Part-B

21. Identify the species, those obey the 18 electron rule, from the following:

(A) Cu—CO   (B) Mn(OC)(CO)   (C) Cr(OC)(CO)(CO)   (D) V(OC)(OC)(CO)(CO)

(a) A and B   (b) B and C   (c) C and D   (d) A and D
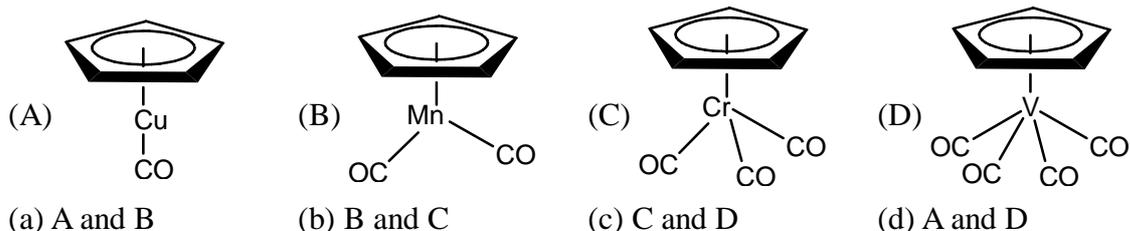
22. The following transformation
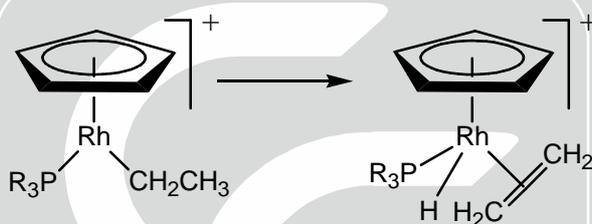
is an example of
(a) oxidative addition   (b) insertion
(c) β-hydride elimination   (d) reductive elimination

23. $[Ni^{II}L_6]^{n+ \text{ or } n-}$ shows absorption bands at 8500, 15400, and 26000 cm^{-1} whereas $\left[Ni^{II}L'_6\right]^{n+ \text{ or } n-}$, at 10750, 17500 and 28200 cm^{-1}. L and L' are respectively

(a) OH^- and N_3^- (b) Cl^- and I^- (c) NCS^- and RCO_2^- (d) H_2O and NH_3

24. The number of microstates present in ^3F term is
(a) 3   (b) 21   (c) 9   (d) 28

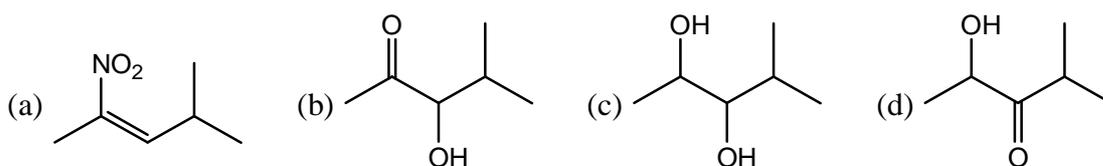25. $CpM\left[Cp \text{ is } \left(\eta^5\text{-}C_5H_5\right)\right]$ fragment isolobal with a BH fragment is

(a) CpGe   (b) CpMn   (c) CpRu   (d) CpCo

26. The number of metal-metal bonds in $\left[Co_2Fe_2(CO)_{11}(\mu_4-PPh)_2\right]$ is
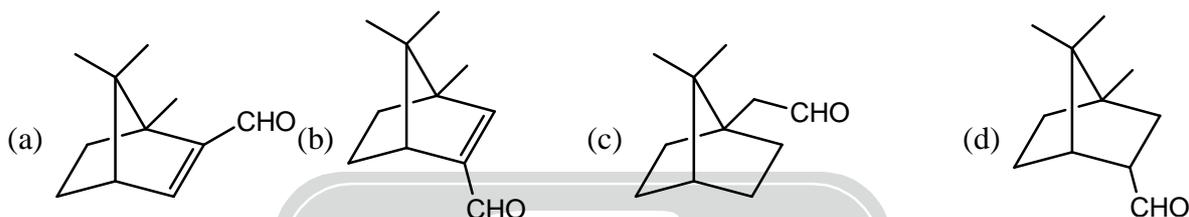(a) 3   (b) 4   (c) 5   (d) 6

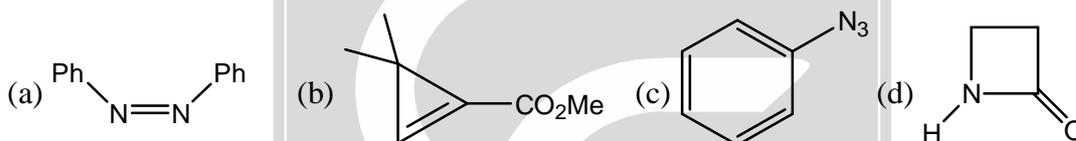27. Correct combination for π and π^* orbitals in B_2 molecule is

	π	π^*
(a)	Gerade	Ungerade
(b)	Ungerade	Gerade
(c)	Gerade	Gerade
(d)	Ungerade	Ungerade

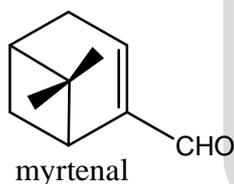28. The correct shape of $[TeF_5]^-$ ion on the basis of VSEPR theory is
    (a) trigonal bipyramidal   (b) square pyramidal
    (c) pentagonal planar   (d) see-saw

29. The numbers of P-S and P-P bonds in the compound P_4S_3 are, respectively
    (a) 6 and 3   (b) 4 and 3   (c) 3 and 6   (d) 6 and 2

30. In the iodometric titration of sodium thiosulfate $(Na_2S_2O_3)$ with acidic dichromate solution, 25 mL of 0.1 M dichromate requires 25 mL of 'x' M thiosulfate. The value of 'x' is
    (a) 0.2   (b) 0.1   (c) 0.6   (d) 0.4

31. Decomposition temperature of $CaCO_3$ in thermogravimetric analysis will be highest in dynamic atmosphere of
    (a) nitrogen   (b) synthesis gas
    (c) 1 : 1 mixture of O_2 and CO   (d) water gas

32. On two sequential electron capture, $_{56}Ba^{131}$ will give
    (a) $_{54}Xe^{131}$ (b) $_{54}Xe^{130}$ (c) $_{56}Ce^{131}$ (d) $_{56}Ce^{130}$

33. The compound which dissolves in $POCl_3$ to give a solution with highest chloride ion concentration, is
    (a) Et_3N (b) KCl   (c) $FeCl_3$ (d) $SbCl_5$

34. In the absence of bound globin chain, heme group on exposure to O_2 gives the iron-oxygen species

    (a) (III)Fe—O—Fe(III)

    (b) (III)Fe—O—O$^{\ominus}$

    (c) (III)Fe—O—O—Fe(III)

    (d) $Fe(IV) = O$

35. For monoionic complex $\left[UO_2 \left(NO_3 \right)_3 \right]^-$, the correct coordination number and geometry respectively, are
    (a) 8 and hexagonal bipyramidal   (b) 5 and square pyramidal
    (c) 8 and square antiprism   (d) 5 and trigonal bipyramidal

36. Chelate effect is
    (a) predominantly due to enthalpy change
    (b) predominantly due to entropy change
    (c) independent of ring size
    (d) due to equal contribution of entropy and enthalpy change

37. The major product formed in the following reaction is

38. The major product formed in the following reaction is

(a) [structure: NO$_2$ substituted alkene]

(b) [structure: ketone with OH]

(c) [structure: diol with two OH]

(d) [structure: OH and ketone]

39. The major product formed in the following reaction is

[structure: camphor-type tosylhydrazone]

$$\xrightarrow[\text{(ii) DMF}]{\text{(i) n-BuLi(2.1 equiv.)}}$$

(a) [bicyclic structure with CHO]

(b) [bicyclic structure with CHO]

(c) [bicyclic structure with CHO]

(d) [bicyclic structure with CHO]

40. Among the following, the compound that displays an IR band at 2150 cm^{-1} is

(a) Ph-N=N-Ph

(b) [cyclopropene with CO$_2$Me]

(c) [phenyl azide, N$_3$]

(d) [azetidinone, N–H and C=O]

41. In the ^{1}H NMR spectrum of myrtenal, the two methyl groups are expected to display signals at (chemical shift values (δ) in ppm)

[structure: myrtenal with CHO]
myrtenal

(a) 1.35 (s, 3H) and 5.0 (s, 3H)   (b) 0.74 (s, 3H) and 1.33 (s, 3H)
(c) 1.22 (s, 6H)   (d) 0.70 (s, 6H)

42. Among the following, the compound(s) that can be classified as terpene derivative is(are)

(A) [chromone structure with Ph, OH, O]

(B) [bicyclic structure with N–OH oxime]

(C) [tropane structure with N–CH$_3$ and C=O]
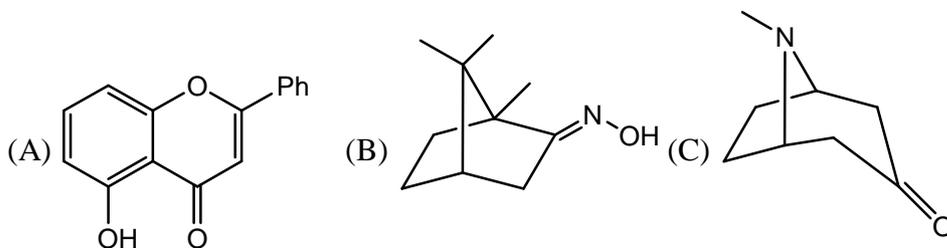
(a) A and B   (b) A only   (c) B only   (d) B and C

43. The frontier orbital interactions involved in the formation of the carbocation intermediate in the reaction of isobutylene with HCl are

(a) π of olefin and σ^* of HCl   (b) π of olefin and σ of HCl

(c) π^* of olefin and σ^* of HCl   (d) π^* of olefin and σ of HCl

44.   The major product formed in the following reaction is

(Cbz = PhCH$_2$OCO)

(a)   (b)

(c)   (d)
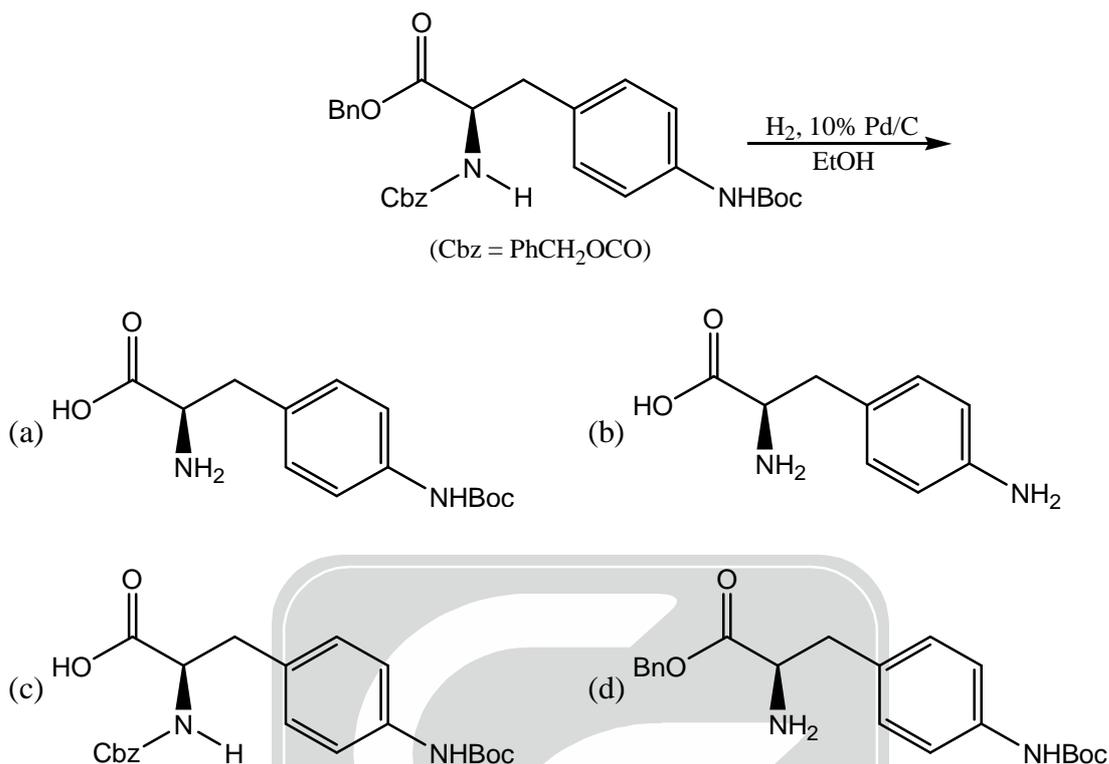
45.   In the UV-visible absorption spectrum of an α, β -unsaturated carbonyl compound, with increasing solvent polarity,

(a) $n - \pi^*$ transitions undergo hypsochromic shift, $\pi - \pi^*$ undergo bathochromic shift

(b) $n - \pi^*$ transitions undergo bathochromic shift, $\pi - \pi^*$ undergo hypsochromic shift

(c) both $n - \pi^*$ and $\pi - \pi^*$ transitions undergo bathochromic shift

(d) both $n - \pi^*$ and $\pi - \pi^*$ transitions undergo hypsochromic shift.

