PART 'B'
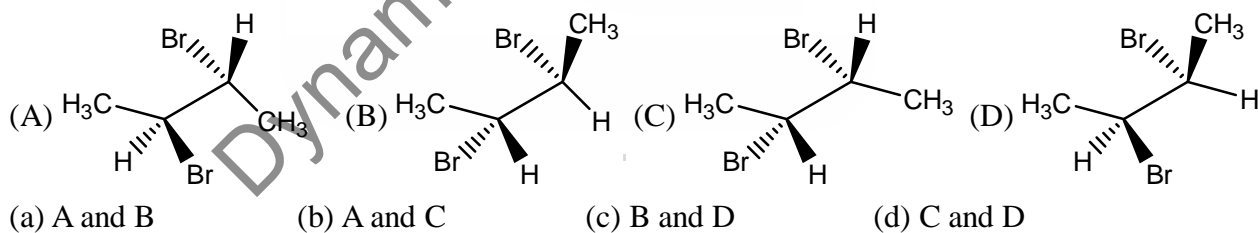
21. The biological functions of cytochrome P_{450} and myoglobin are, respectively
    (a) oxidation of alkene and O_2 storage
    (b) O_2 trasnport and O_2 storage
    (c) O_2 storage and electron carrier
    (d) electron carrier and O_2 transport

22. Deoxy-hemocyanin is
    (a) heme protein and paramagnetic
    (b) colorless and diamagnetic
    (c) O_2 transporter and paramagnetic
    (d) blue colored and diamagnetic

23. The oxidizing power of $[CrO_4]^{2-}$, $[MnO_4]^{2-}$, and $[FeO_4]^{2-}$ follows the order

    (a) $\left[CrO_4 \right]^{2-} < \left[MnO_4 \right]^{2-} < \left[FeO_4 \right]^{2-}$
    (b) $\left[FeO_4 \right]^{2-} < \left[MnO_4 \right]^{2-} < \left[CrO_4 \right]^{2-}$

    (c) $\left[MnO_4 \right]^{2-} < \left[FeO_4 \right]^{2-} < \left[CrO_4 \right]^{2-}$
    (d) $\left[CrO_4 \right]^{2-} < \left[FeO_4 \right]^{2-} < \left[MnO_4 \right]^{2-}$

24. Using crystal field theory, identify from the following complex ions that shows same μ_{eff} (spin only) values

    (A) $\left[CoF_6 \right]^{3-}$
    (B) $\left[IrCl_6 \right]^{3-}$
    (C) $\left[Fe(H_2O)_6 \right]^{2+}$

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

25. The W-W bond order in $\left[W\left(\eta^5 - C_5H_5 \right)\left(\mu - Cl \right)\left(CO \right)_2 \right]_2$ is

    (a) three
    (b) two
    (c) one
    (d) zero

26. The correct statement for Mn–O bond lengths in $\left[Mn\left(H_2O \right)_6 \right]^{2+}$ is

    (a) all bonds are equal

    (b) four bonds are longer than two others

    (c) two bonds are longer than four others

    (d) they are shorter than the Mn-O bond in $\left[MnO_4 \right]^{-}$

27. For the reaction of $\left[Fe\left(\eta^5 - C_5H_5 \right)\left(CH_3 \right)\left(CO \right)_2 \right]$ with PMe_3, the main intermediate is

    (a) $\left[Fe\left(\eta^5 - C_5H_5 \right)\left(CH_3 \right)\left(CO \right)_2\left(PMe_3 \right) \right]$
    (b) $\left[Fe\left(\eta^5 - C_5H_5 \right)\left(COCH_3 \right)\left(CO \right) \right]$
    (c) $\left[Fe\left(\eta^3 - C_5H_5 \right)\left(CH_3 \right)\left(CO \right)_2 \right]$
    (d) $\left[Fe\left(\eta^3 - C_5H_5 \right)\left(COCH_3 \right)\left(CO \right)\left(PMe_3 \right) \right]$

28. Identify the complex ions in sequential order when ferroin is used as an indicator in the titration of iron(II) with potassium dichromate, (phen = 1, 10-phenathroline)

    (a) $\left[Fe\left(phen \right)_3 \right]^{2+}$ and $\left[Fe\left(phen \right)_3 \right]^{3+}$
    (b) $\left[Fe\left(phen \right)_3 \right]^{3+}$ and $\left[Fe\left(phen \right)_3 \right]^{2+}$

    (c) $\left[Fe\left(CN \right)_6 \right]^{4-}$ and $\left[Fe\left(CN \right)_6 \right]^{3-}$
    (d) $\left[Fe\left(CN \right)_6 \right]^{3-}$ and $\left[Fe\left(CN \right)_6 \right]^{4-}$

29. The structures of XeF_2 and XeO_2F_2 respectively are
    (a) bent, tetrahedral
    (b) linear, square planar
   (c) linear, see-saw
    (d) bent, see-saw

30. Spin motion of which of the following gives magnetic moment
(A) electron, (B) proton (C) neutron
Correct answer is
(a) A and B (b) B and C (c) A and C (d) A, B and C

31. Correct statement for coulometry is
(a) it is based on Faraday's law of electrolysis (b) it is a type of voltammetry
(c) it is based on Ohm's law (d) it uses ion selective electrode

32. The order of increasing Bronsted acidity for boron hydrides is
(a) $B_5H_9 < B_6H_{10} < B_{10}H_{14}$ (b) $B_{10}H_{14} < B_5H_9 < B_6H_{10}$
(c) $B_6H_{10} < B_{10}H_{14} < B_5H_9$ (d) $B_{10}H_{14} < B_6H_{10} < B_5H_9$

33. Among the following, species expected to show fluxional behaviour are
(A) $\left[NiCl_4\right]^{2-}$ (tetrahedral) (B) IF_7 (pentagonal bipyramidal)
(C) $\left[CoF_6\right]^{3-}$ (octahedral) (D) $Fe(CO)_5$ (trigonal bipyramidal)
(a) B and C (b) B and D (c) C and D (d) A and D

34. The ring size and the number of linked tetrahedral present in $\left[Si_6O_{18}\right]^{12-}$ are, respectively
(a) 6 and 6 (b) 12 and 6 (c) 12 and 12 (d) 6 and 12

35. The molecule C_3O_2 has a linear structure. This compound has
(a) 4σ and 4π bonds. (b) 3σ and 2π bonds
(c) 2σ and 3π bonds (d) 3σ and 4π bonds.

