

V-66

ENTRANCE EXAMINATIONS – 2019
(Ph.D. Admissions - January 2020 Session)

Ph.D. Chemistry

TIME: 2 HOURS

MAXIMUM MARKS: 80

HALL TICKET NUMBER:

INSTRUCTIONS

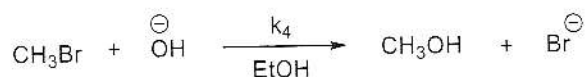
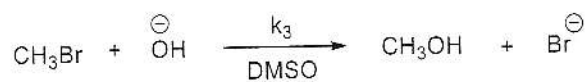
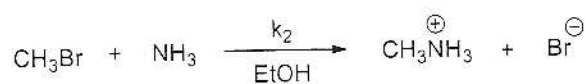
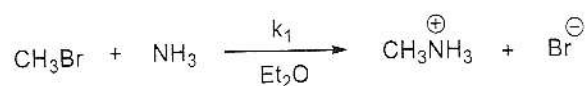
1. Write your **HALL TICKET NUMBER** in the space provided above and also on the **OMR ANSWER SHEET** given to you.
2. Make sure that pages numbered from **1 - 26** are present (including 4 pages assigned for rough work).
3. There are **eighty (80)** multiple choice questions in this paper (**20 in Part-A** and **60 in Part-B**). Each question in Part-A and Part-B carries **two marks**.
4. Attempt all questions in **Part-A** ($20 \times 2 = 40$ marks), and any **20** in **Part-B** ($20 \times 2 = 40$ marks); if more questions are answered in **Part-B**, only the first **20** will be considered for grading.
5. **There is negative marking** for both Part-A and Part-B. **Each wrong answer carries – 0.66 mark.**
6. Answers are to be marked on the OMR answer sheet following the instructions provided on it.
7. Hand over the OMR answer sheet to the invigilator at the end of the examination.
8. In case of a tie, the marks obtained in **Part-A** will be used to determine the order of merit.
8. No additional sheets will be provided. Rough work can be done in the space provided at the end of the booklet.
9. Non-programmable, Standard Calculators are allowed. Mobile phones and all smart devices are **NOT** allowed.
10. Useful constants are provided at the beginning of Part-A in the question paper.
11. OMR without hall ticket number will not be evaluated and University shall not be held responsible.

Useful Constants:

Rydberg constant = 109737 cm^{-1} ; Faraday constant = 96500 C ; Planck constant = $6.625 \times 10^{-34} \text{ J s}$; Speed of light = $2.998 \times 10^8 \text{ m s}^{-1}$; Boltzmann constant = $1.380 \times 10^{-23} \text{ J K}^{-1}$; Gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$; Mass of electron = $9.109 \times 10^{-31} \text{ kg}$; Mass of proton = $1.672 \times 10^{-27} \text{ kg}$; Charge of electron = $1.6 \times 10^{-19} \text{ C}$; $1 \text{ D} = 3.336 \times 10^{-30} \text{ Cm}$; $1 \text{ bar} = 10^5 \text{ N m}^{-2}$; RT/F (at 298.15 K) = 0.0257 V ; Avogadro number = 6.022×10^{23} ; Speed of light = $3.0 \times 10^8 \text{ m s}^{-1}$

PART - A

1. For the following sets of reactions, the correct ordering of the rate constants is:



[A] $k_1 > k_2$ and $k_3 > k_4$

[B] $k_1 > k_2$ and $k_4 > k_3$

[C] $k_2 > k_1$ and $k_4 > k_3$

[D] $k_2 > k_1$ and $k_3 > k_4$

2. The rearrangement reaction that does not require an sp^2 hybridized carbon in the starting material is:

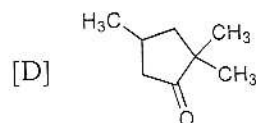
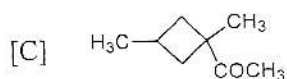
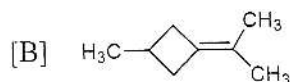
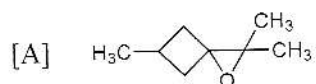
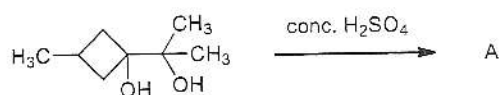
[A] Favorskii rearrangement