46.   The major product formed in the following reaction is

(a)   (b)

(c)   (d)
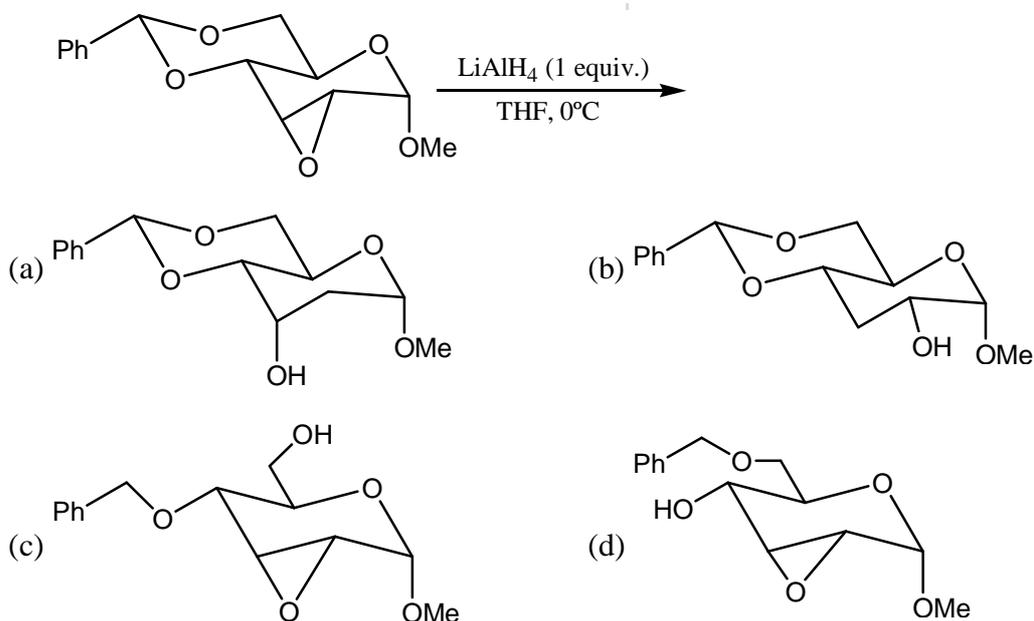
47. In the following compound, the stereochemical descriptor for H_a and H_b is
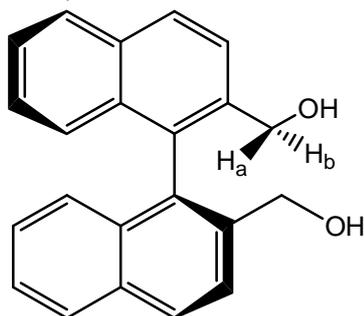
    (a) enantiotopic   (b) diastereotopic   (c) homotopic   (d) constitutionally heterotopic

48. The correct statement are about the reaction of X and Y with $NaNH_2$ are
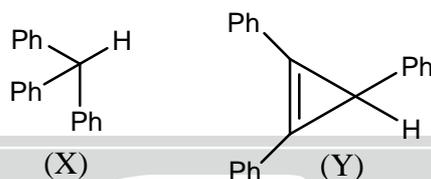
(A) X reacts faster than Y   (B) Y reacts faster than X
(C) X and Y behave as Lewis acids   (D) X is stronger Bronsted acid than Y
    (a) A and C   (b) A and D   (c) B and C   (d) B and D

49. The correct statements about conformations X and Y of 2-butanone are
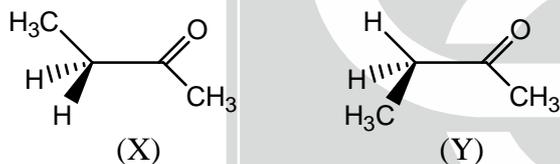
(A) X is more stable than Y   (B) Y is more stable than X
(C) Methyl groups in X are anti   (D) Methyl groups in Y are gauche
    (a) A and D   (b) A and C   (c) B and C   (d) A, C and D

50. The correct order of magnitude of 'A values' for the given substituents in cyclohexane derivatives is

$$X = CH_3$$
$$X = CN$$
$$X = Ph$$
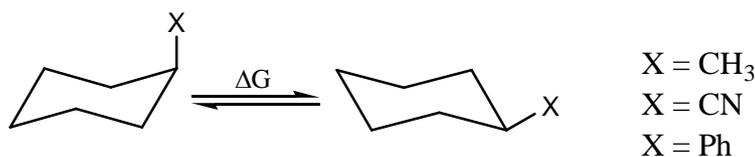
    (a) Ph > CN > Me   (b) Me > Ph > CN   (c) CN > Me > Ph   (d) Ph > Me > CN

51. The correct order of pKa values for the compounds X, Y and Z is

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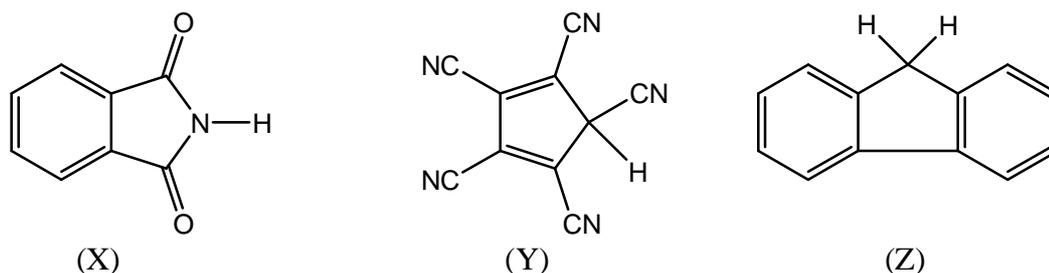
    (a) X > Y > Z   (b) Y > Z > X   (c) Z > X > Y   (d) Y > X > Z

52. The following transformation proceeds through two consecutive electrocyclic processes, which are
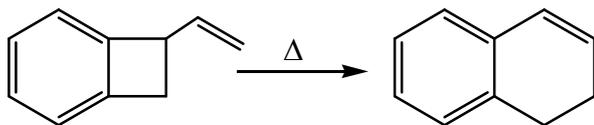

    (a) 4π conrotatory and 6π conrotatory
    (b) 4π disrotatory and 6π conrotatory
    (c) 4π conrotatory and 6π disrotatory
    (d) 4π disrotatory and 6π disrotatory

53. The simultaneous eigenfunctions of angular momentum operators L^2 and L_z are
    (a) all of 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals
    (b) only 2s, $2p_x$ and $2p_y$ orbitals
    (c) only 2s and $2p_z$ orbitals
    (d) only $2p_z$ orbital

54. An ideal gas is composed of particles of mass M in thermal equilibrium at a temperature T in one container. Another container contains ideal gas particles of mass 2M at a temperature 2T. The correct statement about the two gases is
    (a) average kinetic energy and average speed will be same in the two cases
    (b) both the averages will be doubled in the second case
    (c) only the average kinetic energy will be doubled in the second case
    (d) only the average speed will be doubled in the second case

55. The lowest energy term for the d^6 configuration is
    (a) ^2D (b) ^5D (c) ^1P (d) ^1D

56. If the rates of a reaction are R1 and R2 at concentrations C_1 and C_2 of a reactant respectively, the order of reaction, 'n' (assuming that the concentrations of all other reactants and T remain constant) with respect to that reactant is given by

    (a) $n = \dfrac{\log R_1 - \log R_2}{\log C_1 - \log C_2}$
    (b) $n = \dfrac{\log C_1 - \log C_2}{\log R_1 - \log R_2}$
    (c) $n = \dfrac{\log C_1 - \log R_1}{\log C_2 - \log R_2}$
    (d) $n = \dfrac{\log C_2 - \log R_2}{\log C_1 - \log R_1}$

57. Experimentally determined rate law for the chemical reaction,

    $2NO_2F \rightarrow 2NO_2 + F_2$ is $R = k[NO_2F]$

    The rate determining step consistent with the rate law is

    (a) $2NO_2F \rightarrow 2NO_2 + F_2$
    (b) $NO_2F + F \rightarrow NO_2 + F_2$
    (c) $NO_2F \rightarrow NO_2 + F$
    (d) $NO_2 + F \rightarrow NO_2F$

58. The symmetry point group of the most stable geometry of the following molecule $Cl(H)C = C = C(H)Cl$ is
    (a) C_2 (b) C_1 (c) C_{2v} (d) C_{2h}

59. The eigenfunctions of the Hamiltonian H (H = T + V) of a harmonic oscillator are (where T and V are kinetic energy and potential energy operators, respectively)
    (a) eigenfunctions of T as well as V
    (b) eigenfunctions of T, but not of V
    (c) eigenfunctions of V, but not of T
    (d) eigenfunctions of neither T nor V

60. In a potentiometric titration, the end point is characterised by

    (a) $\dfrac{dE}{dV} = 0, \dfrac{d^2E}{dV^2} = 0$
    (b) $\dfrac{dE}{dV} \neq 0, \dfrac{d^2E}{dV^2} = 0$
    (c) $\dfrac{dE}{dV} = 0, \dfrac{d^2E}{dV^2} \neq 0$
    (d) $\dfrac{dE}{dV} \neq 0, \dfrac{d^2E}{dV^2} \neq 0$

    where E is the emf of the titration cell and V is the volume of the titrant added

61. On titrating conductometrically a NaOH solution with a mixture of HCl and CH_3CO_2H solutions, plot of the volume of mixed acid added (b) in y-axis against the conductance (a) in x-axis is expected to look like

(a)   (b)   (c)   (d)
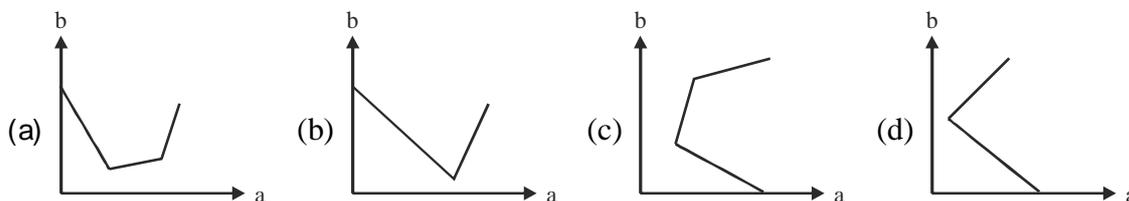
62. $\left(\dfrac{\partial H}{\partial P}\right)_T$ has the dimension of

(a) pressure   (b) volume   (c) temperature   (d) heat capacity

63. In a cubic crystal, the plane [100] is equally inclined to the planes
(a) [010] and [011]   (b) [010] and [110]   (c) [001] and [101]   (d) [110] and [011]

64. The standard electrode potential E^0 at a fixed temperature and in a given medium is dependent on
(a) only the electrode composition
(b) the electrode composition and the extent of the reaction
(c) the extent of the electrode reaction only
(d) the electrode reaction and the electrode composition

65. In a titration, the percentage uncertainties in the measured aliquot volume and the measured titre volume are $\pm x$ and $\pm y$ respectively. The percentage error in the calculated concentration of aliquot is

(a) $x + y$ (b) xy (c) $\left(xy\right)^{1/2}$ (d) $\left(x^2 + y^2\right)^{1/2}$

66. For an ideal gas at 300K

(a) $\left(\dfrac{\partial U}{\partial V}\right)_T = 0$ (b) $\left(\dfrac{\partial U}{\partial T}\right)_V = 0$ (c) $\left(\dfrac{\partial H}{\partial T}\right)_P = 0$ (d) $\left(\dfrac{\partial G}{\partial T}\right)_P = 0$

67. The first excited state of hydrogen molecule is

(a) $^1\Sigma_g^+$ (b) $^1\Sigma_u^-$ (c) $^3\Sigma_g^-$ (d) $^3\Sigma_u^+$

68. When river water containing colloidal clay flows into the sea, the major cause of silting is
(a) accumulation of sand at the bottom   (b) flocculation and coagulation
(c) decreased salinity of sea water   (d) micellization

69. Match the metal given in Column-A with its medicinal use as a compound in Column-B

Column-A	Column-B
(A) Gd	(I) Cancer
(B) Au	(II) Maniac depression
(C) Pt	(III) MRI contrast agent
(D) Li	(IV) Arthritis

Correct match is
(a) A-II; B-III; C-IV; D-I   (b) A-IV; B-II; C-I, D-III
(c) A-III; B-IV; C-I; D-II   (d) A-I; B-II; C-III; D-IV

70. At pH 10, tryptophan exists as

(a)

(b)

(c)