36. The metallic radii are abnormally high for which of the following pairs?
(a) Eu, Yb (b) Sm, Tm (c) Gd, Lu (d) Nd, Ho

37. Identify two enantiomers among the following compounds
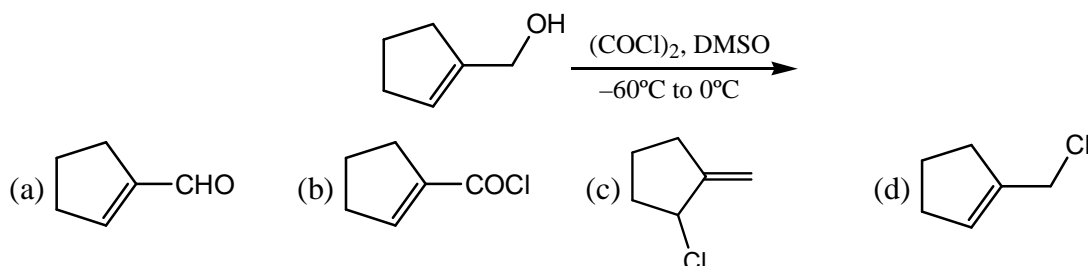
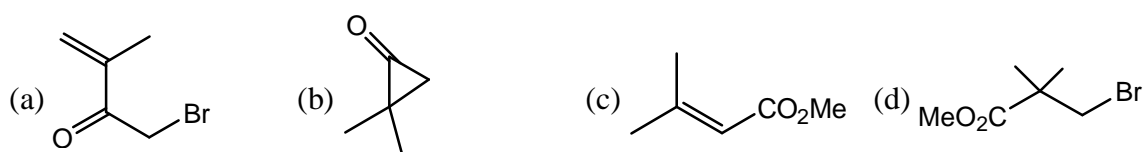(a) A and B (b) A and C (c) B and D (d) C and D
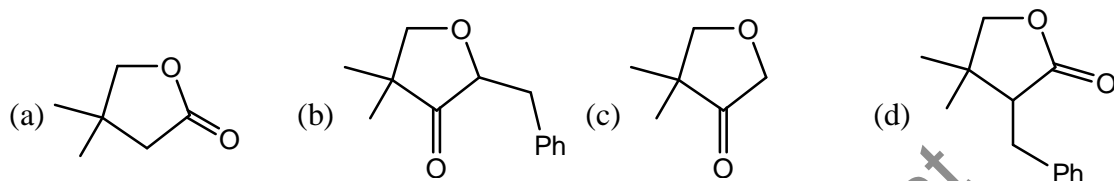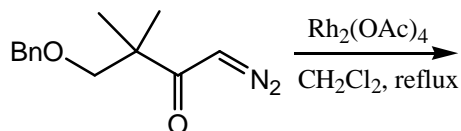
38. The major product formed in the following reaction is

39. The major product formed in the following reaction is
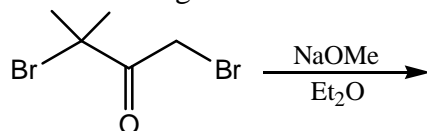
(a)

(b)

(c)

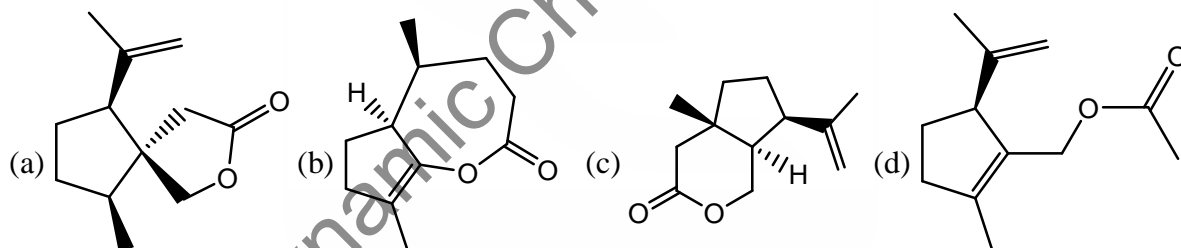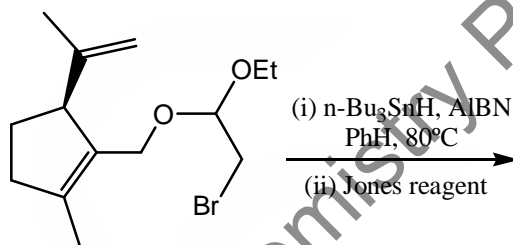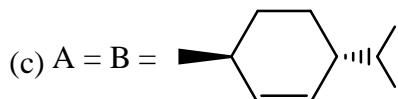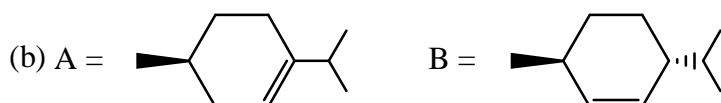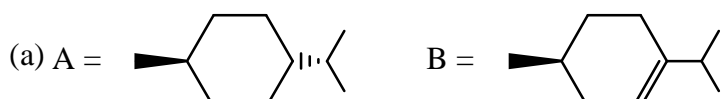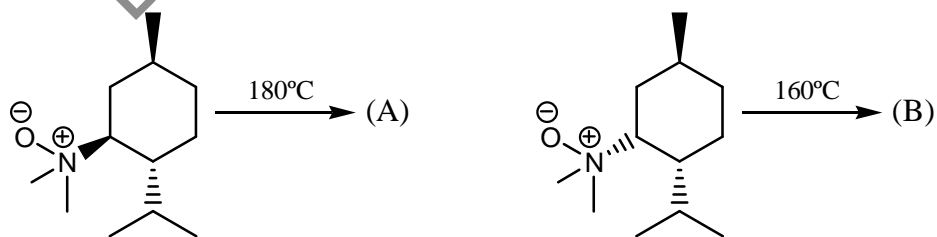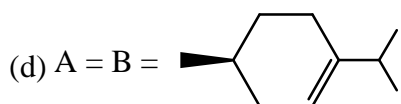(d) MeO$_2$C

