring that follow Pauli's exclusion principle. Given that the radius of benzene is 1.4Å, the longest wavelength of light that is absorbed during an electronic transition in benzene is _____nm. (Upto one decimal place. Use $m_e = 9.1\times10^{-31}$ kg, $h = 6.6\times10^{-34}$ Js, $c = 3.0\times10^8$ ms^{-1})

43. Second-order are constant for the reaction between $\left[Co(NH_3)_5 X\right]^{n+}$ (n = 3 for X = NH$_3$ and H$_2$O; n = 2 for X = Cl$^-$) and $\left[Cr(H_2O)_6\right]^{2+}$ at room temperature varies with the X as

    (a) NH$_3$ > H$_2$O > Cl$^-$ (b) Cl$^-$ > H$_2$O > NH$_3$
    (c) NH$_3$ > Cl$^-$ > H$_2$O   (d) H$_2$O > NH$_3$ > Cl$^-$

44. The Latimer diagram of oxygen is given below. The value of x is _____V. (Upto two decimal places)

$$O_2 \xrightarrow{+0.70\ V} H_2O_2 \xrightarrow{+1.76\ V} H_2O$$
$$x V$$
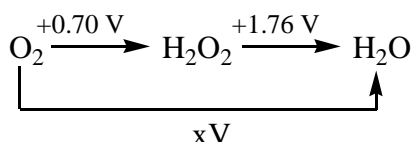
45. The major product formed in the following retro-aldol reaction is

TsOH, 50% aq. dioxane

(a)

(b)

(c)

(d)
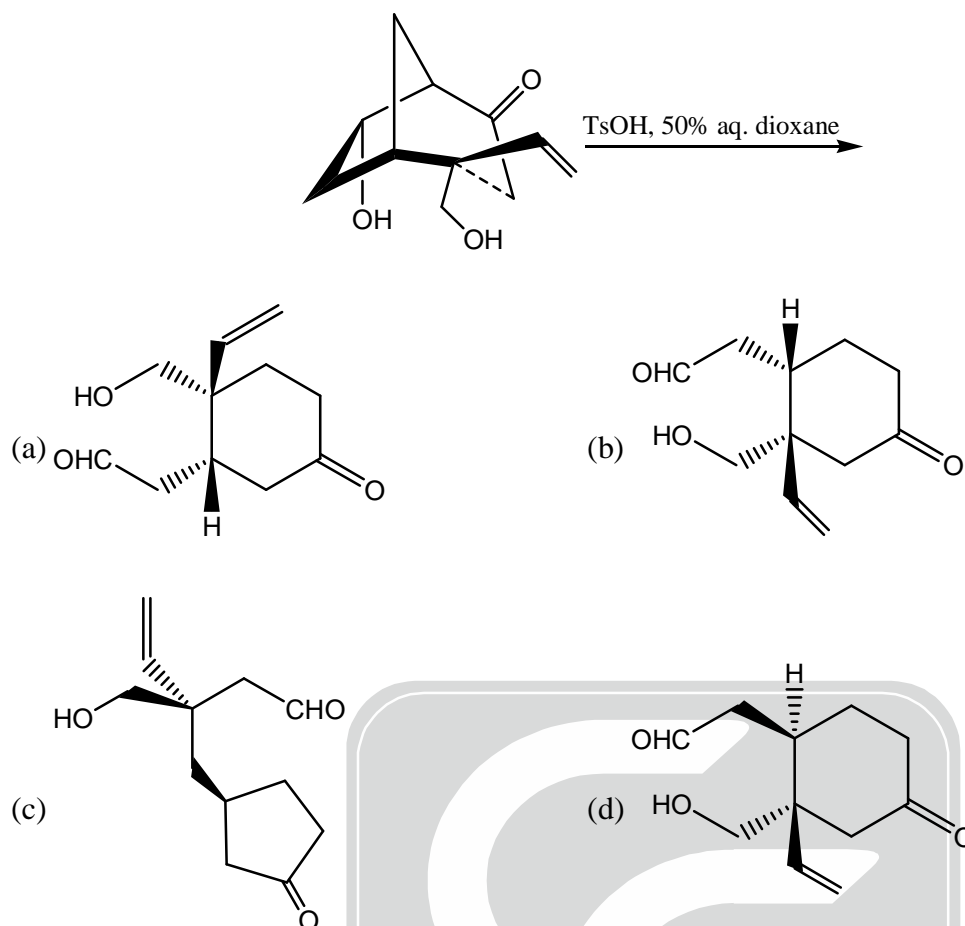
46. The enthalpy of vaporization of a liquid at its boiling point $\left(T_b = 200 \text{ K}\right)$ is 15.3 kJ mol^{-1}. If the molar volumes

    of the liquid and the vapour at 200 K are 110 and 12000 cm^3 mol^{-1}, respectively, then the slope $\dfrac{dP}{dT}$ of the

    liquid-boundary is _____ kPa K^{-1} (Upto two decimal places. Note : 1 Pa = 1 J m^{-1})