(d)
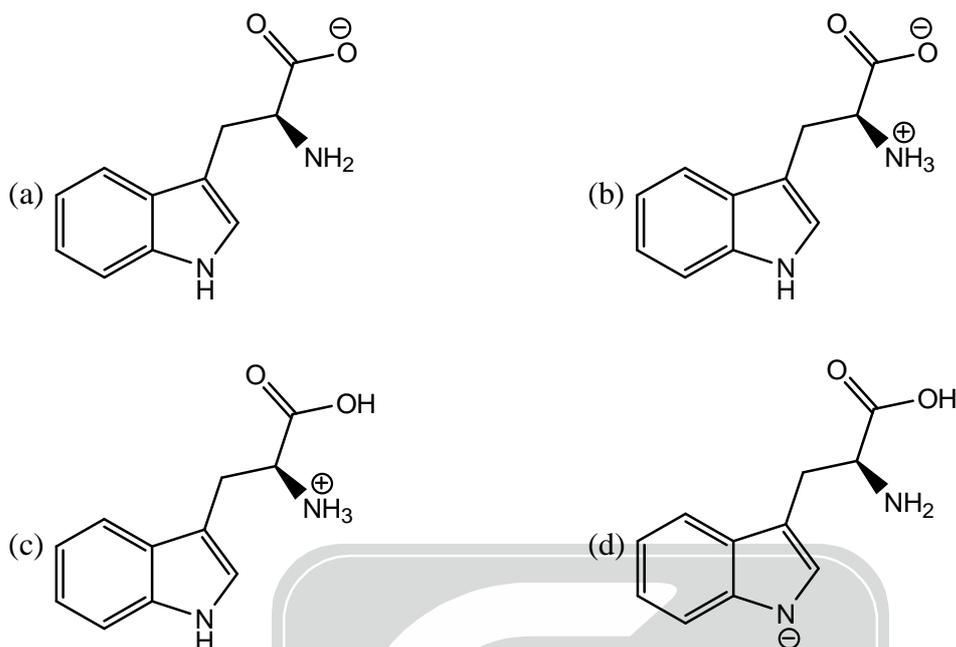
PART-C

71. Complex $\left[Cr\left(bipyridyl \right)_3 \right]^{3+}$, shows red phosphorescence due to transition

(a) ${}^4T_{2g} \leftarrow {}^4A_{2g}$ (b) ${}^4T_{1g} \leftarrow {}^4A_{2g}$ (c) ${}^4A_{2g} \leftarrow {}^2E_g$ (d) ${}^2E_g \leftarrow {}^4A_{2g}$

72. Choose the correct option for carbonyl fluoride with respect to bond angle and bond length

(a) $\angle F-C-F > \angle F-C-O$ and $C-F > C-O$

(b) $\angle F-C-F > \angle F-C-O$ and $C-F < C-O$

(c) $\angle F-C-F < \angle F-C-O$ and $C-F > C-O$

(d) $\angle F-C-F < \angle F-C-O$ and $C-F < C-O$

73. Which of the following react(s) with AsF_5 in liquid BrF_3?
(a) XeF_6 only   (b) XeF_6 and XeF_4 (c) XeF_6 and XeF_2 (d) XeF_4 and XeF_2

74. Consider the following reactions:

(A) $NOCl + Sn \xrightarrow{N_2O_4}$

(B) $NOCl + AgNO_3 \longrightarrow$

(C) $NOCl + BrF_3 \longrightarrow$

(D) $NOCl + SbCl_5 \longrightarrow$

Reactions which will give $\left[NO \right]^+$ as a major product are:

(a) A and B   (b) C and D   (c) A and C   (d) B and D

75. The complex that shows orbital contribution to the magnetic moment, is

(a) $\left[Cu\left(H_2O \right)_6 \right]^{2+}$ (b) $\left[Ni\left(H_2O \right)_6 \right]^{2+}$ (c) $\left[Co\left(H_2O \right)_6 \right]^{2+}$ (d) $\left[Cr\left(H_2O \right)_6 \right]^{2+}$

76. Among KF, SnF_4 and SbF_5, solute(s) that increase(s) the concentration of BrF_4^- in BrF_3, is/are
    (a) KF only   (b) KF and SnF_4 (c) SnF_4 and SbF_5 (d) KF, SnF_4 and SbF_5

77. Paramagnetic susceptibility of the order of 10^{-6} cm^3 mol^{-1} observed for $KMnO_4$ is due to
    (a) random spin alignment   (b) antiferromagnetic exchange interaction
    (c) paramagnetic impurity   (d) temperature independent paramagnetism

78. Correct order of M-C bond length of metallocenes (a-c)

    (A) $\left[Fe\left(\eta^5 - Cp\right)_2 \right]$ (B) $\left[Ni\left(\eta^5 - Cp\right)_2 \right]$ (C) $\left[Co\left(\eta^5 - Cp\right)_2 \right]$ is
    (a) A > B > C   (b) B > C > A   (c) C > B > A   (d) A > C > B

79. A 100 mL solution of 2.5×10^{-3} M in Bi(III) and Cu(II) each, is photometrically titrated at 745 nm with 0.1 M EDTA solution. Identify correct statements for this titration
    (A) Total volume of EDTA solution used in 5 mL
    (B) 3 mL of EDTA is required to complex Bi(III) and 2 mL for Cu(II)
    (C) 2.5 mL of EDTA is used for each metal ion
    (D) First break in titration curve is for Cu(II)
    Correct statements are
    (a) A and B   (b) A and C   (c) A, B and C   (d) B, C and D

80. On continuous exposure of ^{10}B sample to a slow neutron flux of 10^{16} m^2s^{-1}, its 3% weight fraction disappears in 3×10^7 s. Cross section for neutron capture (in barns) by ^{10}B is
    (a) 1000   (b) 3000   (c) 10, 000   (d) 30, 000

81. The ^1H NMR spectrum of $\left[Ru\left(\eta^4 - C_8H_8\right)(CO)_3 \right]$ at 23°C consists of a sharp single line. The number of signals observed at low temperature (–140 °C) in its spectrum is
    (a) 8   (b) 6   (c) 4   (d) 2

82. The g values for $Ce^{3+}(4f^1)$ and Pr^{3+} $(4f^2)$ are, respectively
    (a) 3/7 and 2/5   (b) 5/7 and 4/5   (c) 6/7 and 3/5   (d) 6/7 and 4/5

83. The room temperature magnetic moment (μ_{eff} in BM) for a monomeric Cu(II) complex is greater than 1.73. This may be explained using the expression:

    (a) $\mu_{eff} = \mu_s \left(1 - \dfrac{\alpha\lambda}{\Delta} \right)$ (b) $\mu_{eff} = \sqrt{n(n+2)}$

    (c) $\mu_{eff} = \sqrt{4s(s+1) + L(L+1)}$ (d) $\mu_{eff} = g\sqrt{J(J+1)}$

84. The number of 3c-2e bonds present in $Al(BH_4)_3$ is
    (a) four   (b) three   (c) six   (d) zero

85. The numbers of skeletal electrons present in the compounds $C_2B_3H_5$, $C_2B_4H_6$ and B_5H_9 are, respectively
    (a) 10, 12 and 12   (b) 12, 14 and 14   (c) 10, 12 and 14   (d) 12, 14 and 12

86. Identify correct statements for the EPR spectrum of $VO(acac)_2$ [with square pyramidal geometry at vanadium] at 77K [$I(^{51}V)$ = 7/2].
    (A) It has two g values   (B) It has 8 lines only
    (C) It has one g value   (D) It has two patterns of 8 lines each.
    (a) A and D   (b) A and C   (c) B and C   (d) B and D

87. The numbers of lines shown by the BH_3 part of the molecule $Ph_3P.\,^{11}BH_3$ in the ^1H and ^{11}B NMR spectra are, respectively $[I(^{11}B) = 3/2;\ I(^{31}P) = \frac{1}{2}]$
    (a) 8 and 8   (b) 4 and 8   (c) 3 and 6   (d) 6 and 3

88. To record Mössbauer spectrum of Fe containing samples, a source 'X' is used. X after a nuclear transformation (Y), gives γ-radiation used in Mössbauer spectroscopy.

    (a) ^{57}Fe, β-emission   (b) ^{57}Co, β-emission

    (c) ^{57}Co, electron capture   (d) ^{57}Fe, electron capture

89. Correct combination of number and size of rings present in a metal ion-porphine complex (inlcuding metal ion bearing chelate rings) is

    (a) four 5-membered and four 6-membered
    (b) two 5-membered and six 6-membered
    (c) six 5-membered and two 6-membered
    (d) five 5-membered and three 6-membered

90. In human body cis-platin hydrolyzes to diaqua complex and modifies the DNA structure by binding to
    (a) N-atom of guanine base   (b) O-atom of cytosine base
    (c) N-atom of adenine base   (d) O-atom of thymine base

91. For fluxional $Fe(CO)_5$ (structure given below) in solution, the exchange of numbered CO groups will be between
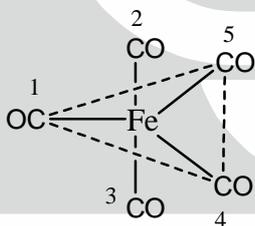
    (a) 2 and 5; 3 and 4   (b) 2 and 3; 4 and 5   (c) 2 and 3; 1 and 5   (d) 1 and 2; 4 and 5

92. In the following reaction sequence

    $$HNEt_2 + CS_2 \xrightarrow{KOH} P \xrightarrow[I_2]{aq.\,soln} R \xrightarrow{[CpMo(CO)_3]_2} S$$
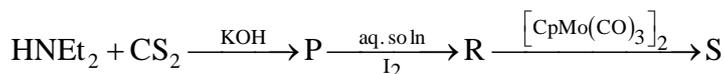
    where dtc = dithiocarbamate and tds = thiuramdisulfide.

    Identify P, R and S. $Cp = \eta^5 - C_5H_5$

	P	R	S
(a)	$Et_2dtc^-K^+$	Et_4tds	$CpMo(Et_2dtc)(CO)_2$
(b)	$Etdtc^-K^+$	Et_3tds	$CpMo(Et_3dtc)(CO)_2$
(c)	$Et_4dtc^-K^+$	Et_2tds	$CpMo(Et_4dtc)(CO)$
(d)	$Etdtc^-K^+$	$Ettdc$	$CpMo(Etdtc)(Co)$

93. Reaction of $Cr(CO)_6$ with LiC_6H_5 gives A which reacts with $[Me_3O][BF_4]$ to give B. The structures of A and B respectively, are

(a) and

(b) and

(c) and

(d) and
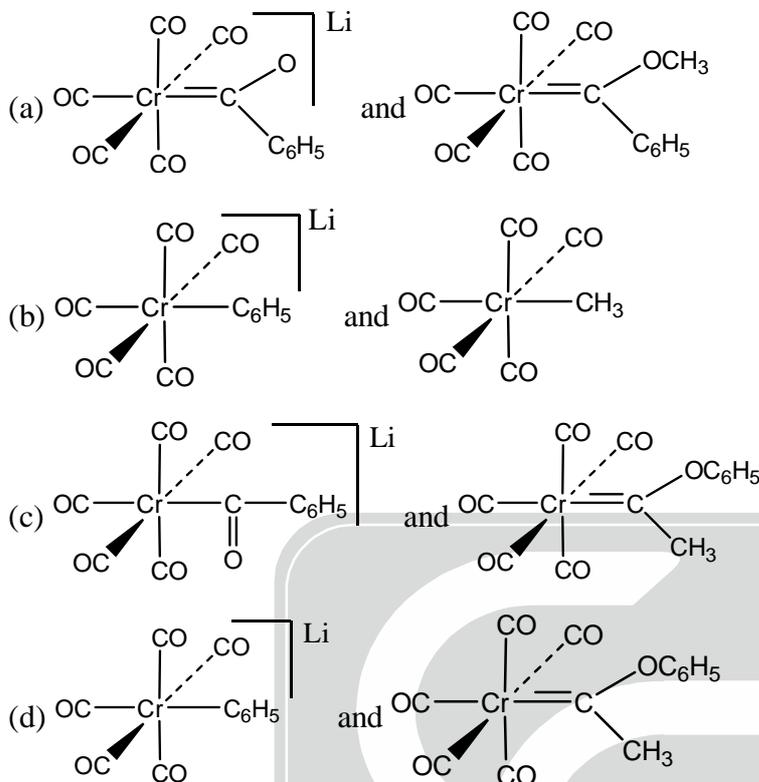
94. Heating a sample of $\left[\left(\eta^5 - C_5H_5\right)Mo(CO)_3\right]_2$ results in the formation of $\left[\left(\eta^5 - C_5H_5\right)Mo(CO)_2\right]_2$ with elimination of 2 equivalents of CO. The Mo-Mo bond order in this reaction changes from

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

95. A plausible intermediate involved in the self metathesis reaction of $C_6H_5 - C \equiv C - C_6H_4 - p - Me$ catalyzed by $\left[\left(^tBuO\right)_3 W \equiv C - ^tBu\right]$ is
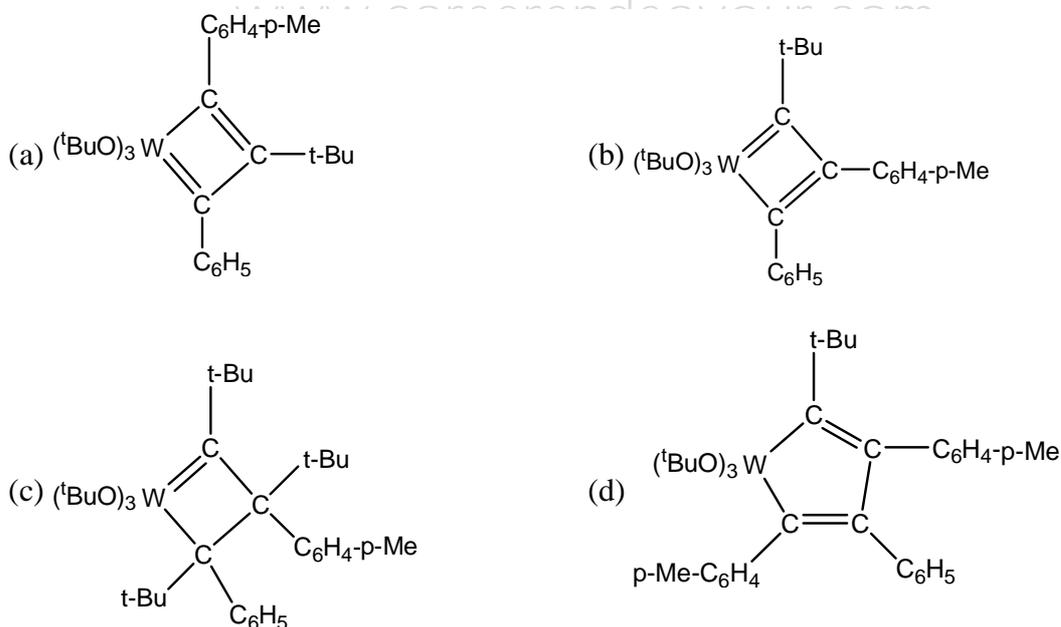
96. The major product formed in the following reaction is