40. The major product formed in the following reaction is

$$\text{BnO} \quad \xrightarrow[\text{CH}_2\text{Cl}_2,\ \text{reflux}]{\text{Rh}_2(\text{OAc})_4}$$

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

41. The major product formed in the following reaction is

(i) n-Bu$_3$SnH, AIBN
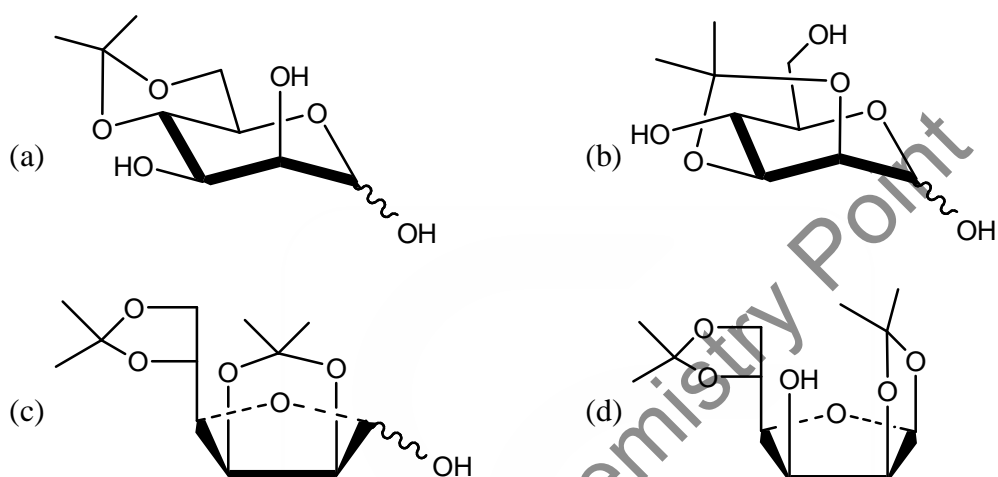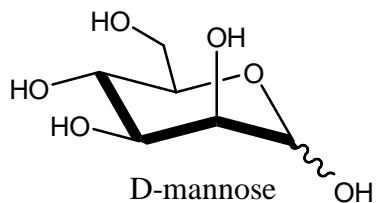PhH, 80ºC
(ii) Jones reagent

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

42. The major product A and B in the following reactions are

 $\xrightarrow{180ºC}$ (A)

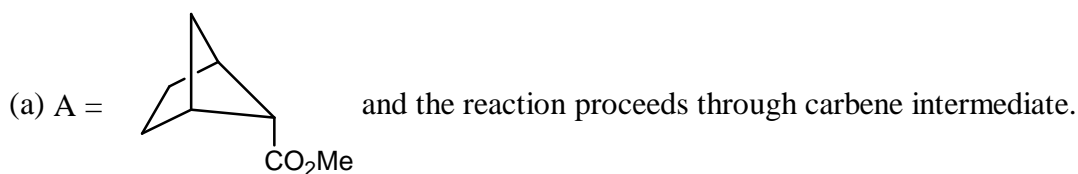 $\xrightarrow{160ºC}$ (B)

(a) A =   B =

(b) A =   B =

(c) A = B =

(d) A = B =

43. D-Mannose upon refluxing in acetone with CuSO$_4$ and H$_2$SO$_4$ gives

D-mannose

(a)

(b)

(c)

(d)

44. The major product formed by photochemical reaction of (2E, 4Z, 6E)-decatriene is

(a)

(b)

(c)

(d)
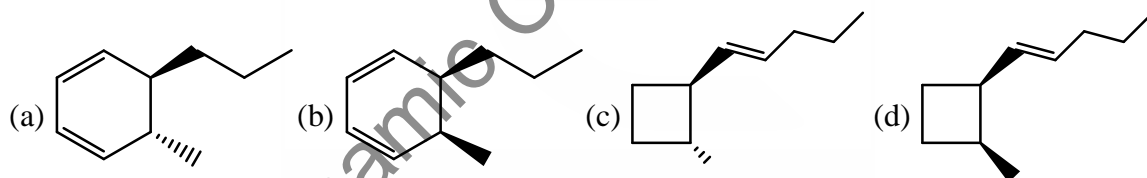
45. The correct statement about the following reaction is that

$$\xrightarrow[\text{h}\nu]{\text{MeOH}} \text{(A)}$$

(a) A =

CO$_2$Me

and the reaction proceeds through carbene intermediate.

(b) A =

CO$_2$Me

and the reaction proceeds through nitrene intermediate.

(c) A = and the reaction proceeds through Norrish type II path.

(d) A = and the reaction proceeds through Norrish type I path.
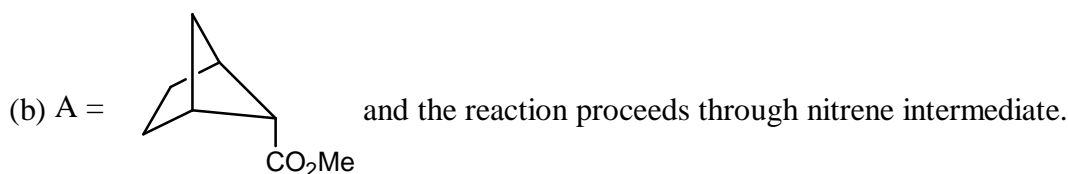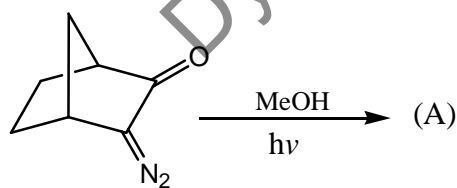
46. The structure of the compounds that matches the ^{1}H NMR data given below is

^{1}H NMR $(DMSO-d_6): \delta \ 7.75 \,(dd, J = 8.8, 2.4 \ Hz, 1H)$, 7.58 (d, J = 2.4 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 6.50 (broad s, 2H), 3.80 (s, 3H).