[B] Pinacol rearrangement

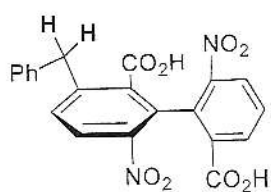
[C] Wittig-Still rearrangement

[D] Oxy-Cope rearrangement

3. The major product **A** obtained in the following transformation is:



4. The topicity of the benzylic protons (indicated **bold**) in the following structure is:



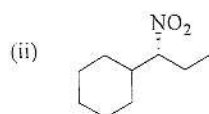
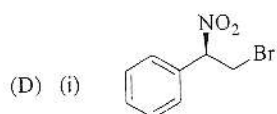
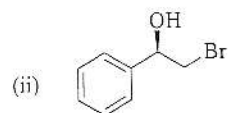
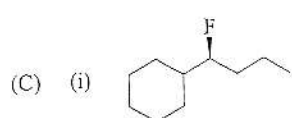
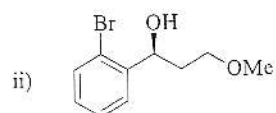
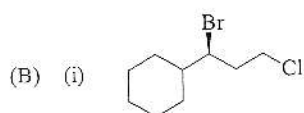
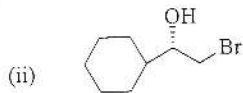
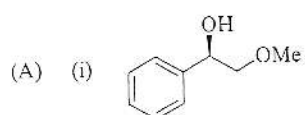
[A] Homotopic

[B] Enantiotopic

[C] Diastereotopic

[D] Do not exhibit topicity

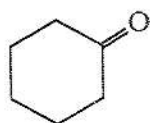
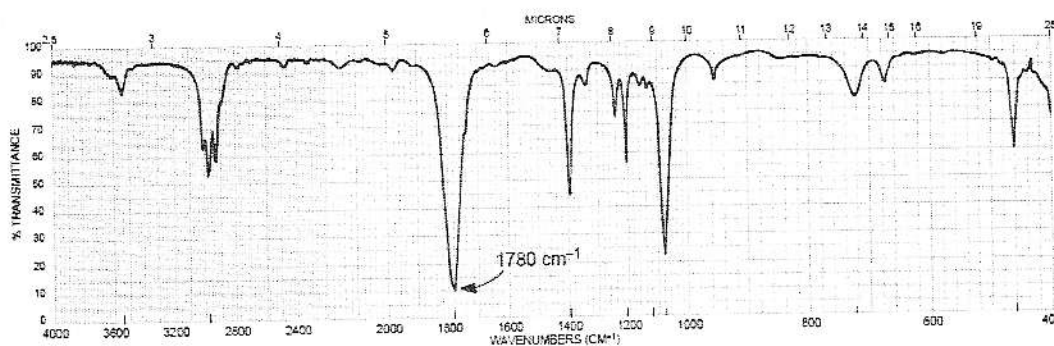
5. A set of two compounds, each having (*R*)-configuration among the following is:



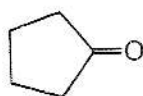
6. A set of two most appropriate oxidizing agents for the conversion of a secondary alcohol into a ketone is:

- [A] i) $\text{Al}(\text{O}i\text{Pr})_3/\text{acetone}$ ii) CrO_3
 [B] i) $\text{CrO}_3/\text{pyridine}$ ii) *m*-chloroperbenzoic acid
 [C] i) $\text{Al}(\text{O}i\text{Pr})_3/2\text{-propanol}$ ii) CrO_3
 [D] i) pyridinium chlorochromate ii) SeO_2

7. The ketone that gives the following IR spectrum is:



A



B

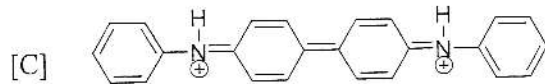
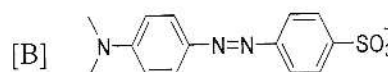
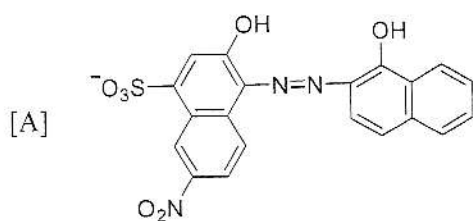


C

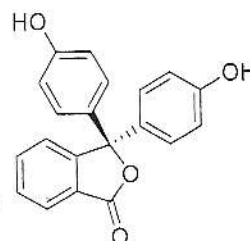


D

8. The metallochromic indicator used in the estimation of Mg^{2+} with ethylenediamine tetraacetic acid is:



[D]



9. Hemerythrin and hemocyanin, respectively are:

- [A] both dinuclear iron metalloproteins
- [B] dinuclear copper and mononuclear iron-porphyrin metalloproteins
- [C] dinuclear iron and dinuclear copper metalloproteins
- [D] multinuclear iron and trinuclear iron metalloproteins

10. The deficiencies of the metals, Zn and Cu in human beings, respectively cause:

- [A] bone deterioration and anemia
- [B] glucose intolerance and skin disease
- [C] hair loss and growth retardation
- [D] growth retardation and brain disease

11. Magnetic resonance imaging (MRI) in humans use the coordination complexes of:

- [A] Cd(II) and Zn(II)
- [B] Ni(II) and Co(II)
- [C] Mn(II) and Gd(III)
- [D] Mo(V) and W(V)

12. The primary role of chlorophyll in photosynthesis is:

- [A] absorption of light
- [B] absorption of water
- [C] storage of energy
- [D] production of chemical energy and its storage