(a)   (b)

(c)   (d)

97. The major product formed in the following reaction sequence is

(i) HOCH₂CH₂OH, TsOH

(ii)

(iii) H₃O⁺

(a)   (b)

(c)   (d)
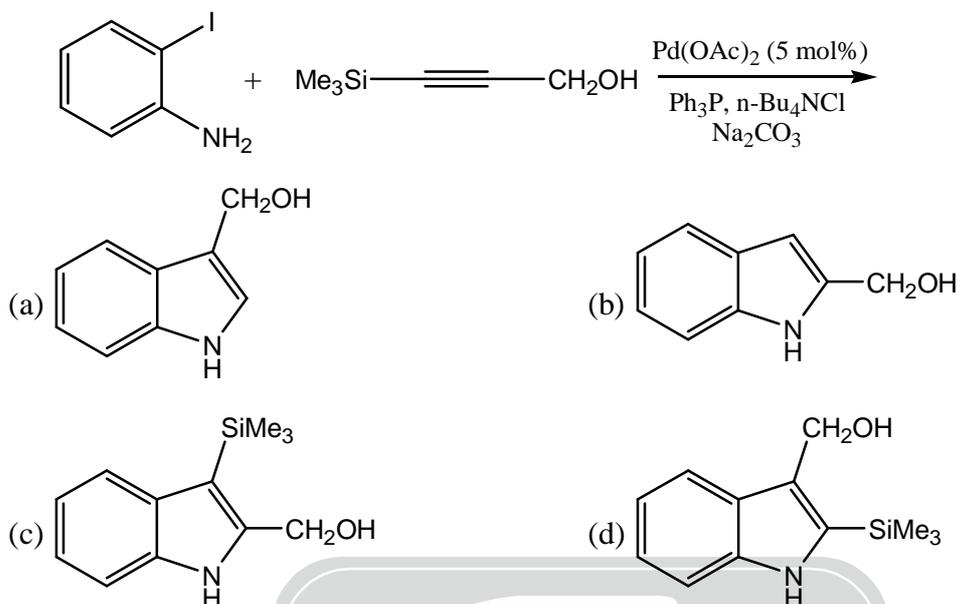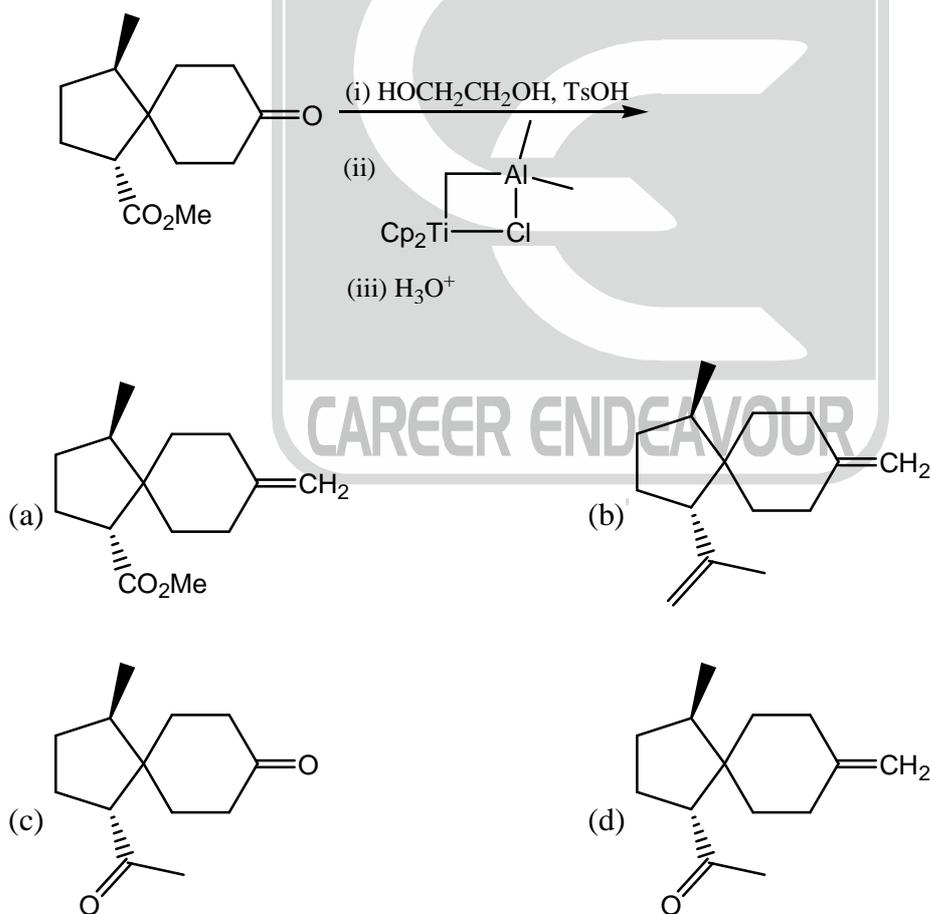
98.　The major product formed in the following reaction is

(a)　

(b)　

(c)　

(d)　

99.　The major products A and B in the following reaction sequence are
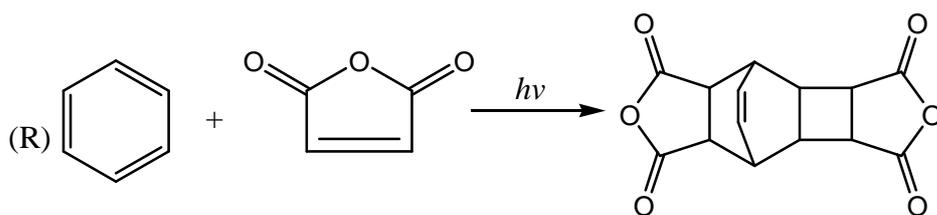

(a) A =　　B =

(b) A =　　B =

(c) A =　　B =

(d) A =　　B =
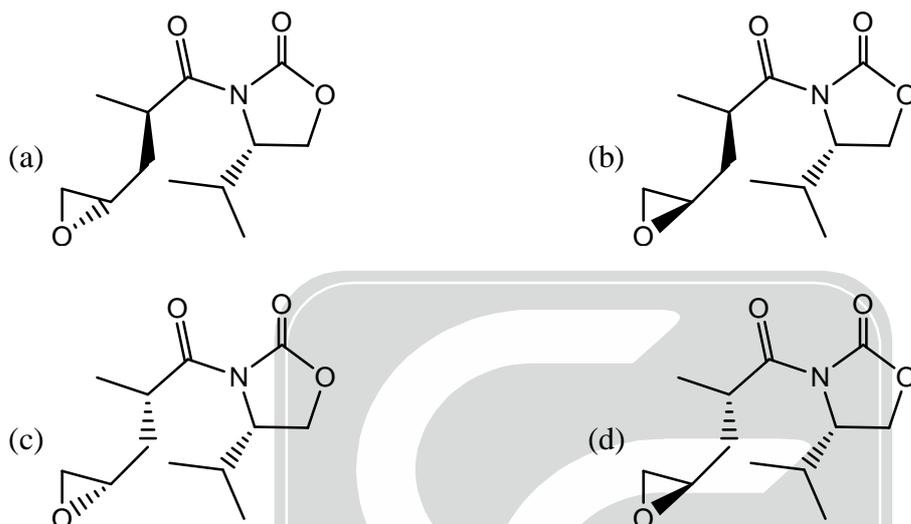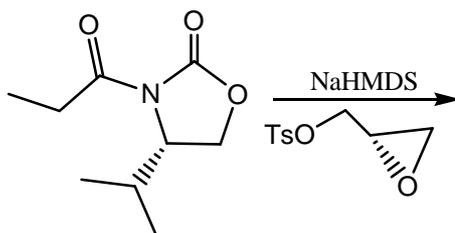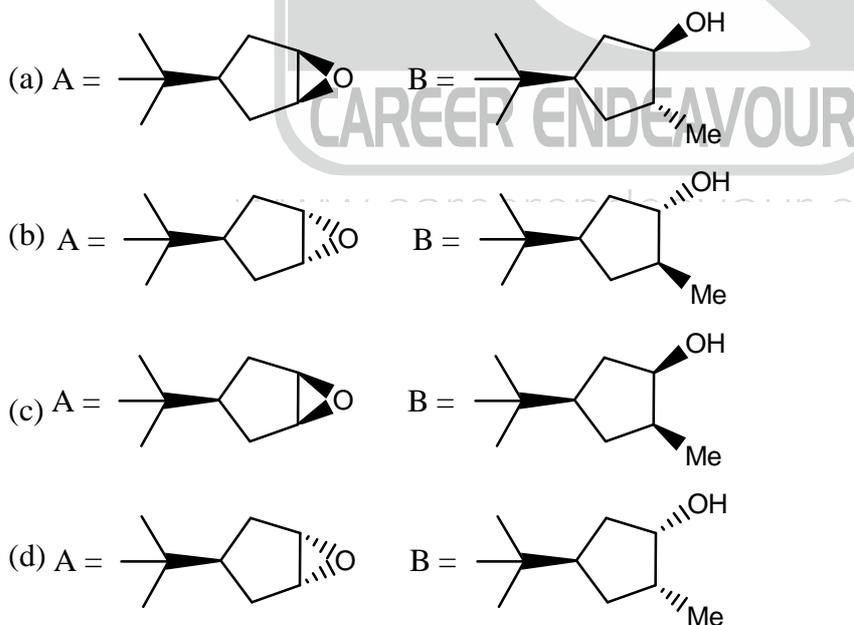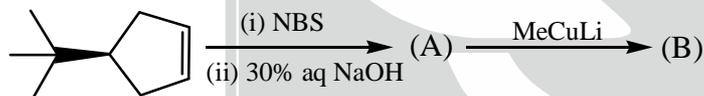
100. The major product formed in the following reaction sequence is

(a)

(b)

(c)

(d)
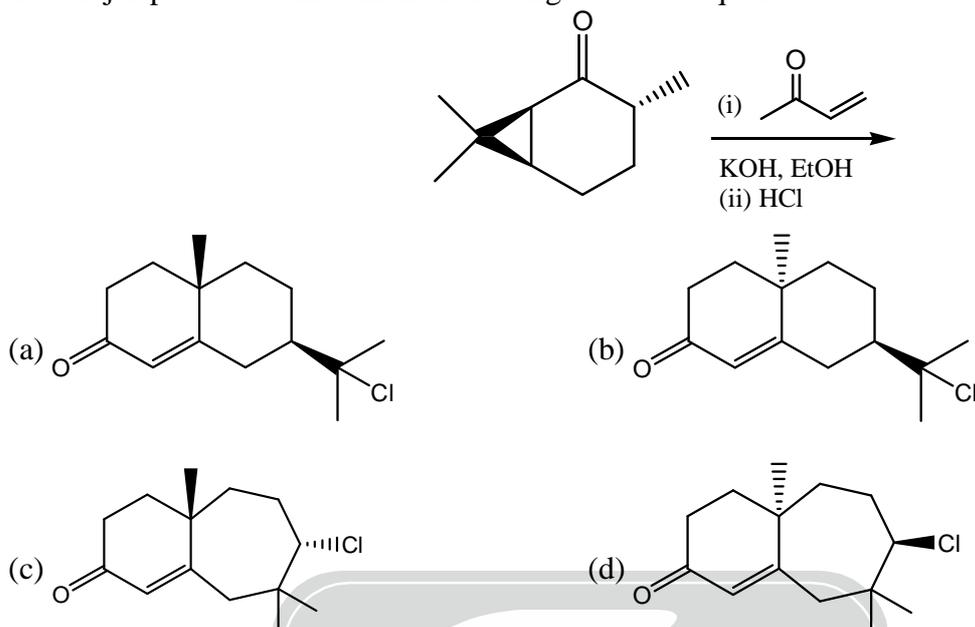
101. The major products A and B in the following reaction sequence are