47. The O$_2$ coordinated to metal ion centres in oxy-myoglobin and oxy-hemocyanin exists, respectively, as
    (a) superoxide and peroxide   (b) superoxide and superoxide
    (c) peroxide and peroxide   (d) superoxide and oxygen

48. For an inverse spinel, AB$_2$O$_4$, the A and B, respectively, can be
    (a) Ni(II) and Ga(III)   (b) Zn(II) and Fe(III)
    (c) Fe(II) and Cr(III)   (d) Mn(II) and Mn(III)

49. The molar conductivity of a 0.01 M weak acid (HX) at 298K, measured in a conductivity cell with cell constant of 0.4 cm^{-1}, is 64.4 Scm^2 mol^{-1}. The limiting molar conductivities at infinite dilution of H$^+$ and X$^-$ at 298K are 350 and 410 S cm^2 mol^{-1}. Ignoring activity coefficients, the pK$_a$ of HX at 298K is _____ (Upto two decimal places)

50. The spacing between the two adjacent lines of the microwave spectrum of H^{35}Cl, is 6.35×1011 Hz, given that bond length D^{35}Cl is 5% greater than that of H^{35}Cl the corresponding spacing for D^{35}Cl is _____ ×10^{11} Hz. (Upto two decimal places)

51. Generally, the coordination number and the nature of the electronic absorption band $(f \rightarrow f \text{ transition})$ of lanthanide (III) ion in their complexes are, respectively
    (a) greater than 6 and sharp
    (b) 6 and broad
    (c) less than 6 and sharp
    (d) greater than 6 and broad

52. A tetrapeptide, made up of natural amino acids, has alanine as the N-terminal residue which is coupled to a chiral amino acid. Upon complete hydrolysis, the tetrapeptide gives glycine, alanine, phenylalanine and leucine. The number of possible sequences of the tetrapeptide is _____

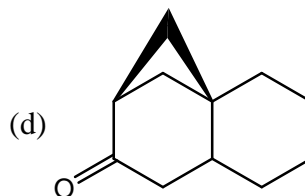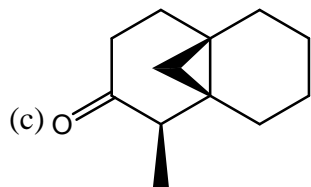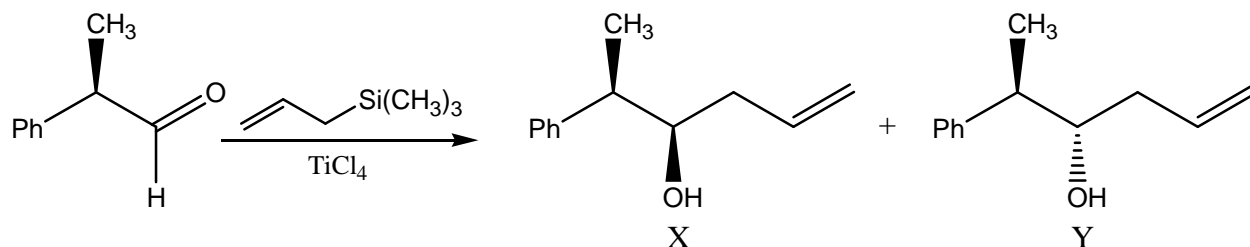53. The major product formed in the following reaction sequence is
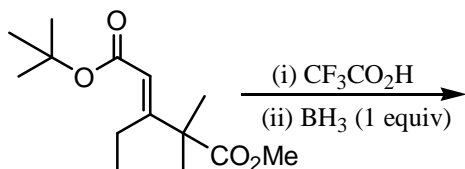
54. The major product formed in the following reaction sequence is

(c)

(d)
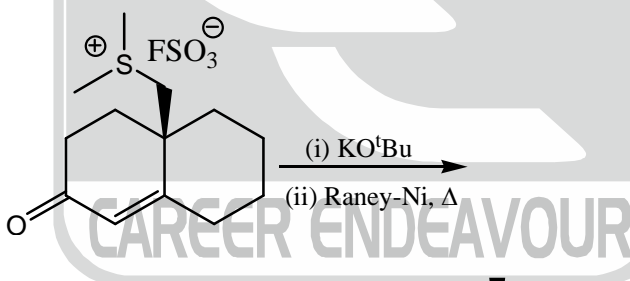
55. In the following reaction,

(a) X is the major product and Y is the minor product

(b) X is the only product

(c) Y is the only product

(d) X is the minor product and Y is the major product

***** END OF THE QUESTION PAPER *****