(a)   (b)   (c)   (d)
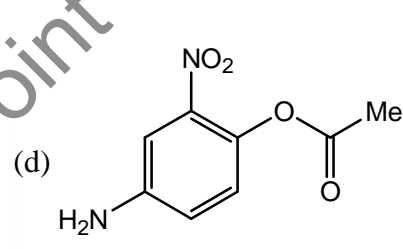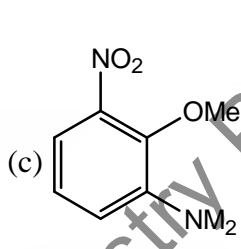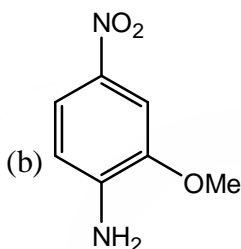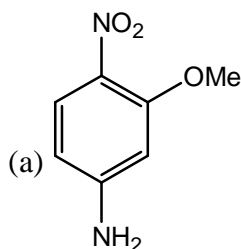
47. Correctly matched structure and carbonyl stretching frequency set is

COLUMN - A   **COLUMN -B**
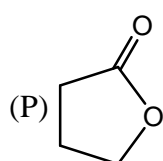
(P)   (X) 1750 cm^{-1}
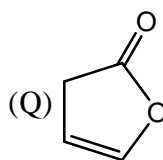
(Q)   (Y) 1770 cm^{-1}
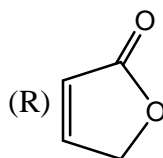
(R)   (Z) 1800 cm^{-1}

(a) P-Y, Q-Z, R-X   (b) P-Y, Q-X, R-Z   (c) P-Z, Q-Y, R-X   (d) P-X, Q-Z, R-Y

48. The number of chemical shift non-equivalent protons expected in ^{1}H NMR spectrum of α-pinene is
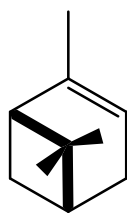
α-pinene

(a) 7   (b) 8   (c) 9   (d) 10

49. In the mass spectrum of 1, 2-dichloroethane, approximate ratio of peaks at m/z values 98, 100, 102 will be

(a) 3 : 1 : 1 (b) 9 : 6 : 1 (c) 1 : 1 : 2 (d) 1 : 2 : 1

50. The major product formed in the following reaction is
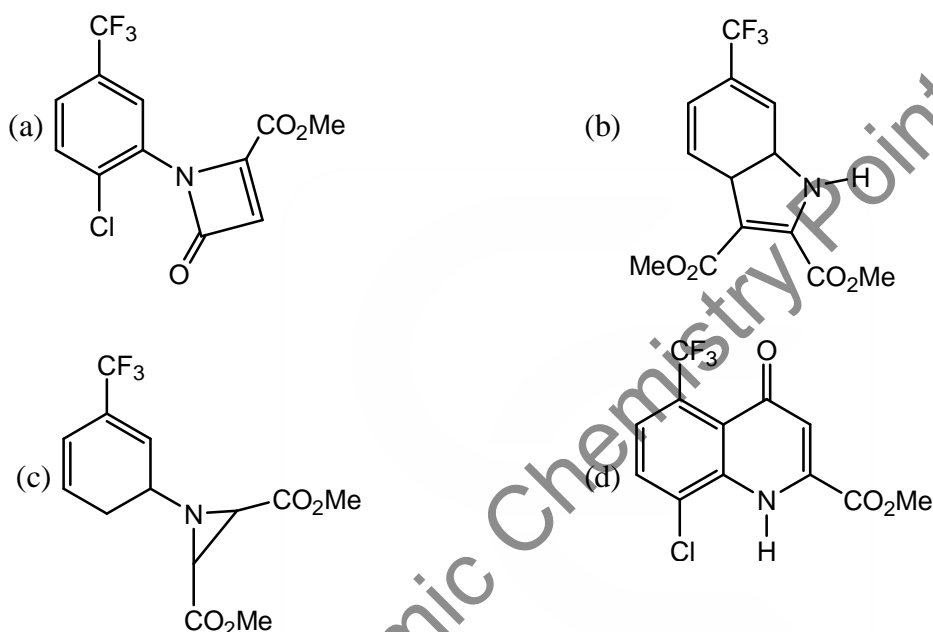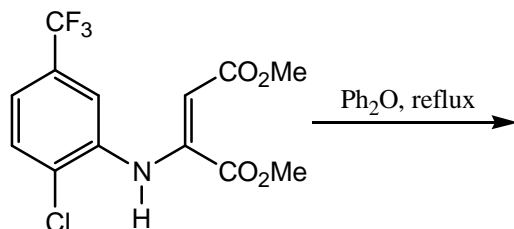
51. The major product formed in the following reaction is
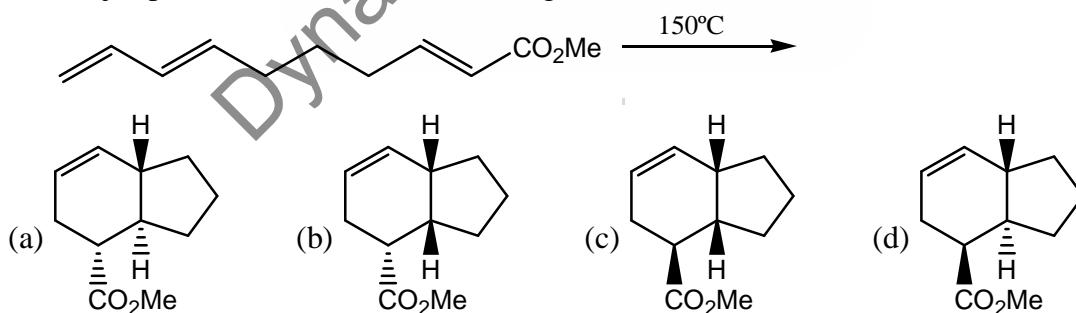
52. The major product formed in the following reaction is

(c)