(a) A =   B =

(b) A =   B =

(c) A =   B =

(d) A =   B =
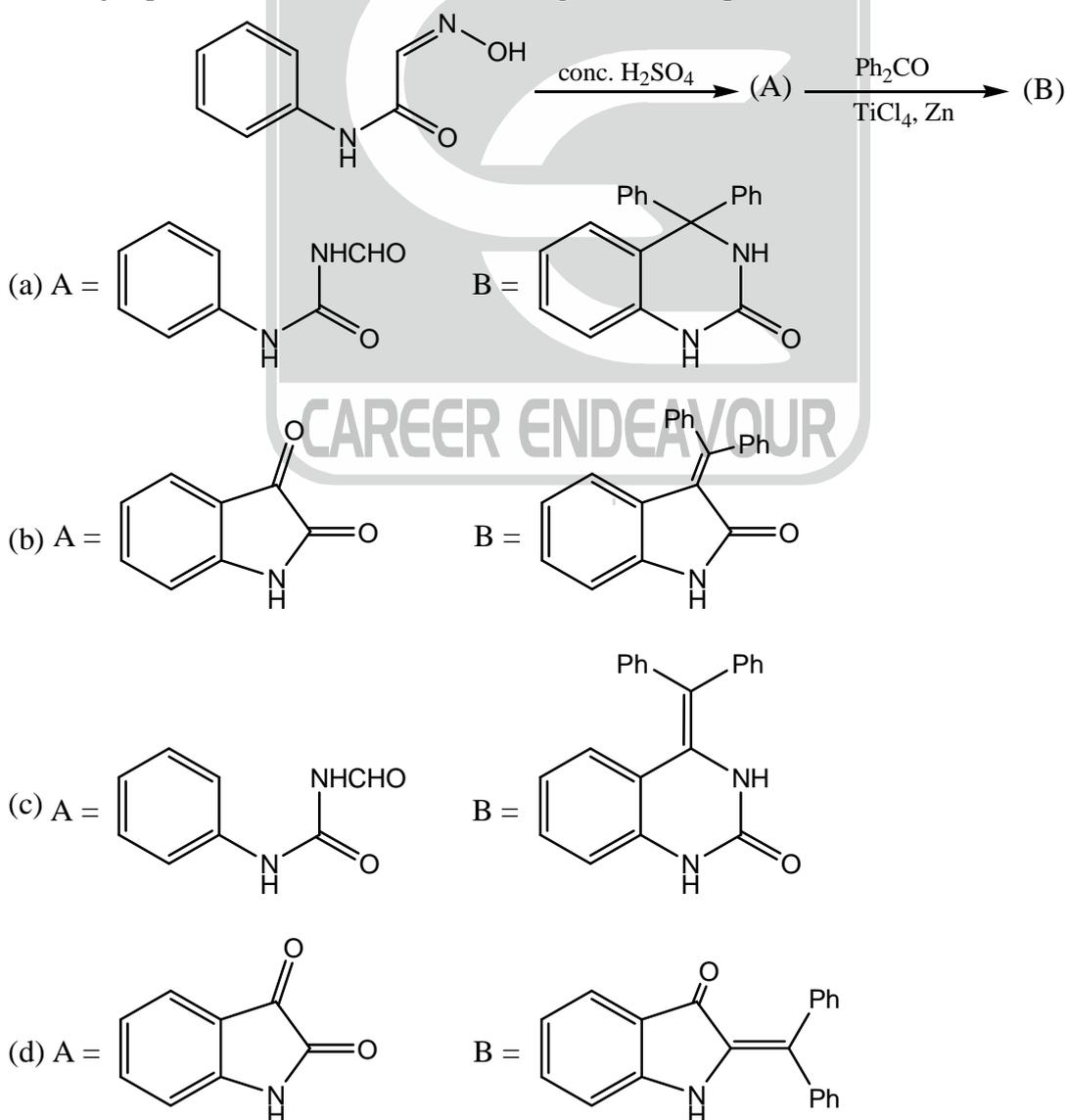
102. The major product in the following reaction is

(a)
(b)
(c)
(d)
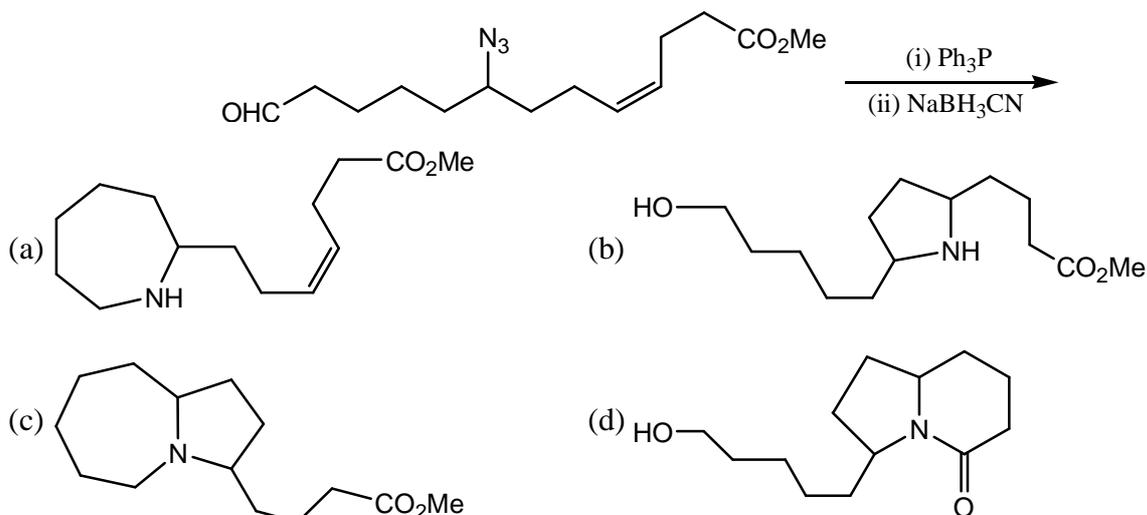
103. The correct reagent combination to effect the following reaction is

(a) (i) NaBH$_4$, CeCl$_3$, MeOH, 0°C; (ii) H$_2$, [Ir(COD) (py)P(Cy)$_3$]PF$_6$; (iii) Ph$_3$P, PhCO$_2$H, DEAD; (iv) LiAlH$_4$.

(b) (i) Li, liquid NH$_3$; (ii) H$_2$, [Ir(COD)(py)P(Cy)$_3$]PF$_6$; (iii) Ph$_3$P, PhCO$_2$H, DIAD; (iv) NaBH$_4$, CeCl$_3$, MeOH, 0°C.

(c) (i) H$_2$, Pd/C; (ii) LIAlH$_4$, –78°C

(d) (i) H$_2$, Pd/C; (ii) Li, liquid NH$_3$.
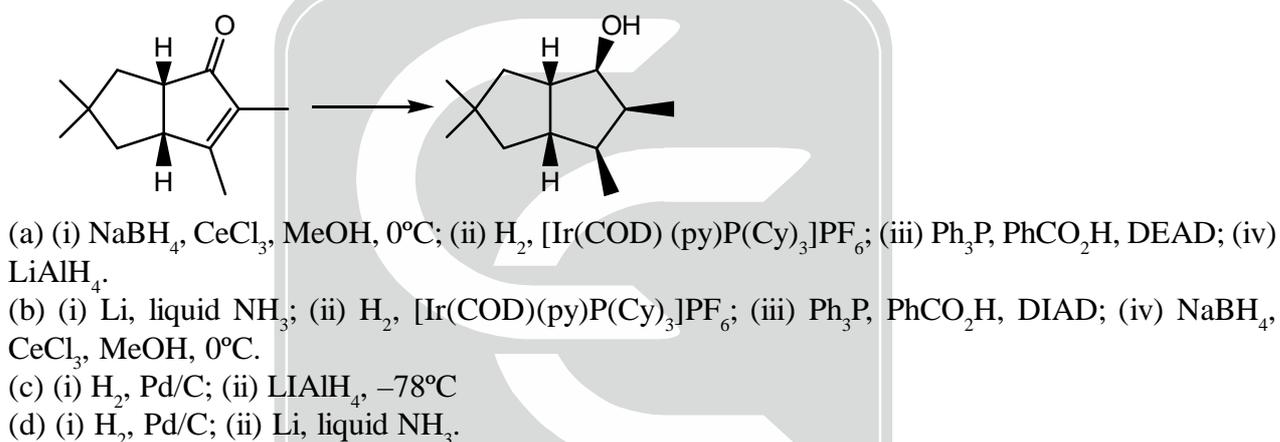
104. The major products A and B in the following reaction sequence are

(a) A =
B =

(b) A =
B =

(c) A =

B =

(d) A =

B =
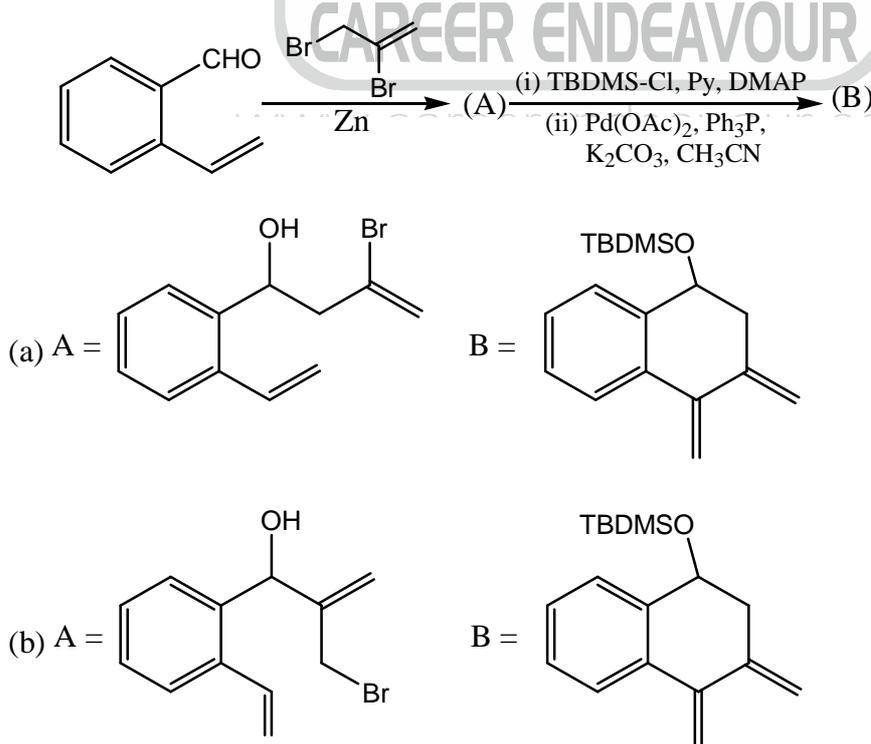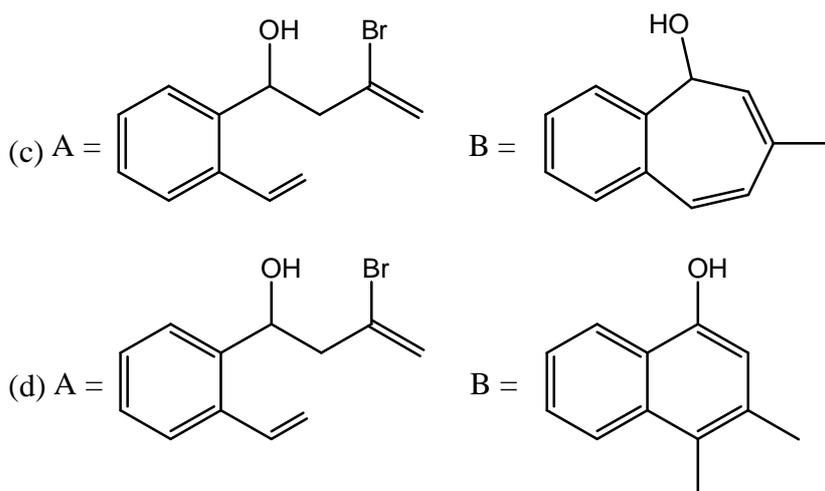
105. Structures of the intermediate A and the major product B in the following reaction sequence are

$$\xrightarrow[\text{Et}_3\text{N}]{(\text{PhO})_2\text{P(O)N}_3} \text{(A)} \xrightarrow{\text{t-BuOH}} \text{(B)}$$

(a) A =

        NCO   B =

                          NHBoc

(b) A =

        PO(OPh)$_2$ B =

                              NH$_2$

(c) A =

        CON$_3$ B =

                          OtBu

(d) A =

        PO(OPh)$_2$ B =

                              OtBu
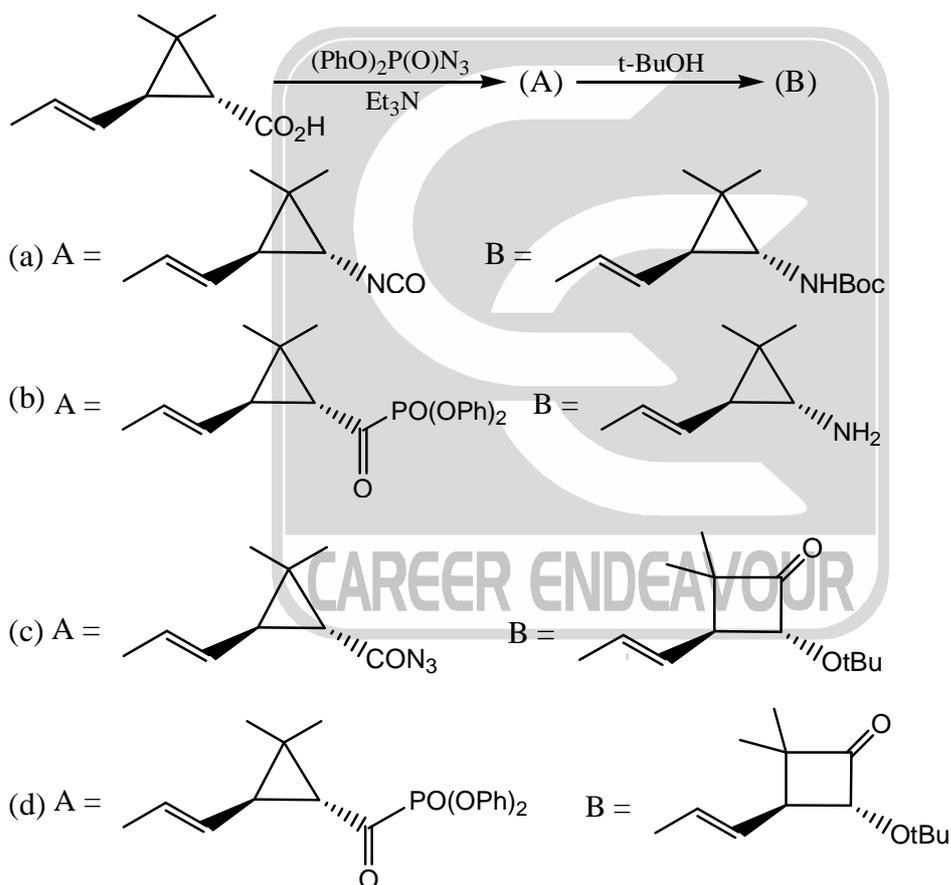
106. The correct match for the following transformations P-S with the processes I-IV is
      Reactions:

(P) Et

        $\xrightarrow{h\nu}$ Et

                              + H$_2$C=CH$_2$

(Q) Ph

        Ph $\xrightarrow{h\nu}$ Ph

                                      Ph   + CO

(R)

(S)
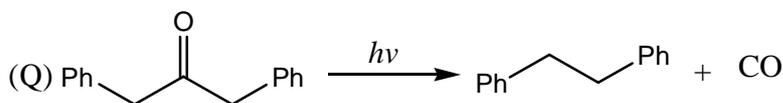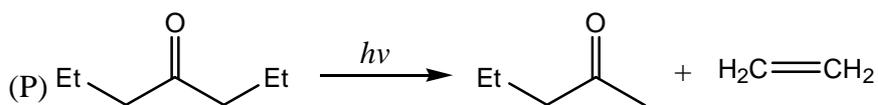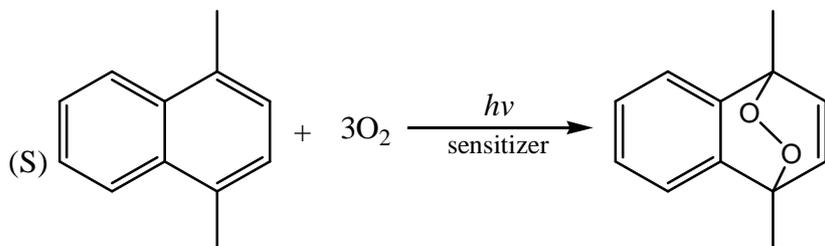
Processes:
(I) Diels-Alder
(II) Norrish Type-I
(III) Photocycloaddition followed by Diels-Alder
(IV) Norrish Type-II
(a) P-II; Q-IV; R-III; S-I   (b) P-II; Q-IV; R-I; S-II
(c) P-IV; Q-II; R-III; S-I   (d) P-IV; Q-II; R-I; S-III

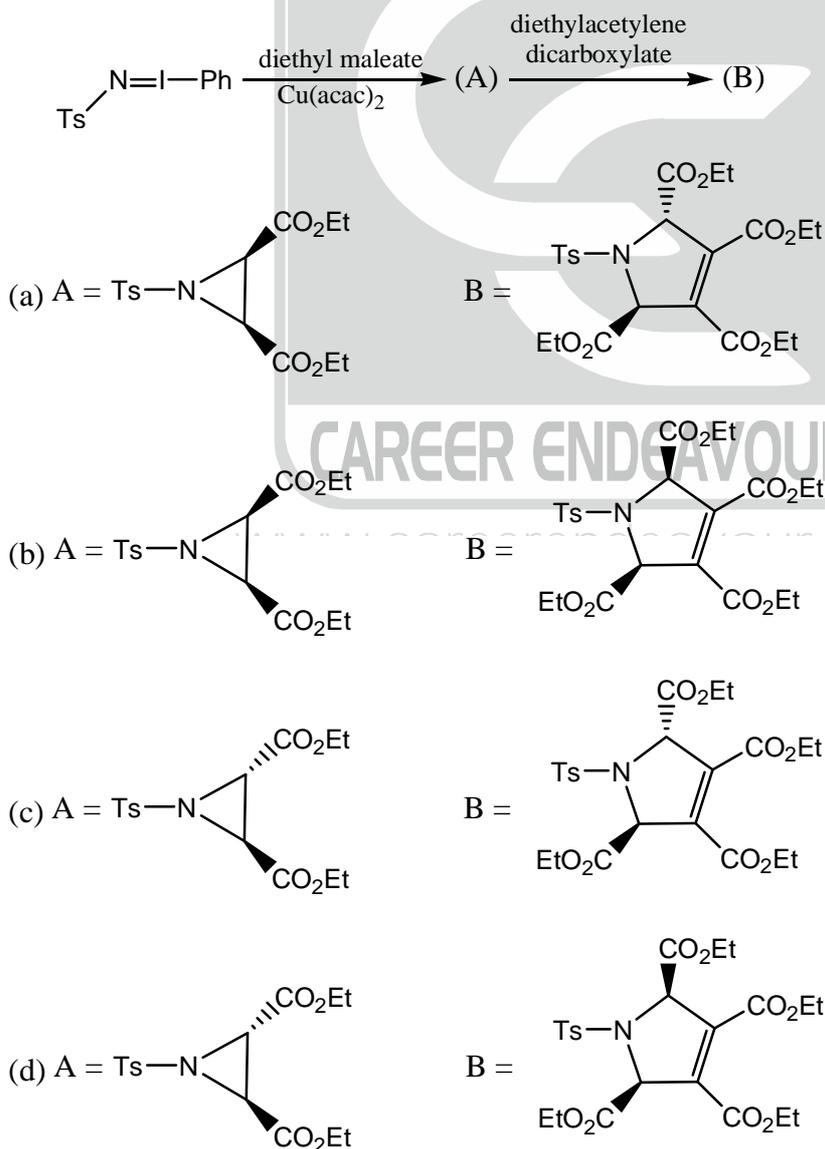107. The correct match for the reactions P-S with the names of cyclizations I-IV is
Reactions:

(P)

(Q)

(R)

(S)
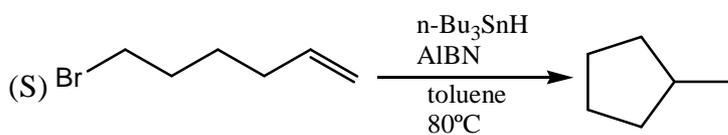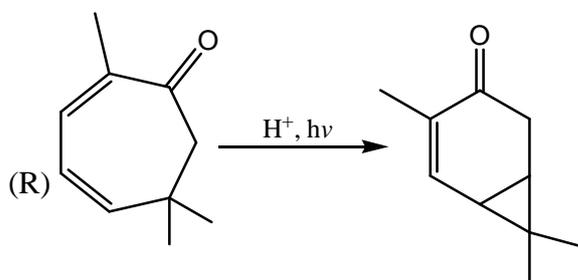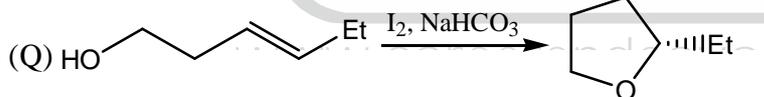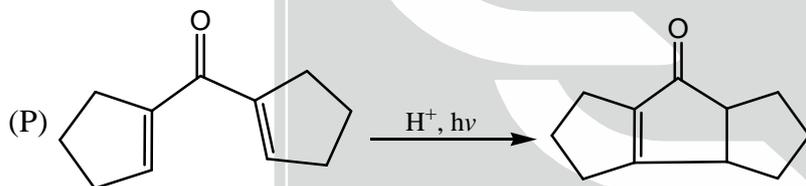
Name of Cyclizations:
(I) halocyclization
(II) Nazarov cyclization
(III) radical cyclization
(IV) electrocyclization

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

108. The correct structure of the intermediate, which leads to the product in the following reaction is
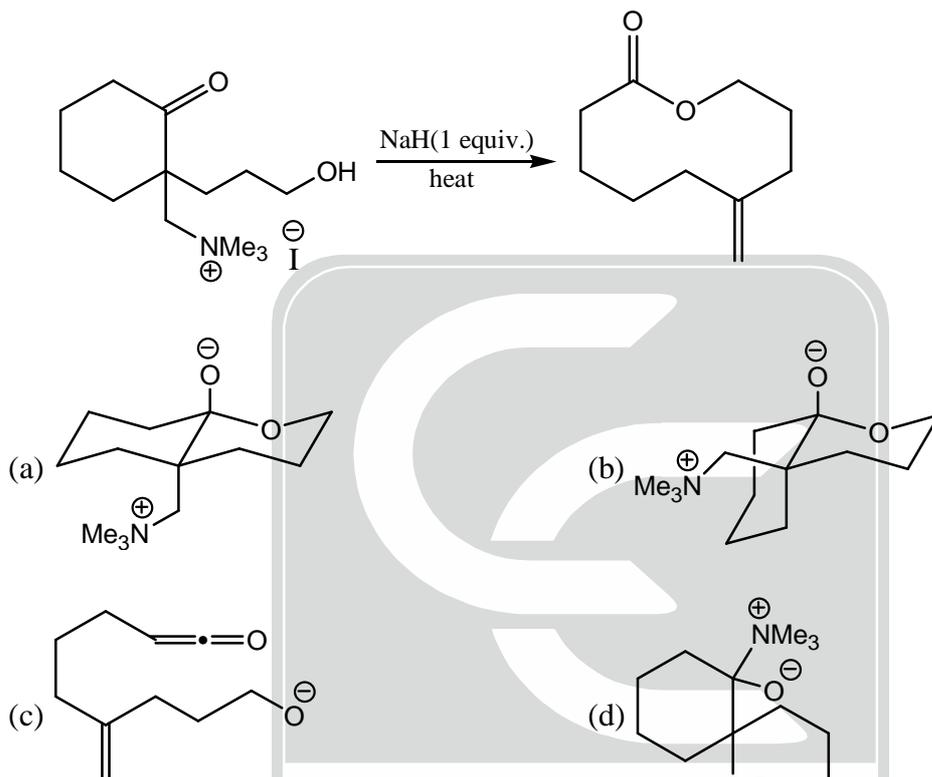
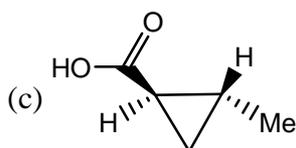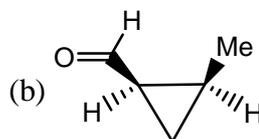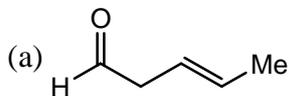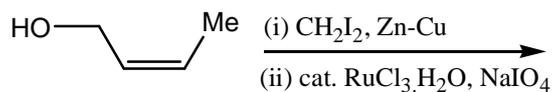109. The major product formed in the following reaction is
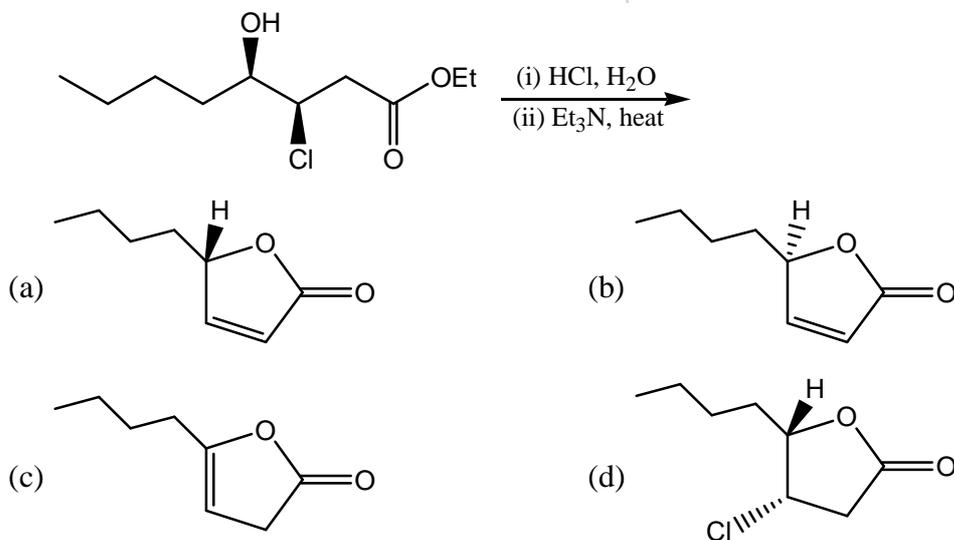
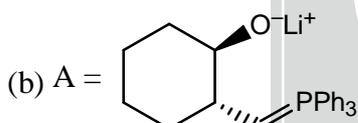110. The major product formed in the following reaction is
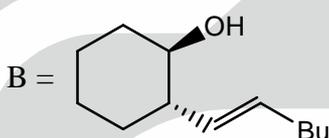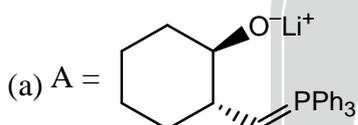

(a)

(b)

(c)