13. The decomposition temperature of carbonates of Group II elements vary in the order:

- [A] $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3 < \text{SrCO}_3$
- [B] $\text{BeCO}_3 > \text{MgCO}_3 > \text{CaCO}_3 > \text{SrCO}_3$
- [C] $\text{BeCO}_3 < \text{MgCO}_3 > \text{CaCO}_3 > \text{SrCO}_3$
- [D] $\text{BeCO}_3 > \text{MgCO}_3 < \text{CaCO}_3 < \text{SrCO}_3$

14. The boiling point of hydrides of group IV elements vary in the order:

- [A] $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4$ [B] $\text{CH}_4 < \text{SiH}_4 > \text{GeH}_4 < \text{SnH}_4$
[C] $\text{CH}_4 > \text{SiH}_4 > \text{GeH}_4 > \text{SnH}_4$ [D] $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 > \text{SnH}_4$

15. The electronic ground state of nitric oxide is:

- [A] $^1\Sigma$ [B] $^2\Sigma$
[C] $^1\Pi$ [D] $^2\Pi$

16. The highest symmetry element of allene ($\text{H}_2\text{C}=\text{C}=\text{CH}_2$) is:

- [A] C_2 [B] C_4
[C] S_2 [D] S_4

17. In the process of nucleation and crystal growth, formation of the nucleus (homogeneous nucleation) is controlled by its:

- [A] surface free energy
[B] bulk free energy
[C] surface and bulk free energies
[D] only surface tension

18. Work function of a solid has the units of:

- [A] entropy
[B] energy
[C] potential
[D] force

19. The rate constant of a reaction decreases with increase in temperature. This indicates that the:

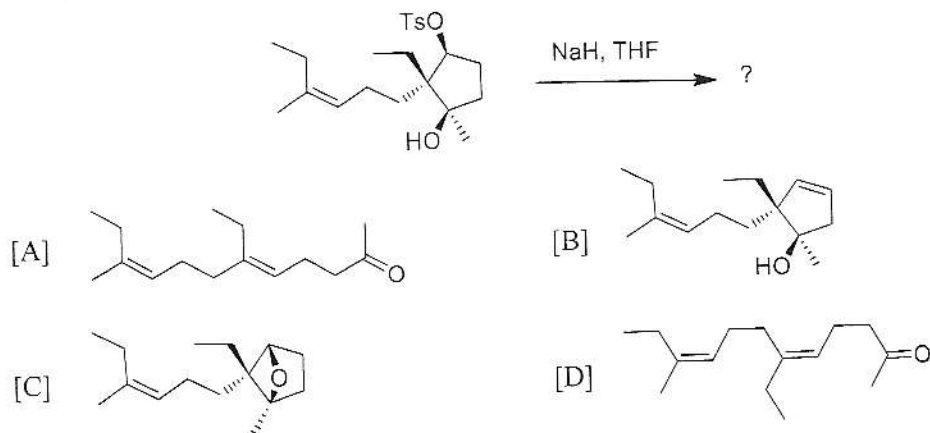
- [A] reaction is exothermic
[B] frequency factor of the reaction is low
[C] reaction proceeds in multiple steps
[D] reaction occurs by a tunneling mechanism

20. The correct unit of gyromagnetic ratio of a nucleus is:

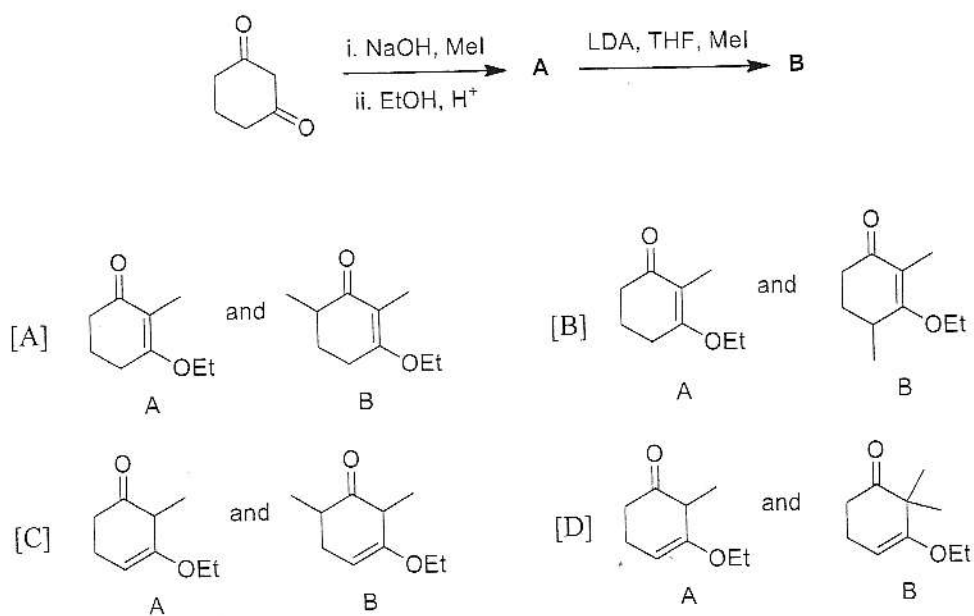
- [A] radian s^{-1}
- [B] radian $M^{-1} s^{-1}$
- [C] MHz T^{-2}
- [D] radian $T^{-1} s^{-1}$