(d)
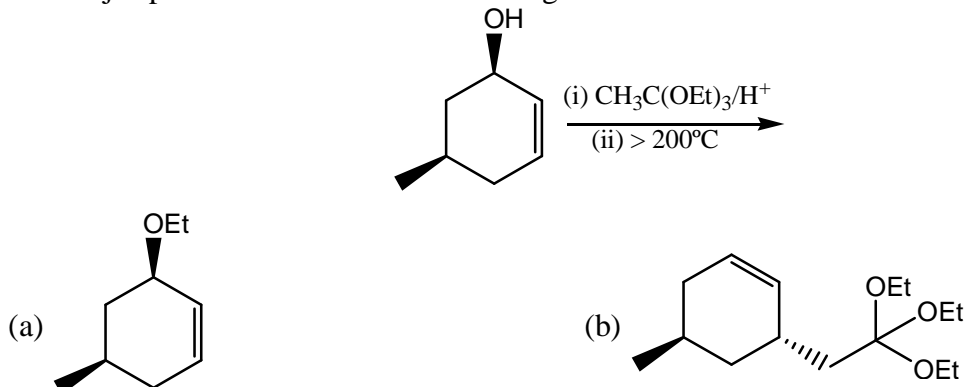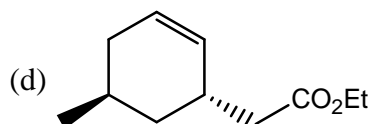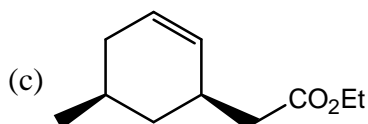
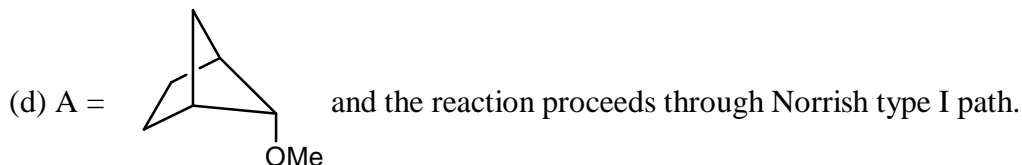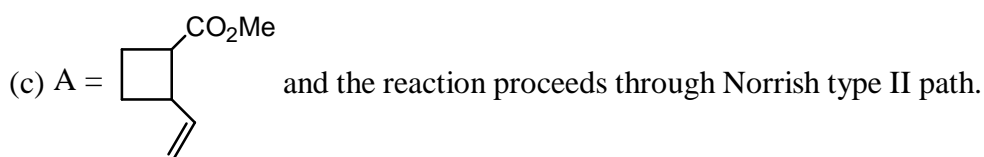53. The concentration of a reactant R varies with time for two different reactions as shown in the following plots :

(I) (II)
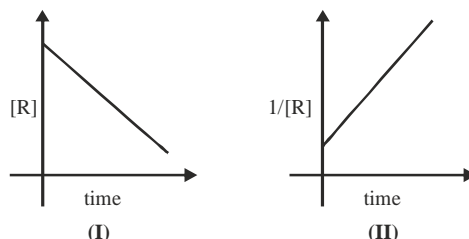
The orders of these two reactions I and II, respectively are
(a) zero and one   (b) one and zero   (c) zero and two   (d) two and zero

54. For a simple cubic crystal lattice, the angle between the [2 0 1] plane and the *xy* plane is
(a) less than 30°   (b) between 30° and 45°   (c) between 45° and 60°   (d) greater than 60°

55. For the following reaction,

$$A \xrightleftharpoons[k_{-1}]{k_1} 2B \; ; \; B \xrightarrow{k_2} C$$
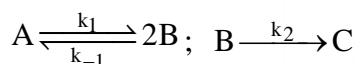
$\dfrac{d[B]}{dt}$ is given by

(a) $k_1[A] - k_{-1}[B]^2 - 2k_2[B]$

(b) $2k_1[A] - k_{-1}[B]^2 - k_2[B]$

(c) $\dfrac{1}{2}k_1[A] - \dfrac{1}{2}k_{-1}[B]^2 - k_2[B]$

(d) $2k_1[A] - 2k_{-1}[B]^{1/2} - k_2[B]$

56. If the reduced mass of a diatomic molecule is doubled without changing its force constant, the vibrational frequency of the molecule will be

(a) $\sqrt{2}$ times the original frequency

(b) $\dfrac{1}{\sqrt{2}}$ times the vibrational frequency

(c) twice the original frequency

(d) unchanged

57. The standard deviation of speed (σ_c) for Maxwell's distribution satisfies the relation

(a) $\sigma_c \propto T$ (b) $\sigma_c \propto \sqrt{T}$ (c) $\sigma_c \propto 1/T$ (d) $\sigma_c \propto 1/\sqrt{T}$

58. The value of $\Delta U - \Delta H$ for the reaction $Fe_2O_3(s) + 3C(s) \longrightarrow 2Fe(s) + 3CO(g)$ is
(a) -3RT   (b) +3RT   (c) +RT   (d) –RT

59. If the pressusre *p*(system) is greater than the p(surroundings), then
(a) work is done on the system by the surroundings
(b) work is down on the surroundigs by the systems
(c) work done on the system by the surroundings is equal to the work done on the surroundings by the system
(d) internal energy of the system increases

60. Two different non-zero operators $\hat{A}$ and $\hat{B}\left(\hat{A} \neq \hat{B}\right)$ satisfy the relation $\left(\hat{A}+\hat{B}\right)\left(\hat{A}-\hat{B}\right)=\hat{A}^2-\hat{B}^2$

(a) $\hat{A}\hat{B}=\hat{A}^2$ and $\hat{B}\hat{A}=\hat{B}^2$

(b) $\hat{A}\hat{B}+\hat{B}\hat{A}=0$

(c) $\hat{A}$ and $\hat{B}$ are arbitrary

(d) $\hat{A}\hat{B}-\hat{B}\hat{A}=0$

61. The degeneracy of an excited state of a particle in 3-dimensional cubic box with energy 3 times its ground state energy is