(d)
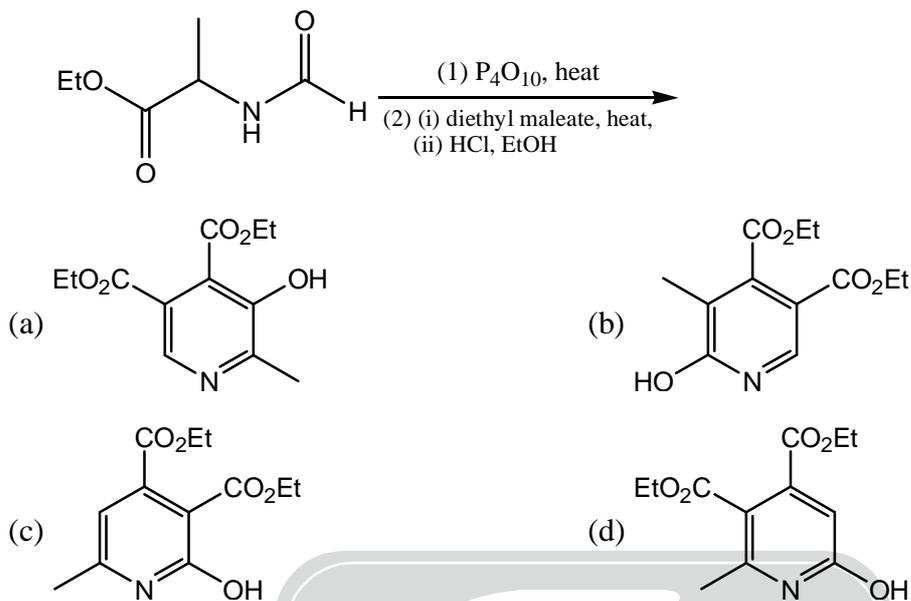
111. The major product A and B formed in the following reaction sequence are

(a) A =   B =

(b) A =   B =

(c) A =   B =

(d) A =   B =

112. The major product formed in the following reaction is

HO⎯⎯\=/⎯Me   (i) CH₂I₂, Zn-Cu
                  ⟶
                  (ii) cat. RuCl₃.H₂O, NaIO₄

(a)

(b)

(c)

(d)
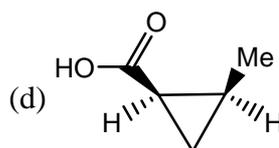
113. The intermediate A and the major product B in the following reaction sequence are

(a) A =   B =

(b) A =   B =

(c) A =   B =

(d) A =   B =
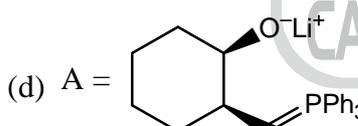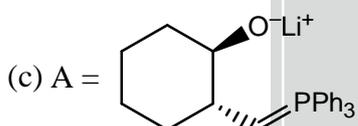
114. The correct structure of the compound, which shows following ^{13}C NMR DEPT-135 data is ^{13}C NMR DEPT-135: negative peaks at δ 30.2, 31.9, 61.8, 114.7 ppm; positive peak at 130.4 ppm

(a)

(b)

(c)

(d)
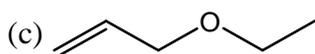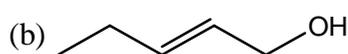
115. A compound displays the following spectral data. The correct structure of the compound is IR : 1690 cm^{-1}.

^{1}H NMR : δ 2.5 (s, 3H), 3.8 (s, 3H), 6.9 (d, J=8Hz, 2H), 7.8 (d, J = 8 Hz, 2H) ppm

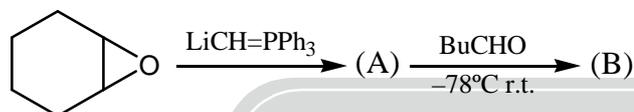^{13}C NMR : δ 197, 165, 130, 129, 114, 56, 26 ppm

(a)

(b)

(c)

(d)
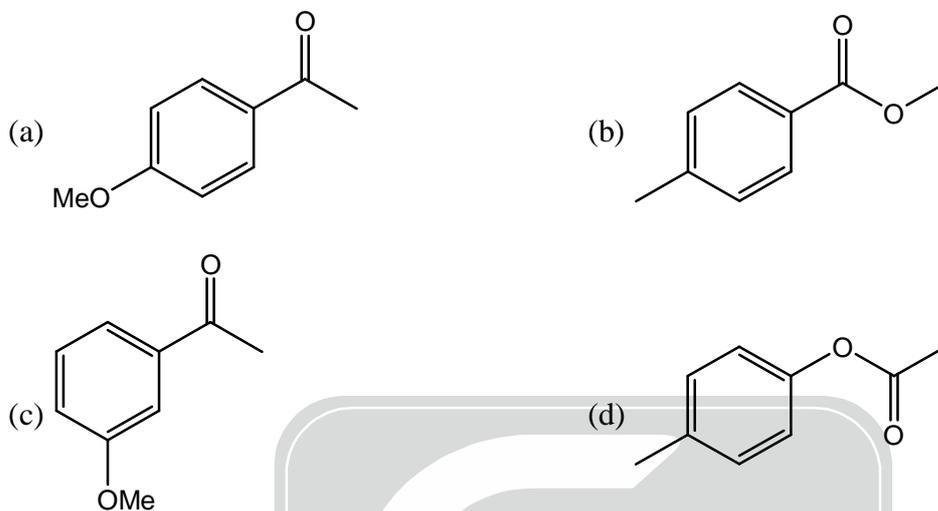
116. The major products A and B formed in the following reaction sequence are

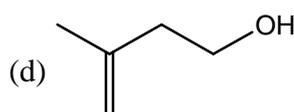(a) A =   B =

(b) A =   B =

(c) A =   B =

(d) A =   B =

117.   The major product formed in the following reaction is

(i) s-BuLi (2 equiv.), –78ºC

(ii)

(a)   (b)   (c)   (d)
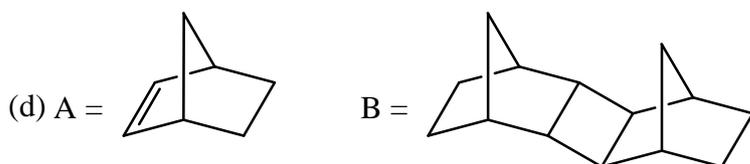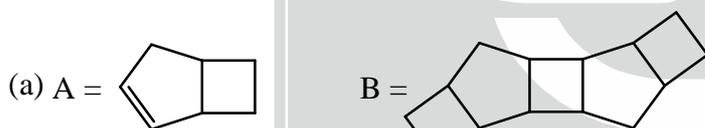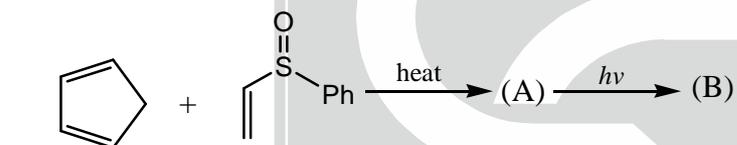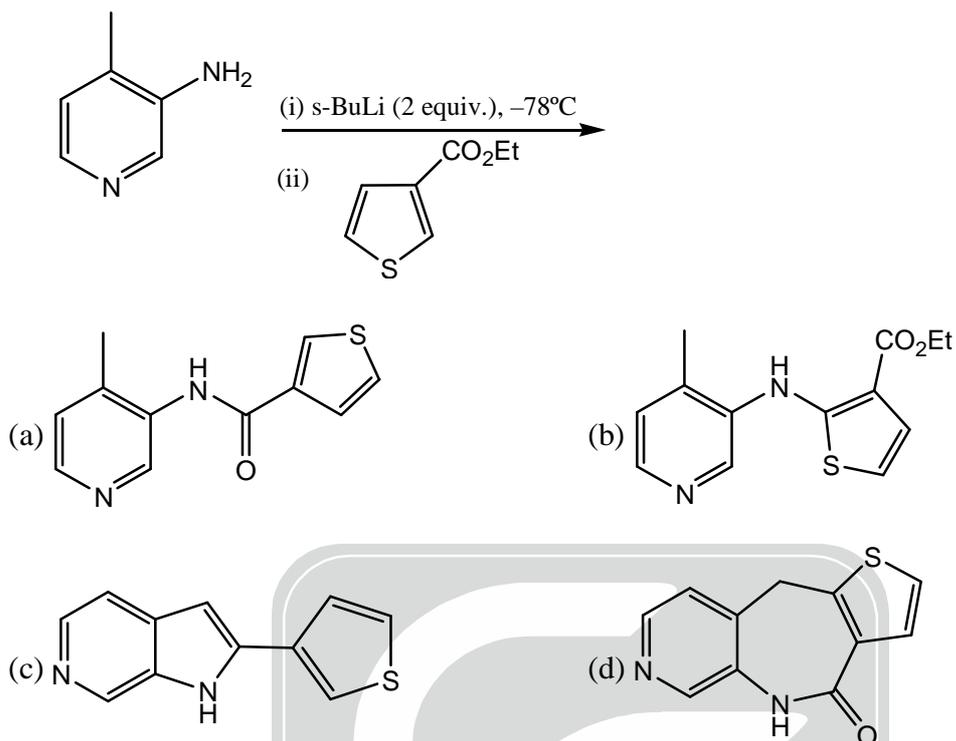
118.   The major product formed in the following reaction is
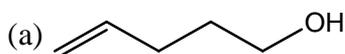

(i) KHMDS

(ii)

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

119. The major product formed in the following reaction is

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

120. The major product formed in the following reaction is

$$\text{Ph} \diagdown \diagup \text{CO}_2\text{Et} \xrightarrow[\text{MeSO}_2\text{NH}_2,\ \text{K}_3\text{Fe(CN)}_6]{\substack{1\ \text{mol\%}\ \text{K}_2\text{OsO}_2(\text{OH})_4 \\ (\text{DHQ})_2-\text{PHAL}}}$$

(a)   (b)   (c)   (d)
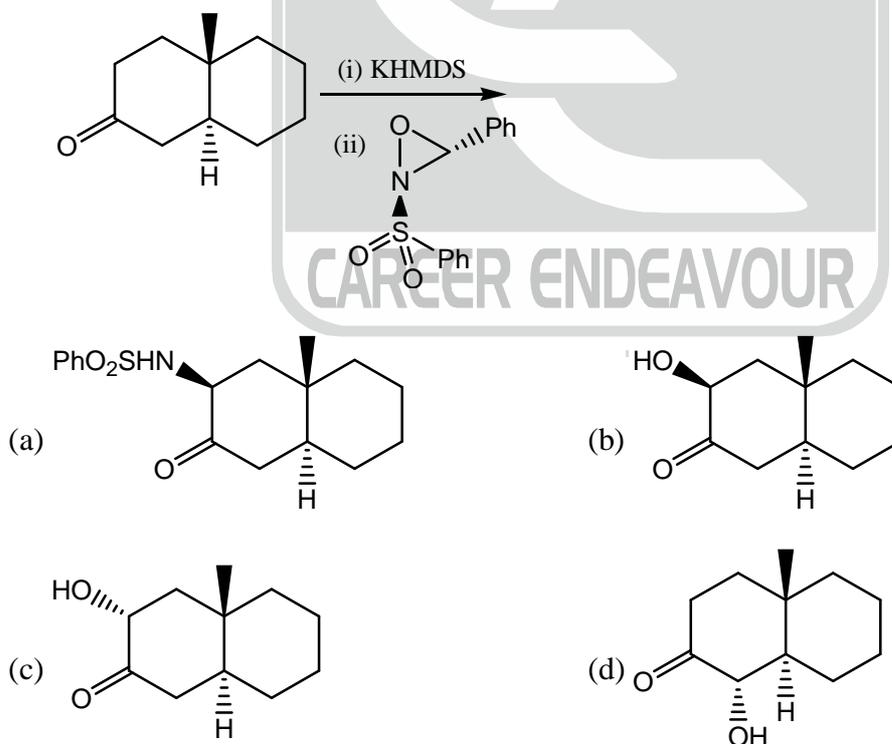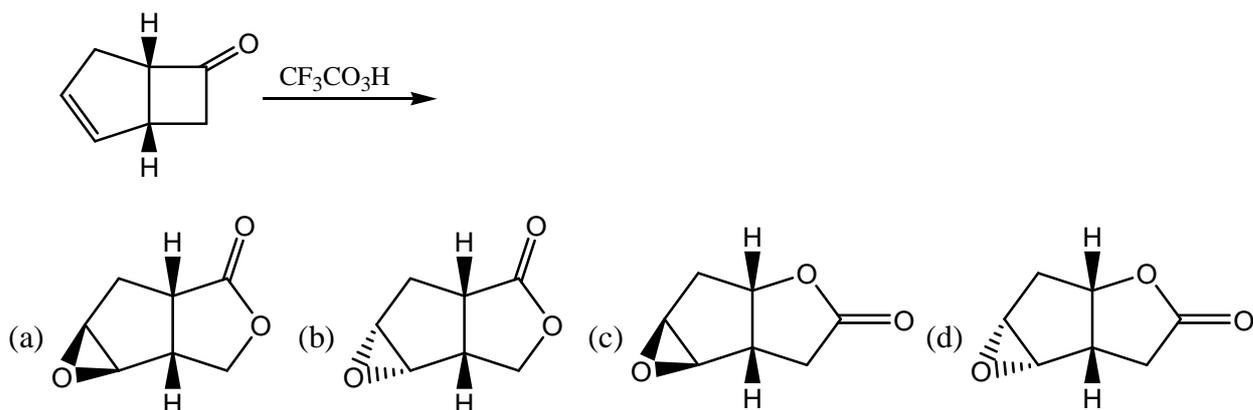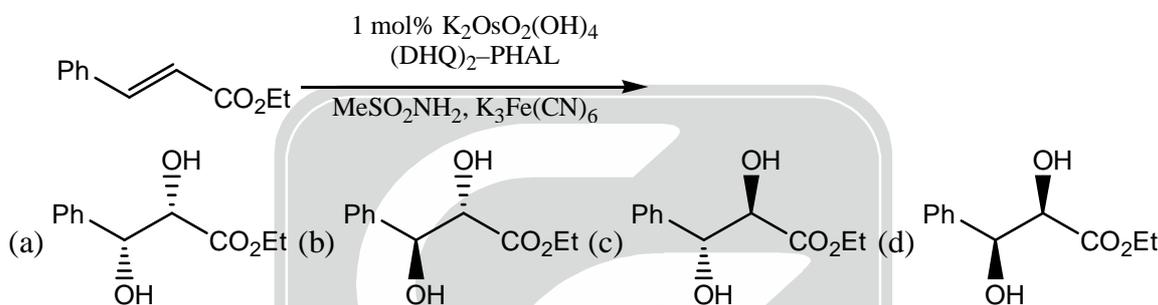
121. The single-particle translational partition function (f) for an ideal gas in a fixed volume V depends

on the thermal de-Broglie wavelength λ_{th} as $f \sim \left(\lambda_{th}\right)^n$ where