PART - B

21. The product of the following reactions is:



22. Products **A** and **B** in the following reaction sequence are:



23. Reagents used in the Cadogan and Schmidt reaction, respectively are:

- [A] triethyl phosphite, N_3H [B] triethyl orthoformate, NH_2OH/H^+
 [C] triethyl borate, TsOH [D] Et_2Zn , NBS

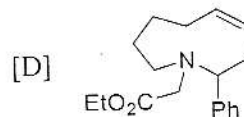
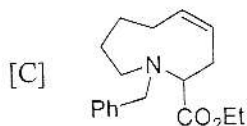
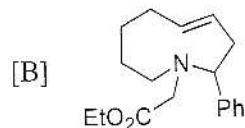
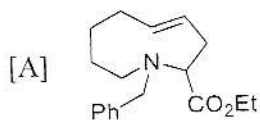
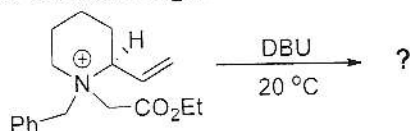
24. The heterocyclic ring present in the amino acid histidine is:

- [A] isoquinoline [B] indole
 [C] pyrrole [D] imidazole

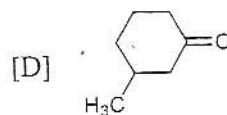
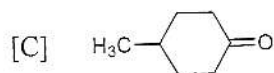
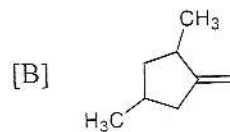
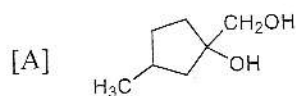
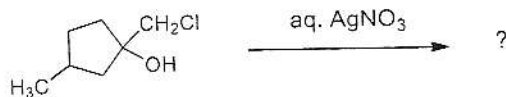
25. Quercetin is a flavonoid widely distributed in nature. The biosynthetic precursor for quercetin in plants is:

- [A] phenylalanine [B] tryptophan
 [C] methionine [D] proline

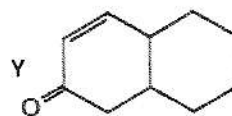
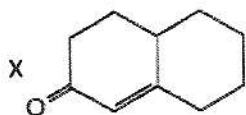
26. The major product formed in the following reaction is:



27. The major product obtained in the following transformation is:



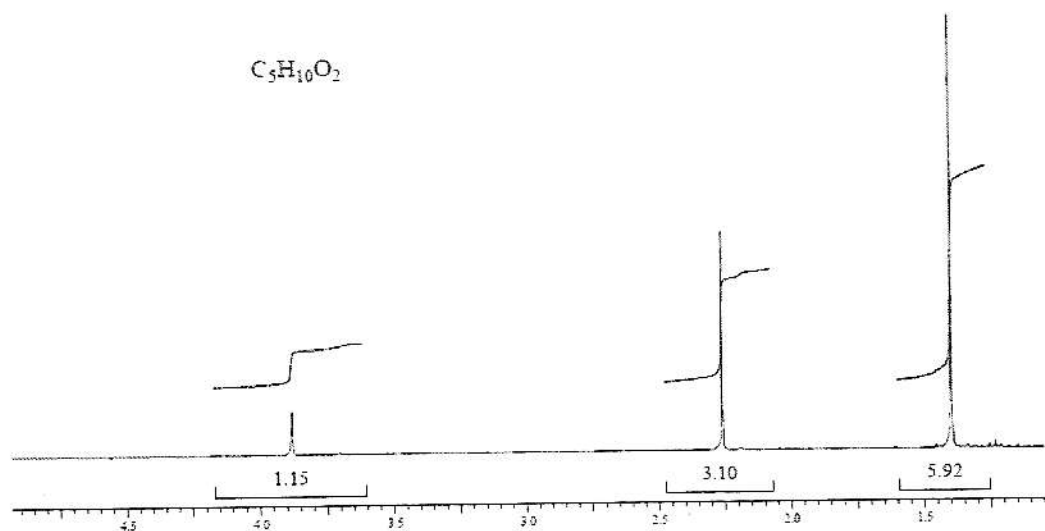
28. The predicted absorption maxima of compounds X and Y, are:



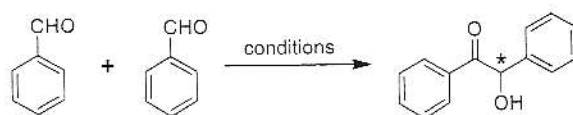
- [A] (X) 239 nm and (Y) 245 nm [B] (X) 244 nm and (Y) 245 nm
 [C] (X) 239 nm and (Y) 227 nm [D] (X) 244 nm and (Y) 227 nm

29. A compound with the molecular formula $C_5H_{10}O_2$ gives the following 1H -NMR spectrum. The resonances at 1.4 δ , 2.25 δ and 3.9 δ are in the intensity ratio, 6:3:1. The most likely structure of the compound is:

- [A] 1-hydroxy-3-methylbutan-2-one [B] 3-hydroxy-3-methylbutan-2-one
 [C] 1-hydroxypentan-3-one [D] 2-hydroxypentan-3-one

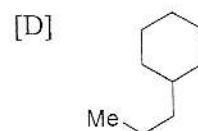
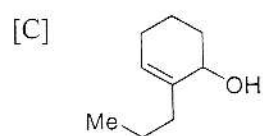
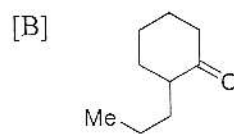
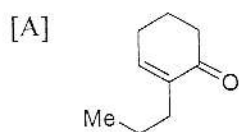
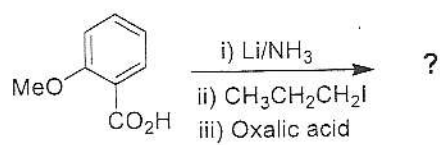


30. The reagent needed for the following transformation is:

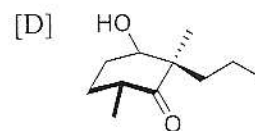
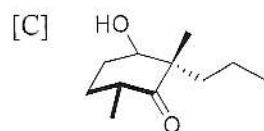
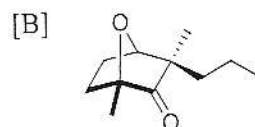
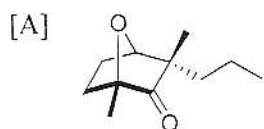
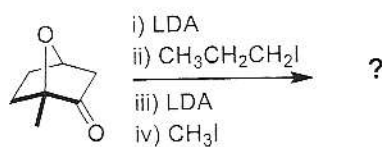


- [A] KOH [B] Quinine
 [C] Proline [D] Thiamine

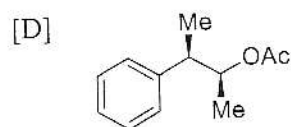
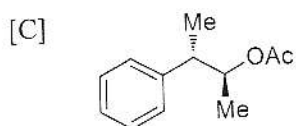
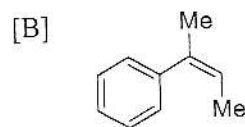
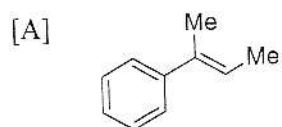
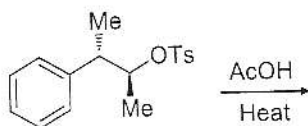
31. The most appropriate product in the following reaction is:



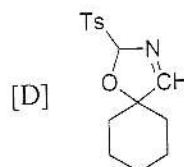
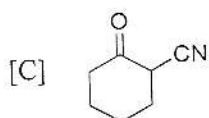
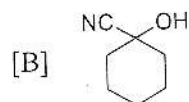
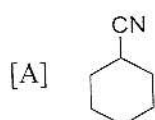
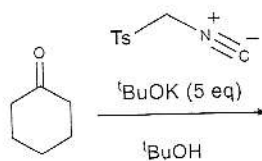
32. The most likely product in the following transformation is:



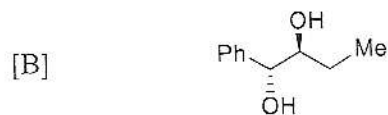
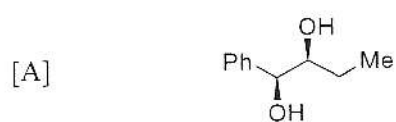
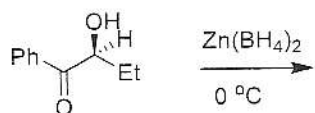
33. The major product in the following transformation is:



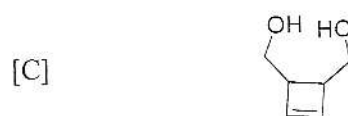
34. The product obtained in the following transformation is:



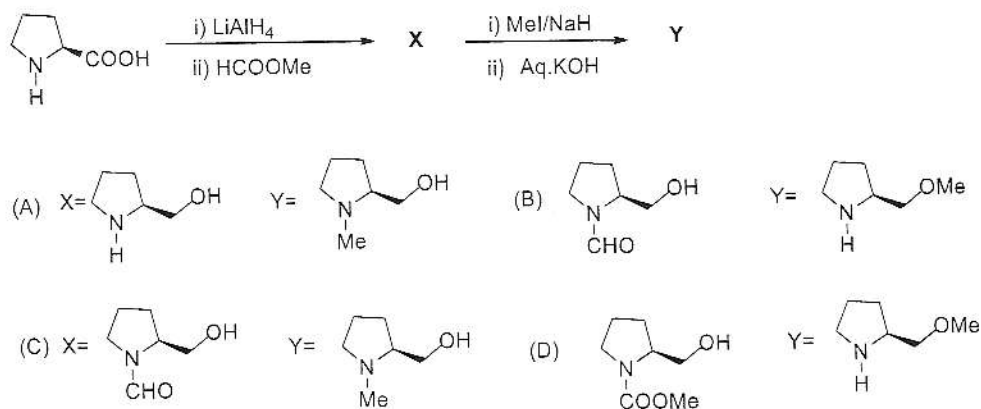
35. The major product formed in the following asymmetric induction is:



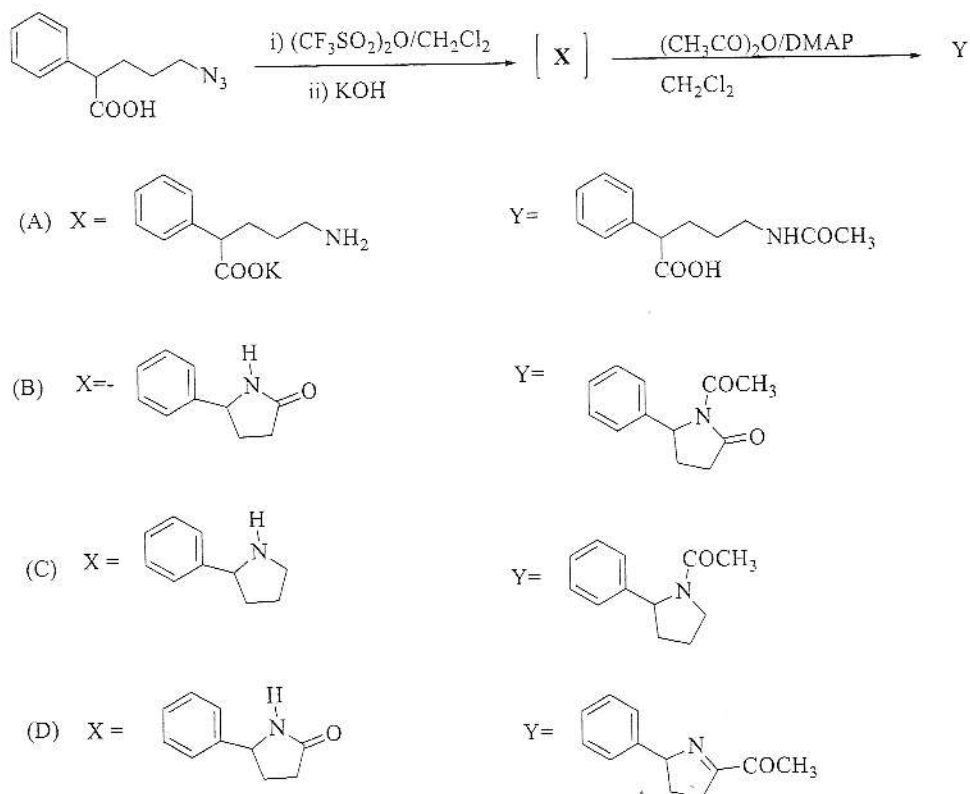
36. The oxepin **X** undergoes valence tautomerism followed by acid-catalyzed ring opening to give:



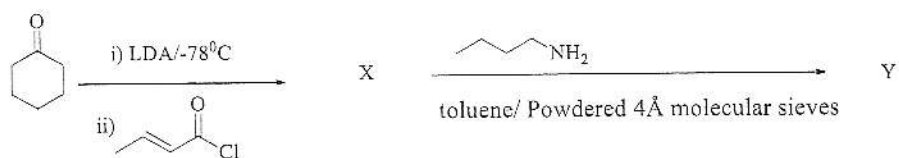
37. The products **X** and **Y** in the following reaction sequence are:



38. The products **X** and **Y** in the following reaction sequence are:

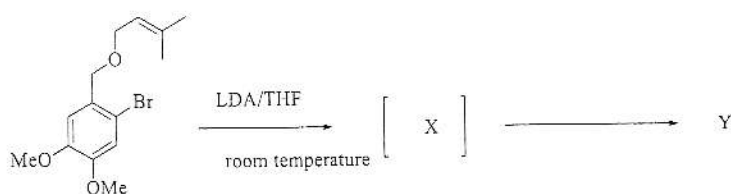


39. The products X and Y in the following reaction sequence are:



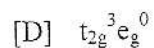
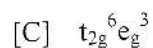
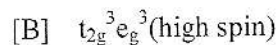
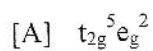
- (A) X = Y =
- (B) X = Y =
- (C) X = Y =
- (D) X = Y =

40. The products X and Y in the following reaction sequence are:



- (A) X = Y =
- (B) X = Y =
- (C) X = Y =
- (D) X = Y =

46. The octahedral d^n configuration which has a contribution from the orbital part to the value of the effective magnetic moment is:



47. The number of improper axis of rotation (S_4) in a tetrahedral AX_4 molecule is:

[A] 2

[B] 4

[C] 3

[D] 1

48. The total number of microstates for a d^3 ion and the 1D term respectively are:

[A] 120 and 5

[B] 120 and 0

[C] 45 and 0

[D] 0 and 45

49. Using Pauling's rules, the pK_a values of $RA_3O_3H_2$ are:

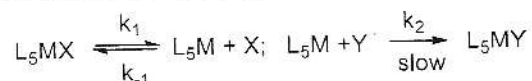
[A] 3.0 and 8.0

[B] 2.3 and 7.3

[C] 4.0 and 7.0

[D] -2.3 and 3.4

50. For the stoichiometric dissociative mechanism for substitution in octahedral complexes with the equations given below, the correct rate expression for the overall reaction is:



[A] $\frac{k_1 k_2 [L_5MX][Y]}{k_{-1}[X] + k_2[Y]}$

[B] $\frac{k_1 k_{-1} [L_5MX][Y]}{k_{-1}[X] + k_2[Y]}$

[C] $\frac{k_{-1}[X] + k_2[Y]}{k_1 k_{-1} [L_5MX][Y]}$

[D] $\frac{k_1 k_2 [L_5MX][Y]}{k_{-1}[X] + k_2[Y] + k_1 [L_5MX]}$

51. The increasing order of *trans*-labilizing effect in the substitution reactions of square planar platinum complexes is:
- [A] pyridine < NH₃ < NO₂⁻ < H⁻ < CO
 [B] NH₃ < pyridine < NO₂⁻ < H⁻ < CO
 [C] NO₂⁻ < NH₃ < pyridine < H⁻ < CO
 [D] NH₃ < pyridine < NO₂⁻ < CO < H⁻
52. The number of lines expected in the X-band ESR spectrum of VO(acac)₂ complex in a solution state at 25°C is:
- [A] 6 [B] 8
 [C] 7 [D] 4
53. The spectroscopic technique useful to distinguish the spin state and oxidation state of iron is:
- [A] IR [B] NMR
 [C] Mössbauer [D] UV-Vis
54. The number of lone electron pairs on the central atom and the shapes of the species ClO₃⁻ and IF₅ are respectively:
- [A] (1, pyramidal); (1, trigonal bipyramidal)
 [B] (0, planar); (1, square pyramidal)
 [C] (1, pyramidal); (1, square pyramidal)
 [D] (0, planar); (1, trigonal bipyramidal)
55. The correct statement with respect to XeF₅⁻ and/or TeF₇⁻ is:
- [A] both have at least one bond angle as 90°
 [B] both have at least one bond angle as 72°
 [C] in XeF₅⁻, there are 90° and 120° bond angles
 [D] TeF₇⁻ has a monocapped octahedral shape

56. The dipole moment of the compounds CH_3Cl , CClF_3 and PF_2Cl_3 are in the order:

- [A] $\text{CH}_3\text{Cl} > \text{PF}_2\text{Cl}_3 > \text{CClF}_3$ [B] $\text{CClF}_3 > \text{PF}_2\text{Cl}_3 > \text{CH}_3\text{Cl}$
 [C] $\text{PF}_2\text{Cl}_3 > \text{CH}_3\text{Cl} > \text{CClF}_3$ [D] $\text{CH}_3\text{Cl} > \text{CClF}_3 > \text{PF}_2\text{Cl}_3$

57. $\text{C}_2\text{B}_4\text{H}_8$ is:

- [A] *nido* carborane [B] *arachno* carborane
 [C] *hypo* carborane [D] *closo* carborane

58. $\text{CaMg}(\text{SiO}_3)_2$ is an example of:

- [A] chain silicate [B] orthosilicate
 [C] cyclic silicates [D] pyrosilicate

59. The bond order of $[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]^+$ and $[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]^{+2}$ are respectively:

- [A] 4 and 3 [B] 3.5 and 4
 [C] 2 and 3 [D] 3 and 2

60. Requirement for an alkene complex to form a metallocyclopropane structure is:

- [A] electron rich metal and electron withdrawing substituents on the alkene carbon
 [B] electron donating substituents on the alkene carbon
 [C] trans effect
 [D] perpendicular orientation of alkene towards the complex plane

61. A molecule with C_3 and σ_h symmetry elements is:

- [A] PF_5 [B] BrF_5
 [C] CH_4 [D] NH_3

62. The bond order of O_2 molecule, when it is in its first ${}^1\Delta_g$ state is:

- [A] 1 [B] 2
 [C] 3 [D] 4

63. The ground state wave function of LiH would be dominated by the configuration ($2s_{\text{Li}}$ and $1s_{\text{H}}$ are the 2s orbital of Li and 1s orbital of H, respectively):
- [A] $2s_{\text{Li}}^2$ [B] $1s_{\text{H}}^2$
[C] $2s_{\text{Li}}^1 \cdot 1s_{\text{H}}^1$ [D] All three configurations with equal weight
64. In the X-ray diffraction experiment on a crystal, the peaks due to the Miller planes ($h_1 k_1 l_1$) and ($h_2 k_2 l_2$) appear at 2θ values, 20° and 30° respectively. Ratio of the corresponding interplanar spacings d_1/d_2 is:
- [A] 1.49
[B] 0.67
[C] 0.51
[D] 0.15
65. Silicon is a semiconductor that absorbs visible light. Its band gap (eV) is approximately:
- [A] 100
[B] 50
[C] 10
[D] 1
66. The magnetic exchange interaction between nearest neighbor spin sites in a ferrimagnetic material is:
- [A] ferromagnetic
[B] antiferromagnetic
[C] Pauli paramagnetic
[D] metamagnetic
67. The packing fraction of a hexagonal 2-dimensional lattice is:
- [A] 0.52
[B] 0.68
[C] 0.74
[D] 0.91