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

62. ΔH of a reaction is equal to slope of the plot of

(a) ΔG versus $\left(1/T\right)$

(b) ΔG versus T

(c) $\left(\Delta G/T\right)$ versus T

(d) $\left(\Delta G/T\right)$ versus $\left(1/T\right)$

63. The correct form for a simple Langmuir isotherm is

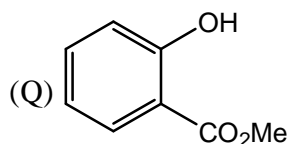(a) $\theta=Kp$ (b) $\theta=\left(Kp\right)^{1/2}$ (c) $\theta=Kp/\left(1+Kp\right)$ (d) $\theta=\left(1+Kp\right)/Kp$

64. In Kohlrausch law, $\Lambda_m=\Lambda_m^0-\kappa\sqrt{c}$, Λ_m^0 and κ

(a) depend only on stoichiometry

(b) depend only on specific identify of the electrolyte

(c) are independent of specific identify of the electrolyte

(d) are mainly dependent on specific identity of the electrolyte and stoichiometry, respectively

65. The correct expression for the product $\left(\left(\bar{M}_n\right)\cdot\left(\bar{M}_w\right)\right)$ [$\bar{M}_n$ and $\bar{M}_w$ are the number-average and weight average molar masses, respectively, of a polymer] is

(a) $N^{-1}\Sigma_i N_i M_i$ (b) $N^{-1}\Sigma_i N_i M_i^2$ (c) $N/\sum_i N_i M_i$ (d) $N/\sum_i N_i M_i^2$

66. The concentration of a $MgSO_4$ solution having the same ionic strength as that of a 0.1 M Na_2SO_4 solution is

(a) 0.05 M   (b) 0.067 M   (c) 0.075 M   (d) 0.133 M

67. sp hybrid orbitals are of the form $C_1 2s+C_2 2p_z$ (2s and $2p_z$ are normalised individually). The coefficients of the normalized form fo the above sp hybrid orbitals are

(a) $C_1=\dfrac{1}{\sqrt{2}}, C_2=\pm\dfrac{1}{\sqrt{2}}$

(b) $C_1=\dfrac{1}{2}, C_2=\pm\dfrac{1}{2}$

(c) $C_1=\dfrac{1}{\sqrt{2}}, C_2=\pm\dfrac{1}{2}$

(d) $C_1=\dfrac{1}{2}, C_2=\pm\dfrac{1}{\sqrt{2}}$

68. The correct statement among the following is

(a) N_2 has higher bond order than N_2^+ and hence has larger bond length compared to N_2^+.

(b) N_2^+ has higher bond order than N_2 and hence has larger bond length compared to N_2.

(c) N_2 has higher bond order than N_2^+ and hence has higher dissociation energy compared to N_2^+.

(d) N_2 has lower bond order than N_2^+ and hence has lower dissociation energy compared to N_2^+ energy.

69. The formation constant for the complexation of M^+ (M = Li, Na, K and Cs) with cryptand, C222 follows the order

(a) $Li^+<Cs^+<Na^+<K^+$

(b) $Li^+<Na^+<K^+<Cs^+$

(c) $K^+<Cs^+<Li^+<Na^+$

(d) $Cs^+<K^+<Li^+<Na^+$

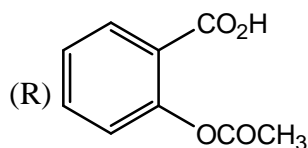70. The correct match for the compounds in **column A** with the description in **column B** is

Column - A   **Column - B**

(P) [structure: 4-isobutyl-α-methylbenzeneacetic acid with CO_2H]

(X) Oil of Wintergreen

(Q) [structure: methyl salicylate with OH and CO_2Me]

(Y) Aspirin

(R) [structure: benzene ring with CO_2H and $OCOCH_3$]
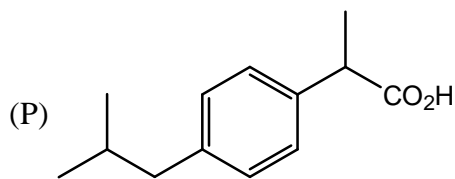
(Z) Ibuprofen

(a) P-Y, Q-Z, R-X   (b) P-Z, Q-X, R-Y   (c) P-Z, Q-Y, R-X   (d) P-X, Q-Z, R-Y

PART-C

71. The resonance Raman stretching frequency (ν_{O-O}, in cm^{-1}) of O_2 is 1580. The ν_{O-O} for O_2 in bound oxy-hemoglobin is close to

(a) 1600   (b) 1900   (c) 800   (d) 1100

72. Match the metalloprotein in **Column-A** with its biological function and metal centre in **Column-B**.

Column-A   **Column-B**

(A) hemoglobin   (I) electron carrier and iron
(B) cytochrome b   (II) electron carrier and copper
(C) vitamin B_{12} (III) O_2 transport and copper
(D) hemocyain   (IV) Group transfer reactions and cobalt
                                        (V) O_2 storage and cobalt
                                        (VI) O_2 transport and iron

The correct match is

(a) A-VI, B-I, C-IV and D-III   (b) A-V, B-I, C-IV and D-III
(c) A-VI, B-V, C-I and D-II   (d) A-V, B-VI, C-II and D-IV

73. Pick the correct statements about Atomic Absorption Spectrometry (AAS) from the following

(A) Hg lamp is not a suitable source for AAS
(B) Graphite furnace is the best atomizer for AAS
(C) Non-metals cannot be determined with AAS
(d) AAS is better than ICP-AES for simultaneous determination of metal ions.

Correct answer is

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

74. Identify radioactive capture from the following nuclear reactions

(a) $^9\text{Be}(\gamma \cdot n)\,^8\text{Be}$ (b) $^{23}\text{Na}(n \cdot \gamma)\,^{24}\text{Na}$

(c) $^{63}\text{Cu}(p \cdot p\, 3n\, 9\alpha)\,^{24}\text{Na}$ (d) $^{107}\text{Ag}(n \cdot n)\,^{107}\text{Ag}$

75. The calibration curve in spectrofluorimetric analysis becomes non-linear when

(a) molecular weight of analyte is high   (b) intensity of light source is high
(c) concentration of analyte is high   (d) molar absorptivity of analyte is high

76. $[MnO_4]^-$ is deep purple in color whereas $[ReO_4]^-$ is colorless. This is due to greater energy required for
    (a) d-d transitions in the Re compound compared to the Mn compound
    (b) d-d transitions in the Mn compound compared to the Re compound
    (c) charge transfer from O to Re compared to O to Mn
    (d) charge transfer from O to Mn compared to O to Re

77. $\left[\left(\eta^3 - C_3H_5\right)Mn\left(CO\right)_4\right]$ shows fluxional behavior. The ^{1}H NMR spectrum of this compound when it is in the non-fluxional state shows
    (a) one signal
    (b) two signals in the intensity ratio of 4 : 1
    (c) three signals in the intensity ratio of 2 : 2 : 1
    (d) five signals of equal intensity.