(a) n = 3   (b) n = 1   (c) n = –1   (d) n = – 3

122. 15 particles are distributed among 4 levels as shown in state I. Heat is given to the system and no work is done. The final state could be
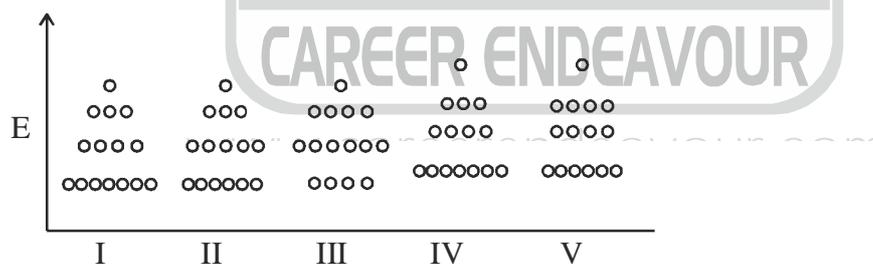
(a) II   (b) III   (c) IV   (d) V

123. In an NMR spectrometer containing a 2.5T magnet, Larmor precession frequency of ^{1}H is 100 MHz. The radiofrequency used in this spectrometer has an associated magnetic field strength of 2.5×10^{-4}T. The duration of a 90° pulse in this instrument is

(a) $25\times10^{-6}s$ (b) $50\times10^{-6}s$ (c) $25\times10^{-5}s$ (d) $50\times10^{-5}s$

124. Upon application of a weak magnetic field, a line in the microwave absorption spectrum of rigid rotor splits into 3 lines. The quantum number (J) of the rotational energy level from which the transition originates is

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

125. Phase diagram of a compound is shown below
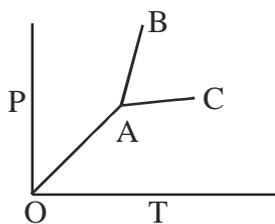
The slopes of the lines OA, AC and AB are $\tan\dfrac{\pi}{4}$, $\tan\dfrac{\pi}{6}$ and $\tan\dfrac{\pi}{3}$, respectively. If melting point

and ΔH of melting are 300K and 3 kJ mole^{-1} respectively, the change in the volume on melting is

(a) $10\tan\dfrac{\pi}{3}$ (b) $10\tan\dfrac{\pi}{4}$ (c) $10\cot\dfrac{\pi}{3}$ (d) $10\cot\dfrac{\pi}{4}$

126. The figure below describes how a Carnot engine works. It starts from the adiabatic compression step denoted by

(a) AB   (b) BC   (c) DC   (d) AD

127. The point group obtained by adding symmetry operation σ_h to the point group C_4 is
(a) S_4 (b) C_{4h} (c) D_{2h} (d) D_4

128. For a particle of mass m confined in a rectangular box with sides $2a$ and a, the energy and degeneracy of the first excited state, respectively, are
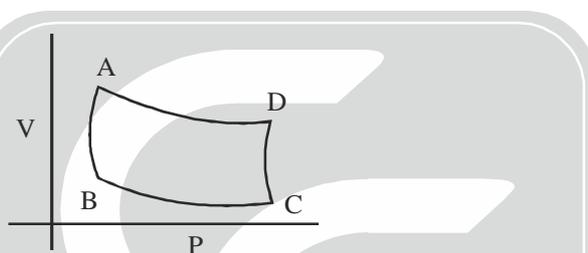
(a) $\dfrac{h^2}{8m}\left(\dfrac{2}{a^2}\right), 1$ (b) $\dfrac{h^2}{8m}\left(\dfrac{17}{4a^2}\right), 2$ (c) $\dfrac{h^2}{8m}\left(\dfrac{5}{4a^2}\right), 1$ (d) $\dfrac{h^2}{8m}\left(\dfrac{5}{a^2}\right), 2$

129. The ionization energy of hydrogen atom in its ground state is approximately 13.6 eV. The potential energy of He$^+$, in its ground state is approximately
(a) –54.4 eV   (b) –27.2 eV   (c) –13.6 eV   (d) –108.8 eV

130. The character table for the D_3 point group is provided below:

D_3	E	$2C_3$	$3C$		
A_1	1	1	1		x^2+y^2, z^2
A_2	1	1	-1	z, R_z	
E	2	-1	0	$(x,y),(R_x,R_y)$	$(x^2-y^2, xy),(xz,yz)$

For this point group, the correct statement among the following is:
(a) it is possible to have a totally symmetric normal mode of vibration which is IR-active
(b) all IR-active normal modes are necessarily Raman inactive
(c) all Raman-active normal modes are necessarily IR-active
(d) it is possible to have a pair of IR-active normal modes that are degenerate.

131.   Suppose $\psi_1, \psi_2, \psi_3 .....$ are wavefunctions of an anharmonic oscillator and $\phi_0, \phi_1, \phi_2, ...$ are wavefunctions of a harmonic oscillator with increasing order of energy. The subscripts denote vibrational quantum numbers in both the cases. Given

$$\psi_0 = a_1\phi_0 + a_2\phi_2 + a_3\phi_4$$
$$\psi_1 = b_1\phi_0 + b_2\phi_4 + b_3\phi_6$$
$$\psi_2 = c_1\phi_1 + c_2\phi_4$$
$$\psi_3 = d_1\phi_3 + d_2\phi_5$$

the FORBIDDEN electric dipole (assuming the dipole operator is linear in normal coordinates) transition among the following is

(a) $\psi_0 \rightarrow \psi_1$ (b) $\psi_0 \rightarrow \psi_2$ (c) $\psi_0 \rightarrow \psi_3$ (d) $\psi_1 \rightarrow \psi_2$

132.   If U is a function of V and T, $\left(\dfrac{\partial U}{\partial T}\right)_P$ is equal to π and α are the internal pressure and the coefficient of thermal expansion, respectively)

(a) C_P (b) C_V (c) $C_P - \pi V\alpha$ (d) $C_P + \pi V\alpha$
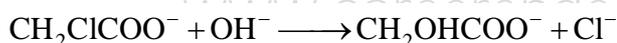
133.   The character table of C_{3V} point group is provided below, along with an additional reducible representation, Γ

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	–1
E	2	–1	0
Γ	6	0	2

Γ is given by

(a) $A_1 + A_2 + 2E$ (b) $2A_1 + 2E$ (c) $2A_2 + 2E$ (d) $2A_1 + 2A_2 + E$

134.   For the chemical reaction in aqueous solution,

$$CH_2ClCOO^- + OH^- \longrightarrow CH_2OHCOO^- + Cl^-$$

the correct statement is
(a) increase of pressure increases the rate constant
(b) increase of dielectric constant increases the rate constant
(c) increase of ionic strength decreases the rate constant
(d) the entropy of activation is positive

135.   If experimentally observed rate constant is greater than the maximum value of rate constant obtained using hard-sphere model of collision theory, then relation between the impact parameter (b) and sum of the radii of two reactants is

(a) $b = r_1 + r_2$ (b) $b < r_1 + r_2$ (c) $b > r_1 + r_2$ (d) $b \leq r_1 + r_2$

136. Half-life $t_{1/2}$ for a third order reaction $3C \rightarrow$ products, where C_0 is the initial concentration of C, will be

(a) $\dfrac{3}{2kC_0^2}$ (b) $\dfrac{3}{kC_0}$ (c) $\dfrac{3}{2kC_0}$ (d) $\dfrac{2}{3kC_0^2}$

137. For a simple cubic lattice, the ratio between the unit cell length and the separation of two adjacent parallel crystal planes can NOT have a value of

(a) $5^{1/2}$ (b) $7^{1/2}$ (c) $11^{1/2}$ (d) $13^{1/2}$

138. Adsorption isotherm of three gases A, B and C are shown in the following figure, where θ is the percentage of surface coverage
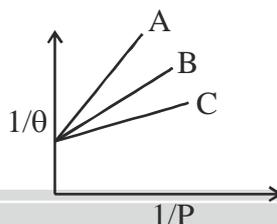
The correct order of the extent of adsorption of these gases is

(a) $A > B > C$ (b) $B > A > C$ (c) $C > A > B$ (d) $C > B > A$

139. Choosing some Hamiltonian H and an orthonormal basis, a linear variation is carried out to get approximately energies $\bar{E}_j$. With 2 basis functions, one obtains $\bar{E}_1(2) \le \bar{E}_2(2)$. Taking 3 basis functions, similarly three ordered energies $\bar{E}_1(3) \le \bar{E}_2(3) \le \bar{E}_3(3)$ are found. The relation which holds from the following is?

(a) $\bar{E}_1(2) \le \bar{E}_1(3);$ $\bar{E}_2(2) \le \bar{E}_2(3)$

(b) $\bar{E}_1(3) \le \bar{E}_1(2);$ $\bar{E}_2(2) \le \bar{E}_2(3)$

(c) $\bar{E}_1(2) \le \bar{E}_1(3);$ $\bar{E}_2(3) \le \bar{E}_2(2)$

(d) $\bar{E}_1(3) \le \bar{E}_1(2);$ $\bar{E}_2(3) \le \bar{E}_2(2)$

140. Average value of momentum for the ground state of a particle in a 1-d box is zero because

(a) $[p, H] = 0$ (b) $V(\text{potential}) = 0$

(c) H is hermitian (d) the state is bound and stationary

141. For a hermitian operator A, which does NOT commute with the Hamiltonian H, let ψ_1 be an eigenfunction of A and ψ_2 be an eigenfunction of H. The correct statement regarding the average value of the commutator of A with $H\left([A, H]\right)$ is

(a) both $\left\langle \psi_1 \left| [A, H] \right| \psi_1 \right\rangle$ and $\left\langle \psi_2 \left| [A, H] \right| \psi_2 \right\rangle$ are non-zero

(b) only $\left\langle \psi_1 \left| [A, H] \right| \psi_1 \right\rangle$ is zero, but $\left\langle \psi_2 \left| [A, H] \right| \psi_2 \right\rangle$ is non-zero

(c) only $\left\langle \psi_2 \left| [A, H] \right| \psi_2 \right\rangle$ is zero, but $\left\langle \psi_1 \left| [A, H] \right| \psi_1 \right\rangle$ is non-zero

(d) both $\left\langle \psi_1 \left| [A, H] \right| \psi_1 \right\rangle$ and $\left\langle \psi_2 \left| [A, H] \right| \psi_2 \right\rangle$ are zero

142. The condensation of a hydroxy acid produces a polyster with the probability of linkage at both ends being p. The mole fraction of k-mer chain formation is

(a) p^k (b) $p(1-p)^{k-1}$ (c) $p^{k-1}(1-p)$ (d) p^{k-1}

143. In simple molecular orbital theory of hydrogen molecule, bonding σ_g and anti-bonding σ_u molecular orbitals are constructed as linear combinations of atomic orbitals of two hydrogen atoms. The spatial part of a purely covalent singlet wavefunction is obtained by

(a) $\sigma_g^2 + \sigma_u^2$ (b) σ_g^2 (c) $\sigma_g^2 - \sigma_u^2$ (d) $\sigma_g^2 + \frac{1}{2}\sigma_u^2$

144. Two aqueous 1:1 electrolyte systems A and B are at different temperatures T_A and T_B and C_A and C_B concentrations, respectively. Their Debye lengths will be equal if

(a) $T_A = 2T_B$ and $C_A = 2C_B$ (b) $T_A = 2T_B$ and $C_A = C_B/2$

(c) $T_A = \sqrt{2}T_B$ and $C_A = 2C_B$ (d) $T_A = 2T_B$ and $C_A = \sqrt{2}C_B$

145. Aqueous solutions of $NaCl$, $CaCl_2$ and $LaCl_3$ show the following plots of logarithms of mean ionic activity coefficient $(\ln \gamma_{\pm})$ vs molar concentration (c)
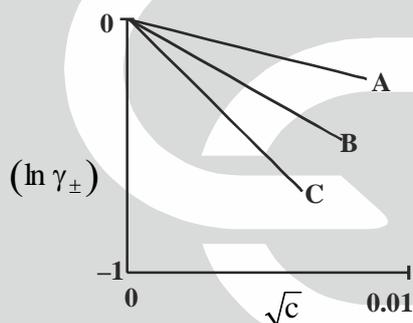
The correct option is then

	NaCl	$CaCl_2$	$LaCl_3$
(a)	C	B	A
(b)	A	B	C
(c)	A	C	B
(d)	C	A	B