68. A reaction which proceeds through the mechanism, $A + B \xrightleftharpoons[k_d]{k_d} X \xrightarrow{k_1} \text{products}$, is diffusion controlled, when:
- [A] $k_1 \ll k_d$
 [B] $k_1 \ll k_d$
 [C] $k_1 \ll k_d$
 [D] $k_1 \gg k_d$
69. Among the following molecules, H_2 , HCl , CH_4 and H_2O , those which show a rotational Raman spectrum are:
- [A] H_2 and HCl only
 [B] H_2 and CH_4 only
 [C] HCl and H_2O only
 [D] H_2 , HCl and H_2O only
70. The vibrational temperature of F_2 molecule ($\tilde{\nu} = 917 \text{ cm}^{-1}$) is nearly equal to (in absolute scale of temperature):
- [A] 132
 [B] 123
 [C] 1320
 [D] 1230
71. The rate of a chemical reaction was found to triple when the temperature is raised from 24°C to 49°C . The activation energy of the reaction is nearly equal to (in kJ mol^{-1}):
- [A] 8.0
 [B] 17.0
 [C] 35.0
 [D] 70.0
72. Sum of the infinite series, $1 + x + x^2 + x^3 + \dots$ is:
- [A] x
 [B] x^{-1}
 [C] $(1 + x)^{-1}$
 [D] $(1 - x)^{-1}$
73. If $\hat{H} = \frac{p^2}{2m} + V(x)$, then $[\hat{x}, \hat{H}]$ equation is given as:
- [A] $\frac{\hbar p}{m}$
 [B] $-\frac{\hbar p}{im}$
 [C] $-\frac{i\hbar p}{m}$
 [D] $\frac{-\hbar p}{m}$

74. The mean free path of carbon dioxide molecule ($\sigma = 0.52 \text{ nm}^2$) at 25°C and 15 atm is nearly equal to (in nm):
- [A] 3.73 [B] 5.22
[C] 2.97 [D] 6.56
75. The activities of Cl^- , F^- , Na^+ and K^+ ions in an aqueous solution containing 0.01 mol kg^{-1} of NaCl and 0.05 mol kg^{-1} of KF are respectively:
- [A] 0.044, 0.088, 0.044 and 0.088 [B] 0.075, 0.0375, 0.075 and 0.0375
[C] 0.044, 0.044, 0.088 and 0.088 [D] 0.0375, 0.0375, 0.075 and 0.075
76. The work done when 20 g of CO_2 undergoes a reversible adiabatic expansion from 200 cm^3 to 2 dm^3 at 298 K [$C_{p,m}(\text{CO}_2) = 37.11 \text{ kJ mol}^{-1}$; assume ideal gas behavior] is:
- [A] -1.71 kJ [B] -0.86 kJ
[C] -0.46 kJ [D] -1.9 kJ
77. 2 V is applied on a cell with KCl solution as the electrolyte and the two electrodes, 4 cm apart. The distance moved by K^+ ion in one hour [conductance of KCl at infinite dilution = $150 \text{ Ohm}^{-1}\text{cm}^2$; consider that K^+ and Cl^- have equal ionic mobility] is:
- [A] 1.4 cm [B] 2.8 cm
[C] 0.57 cm [D] 2.4 cm
78. Oxidation of oxalic acid was carried out by acidic MnO_4^- in a reversible cell. Given, $E_{\text{MnO}_4^-/\text{Mn}^{+2}}^0 = 1.51 \text{ V}$ and $E_{\text{CO}_2/\text{oxalate}}^0 = -0.49 \text{ V}$, the equilibrium constant of the cell reaction at 25°C is close to:
- [A] 10^{339} [B] 10^{170}
[C] 10^{68} [D] 10^{38}

79. The distance from the nucleus, at which the probability of finding the electron in the $1s$ orbital of H atom is maximum, is ($a_0 =$ Bohr radius):

[A] 0

[B] a_0

[C] $\frac{a_0}{2}$

[D] $2a_0$

80. The spin wave function $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$ of the electrons in H_2 molecule is:

[A] not an eigen function of the \hat{S}^2 operator

[B] an eigen function of the \hat{S}^2 operator with eigen value $+\frac{3}{4}\hbar^2$

[C] an eigen function of the \hat{S}^2 operator with eigen value 0

[D] an eigen function of the \hat{S}^2 operator with eigen value $-\frac{3}{4}\hbar^2$

*****End*****