78. The number of lone pair(s) of electrons on the central atom in $[BrF_4]^-$, XeF_6 and $[SbCl_6]^{3-}$ are, respectively
    (a) 2, 0 and 1   (b) 1, 0 and 0   (c) 2, 1 and 1   (d) 2, 1 and 0

79. Consider the following reaction :

    $$N_3P_3Cl_6 + 6HNMe_2 \rightarrow \underset{[A]}{N_3P_3Cl_3\left(NMe_2\right)_3} + 3$$

    $Me_2NH \cdot HCl$

    The number of possible isomers for [A] is
    (a) 4   (b) 3   (c) 2   (d) 5

80. Using Wade's rules predict the structure type of $[C_2B_5H_7]$
    (a) nido   (b) closos   (c) arachno   (d) hypho

81. Among the following complexes
    (A) $\left[Co\left(ox\right)_3\right]^{3-}$
    (B) $trans-\left[CoCl_2\left(en\right)_2\right]^+$
    (C) $\left[Cr\left(EDTA\right)\right]^-$ the chiral one(s) is/are
    (a) A and B   (b) C and B   (c) C only   (d) A and C

82. Mössbauer spectrum of a metal complex gives information about
    (A) oxidation state and spin state of metal
    (B) types of ligands coordinated to metal
    (C) nuclear spin state of metal
    (D) geometrey of metal
    Correct answer is
    (a) A and C   (b) B and C   (c) A, B and D   (d) B and D

83. For uranocene, the correct statement(s) is/are
    (A) oxidation state of uranium is '+4'
    (B) it has cyclooctatetraenide ligands
    (C) it is bent sandwich compound
    (D) it has '–2' charge
    Correct answer is
    (a) A and B   (b) B and C   (c) A and D   (d) B only

84. The final products of the reaction of carbonyl metalates $\left[V(CO)_6\right]^-$ and $\left[Co(CO)_4\right]^-$ with H_3PO_4, respectaively, are

(a) $V(CO)_6$ and $HCo(CO)_4$

(b) $HV(CO)_6$ and $Co_2(CO)_8$

(c) $\left[H_2V(CO)_6\right]^+$ and $HCo(CO)_4$

(d) $V(CO)_6$ and $Co_2(CO)_8$

85. The correct statement about the substitution reaction of $\left[Co(CN)_5Cl\right]^{3-}$ with OH^- to give $\left[Co(CN)_5(OH)\right]^{3-}$ is,

(a) it obeys first order kinetics

(b) its rate is proportional to the concentration of both the the reactants

(c) it follows the S_N^1CB mechanism

(d) its rate is dependent only on the concentration of $\left[OH\right]^-$

86. Aqueous Cr^{2+} effects one electron reduction of $\left[Co(NH_3)_5Cl\right]^{2+}$ giving compound Y. Compound Y undergoes rapid hydrolysis. Y is ,

(a) $\left[Co(NH_3)_5\right]^{2+}$

(b) $\left[Co(NH_3)_5(OH)\right]^+$

(c) $\left[Co(NH_3)_4(OH)_2\right]$

(d) $\left[Cr(H_2O)_5Cl\right]^{2+}$

87. The reaction of BCl_3 with NH_4Cl gives product A which upon reduction by $NaBH_4$ gives product B. Product B upon reacting with HCl affords compound C, which is

(a) $Cl_3B_3N_3H_9$

(b) $\left[ClBNH\right]_3$

(c) $\left[HBNH\right]_3$

(d) $(ClH)_3B_3N_3(ClH)_3$

88. The number of valence electrons provided by $\left[Ru(CO)_3\right]$ fragment towards cluster bonding is

(a) 1   (b) 14   (c) 6   (d) 2

89. Choose the correct statements about Tanabe-Sugano diagrams

(A) E/B is plotted against Δ_0/B

(B) The zero energy is taken as that of the lowest term

(C) Terms of the same symmetry cross each other

(D) Two terms of the same symmetry upon increases of ligand field strength bend apart from each other.

Correct answer is

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

90. Which of the following statements are TRUE for the lanthanides?

(A) the observed magnetic moment of Eu^{3+} at room temperature is higher than that calculated from spin-orbit coupling

(B) Lanthanide oxides are predominantly acidic in nature

(C) The stability of Sm(II) is due to its half-filled sub-shell.

(D) Lanthanide (III) ions can be separated by ion exchange chromatography

Correct answer is

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

91. The intermediate and the final major product of photolysis of **Z**.

(Z)

From the following:

(A) $(OC)_3Mo$ (B) $Mo(CO)_2$ (C) $Mo(CO)_2$ (D) $(OC)_2Mo$
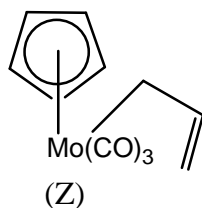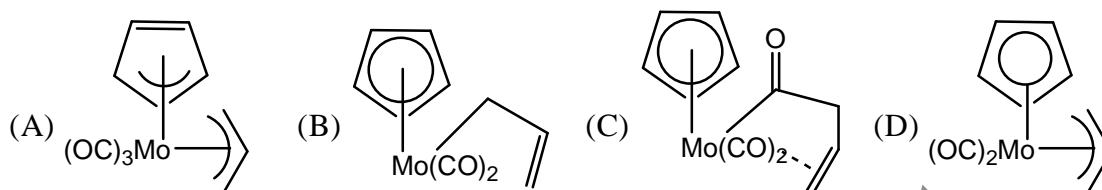
are
(a) A and D   (b) B and D   (c) B and C   (d) A and C

92. Reaction of $[Mn_2(CO)_{10}]$ with I_2 results in A without loss of CO. Compound A, on heating ot 120°C loses a CO ligand to give B, which does not have a Mn–Mn bond. Compound B reacts with pyridine to give 2 equivalents of C. Compounds A, B and C from the following respectively, are
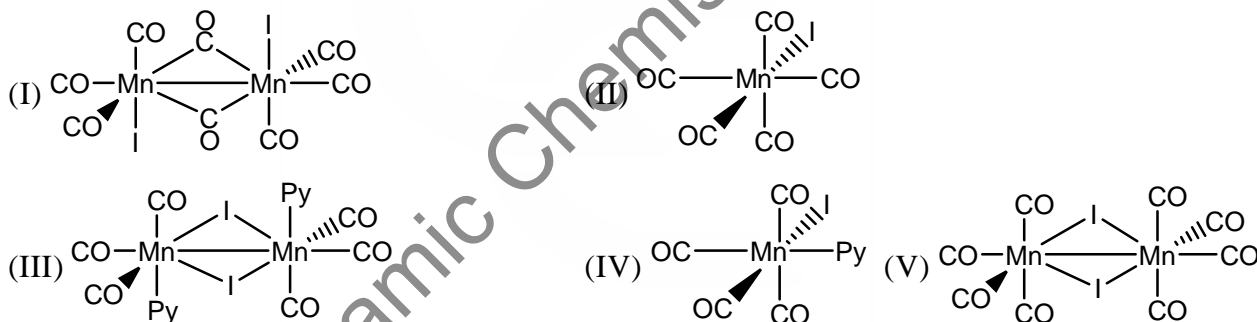
(a) II, V anad IV   (b) II, III and IV   (c) V, III and IV   (d) II, V and III

93. The approximate positions of ν_{CO} bands (cm^{-1}) in the solid-state infrared spectrum and the Fe-Fe bond order in $\left[Fe\left(\eta^5 - C_5H_5\right)\left(\mu - CO\right)\left(CO\right)\right]_2$ (non-centrosymmetric) respectively, are

(a) (2020, 1980, 1800) and one   (b) (2020, 1980, 1800) and two
(c) (2020, 1980) and one   (d) (2143) and one

94. Protonated form of ZSM-5 catalyzes the reaction of ethene with benzene to produce ethylbenzene. The correct statement for this catalytic process is
(a) alkyl carbocation is formed   (b) carbanion is formed
(c) benzene is converted to $(C_6H_5)^+$ group   (d) vinyl radical is formed

95. Three electronic transitions at 14900, 22700 and 34400 cm^{-1} are observed in the absorption spectrum of $\left[CrF_6\right]^{3-}$. The Δ_0 value (in cm^{-1}) and the corresponding transition are

(a) 7800 and $^4A_{2g} \rightarrow {}^4T_{2g}$

(b) 14900 and $^4A_{2g} \rightarrow {}^4T_{2g}$

(c) 14900 and $^4T_{2g} \rightarrow {}^4T_{1g}\left(F\right)$

(d) 7800 and $^4T_{2g} \rightarrow {}^4T_{1g}\left(F\right)$

96. The major product formed in the following reaction is

(a)
(b)
(c)
(d)
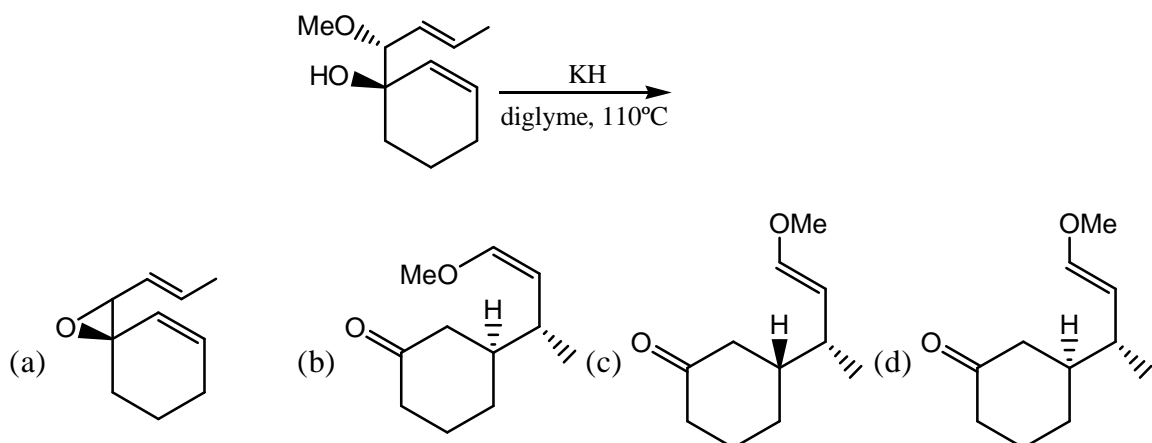
97. The following transformation involves sequential
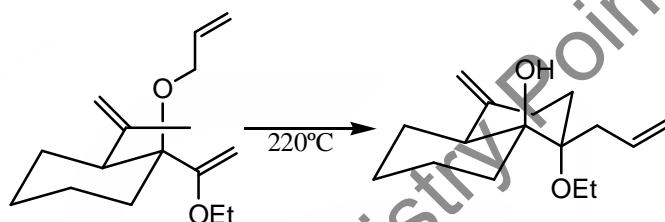
(a) Claisen rearrangement - Cope rearrangement - ene reaction
(b) Cope rearrangement - Claisen rearrangement - ene reaction
(c) Cope rearrangement – ene reaction - Claisen rearrangement.
(d) ene reaction - Claisen rearrangement – Cope rearrangement.

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

(i) m-CPBA
(ii) NaN$_3$, MeOH
(iii) PPh$_3$, MeCN

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

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

$$\xrightarrow[\underset{\text{rt}}{\text{ClH}_2\text{C}-\text{CH}_2\text{Cl}}]{\text{Grubb's catalyst}} \text{(A)} \xrightarrow{\text{LiAlH}_4} \text{(B)}$$

(a) A =   B =

(b) A =   B =

(c) A =   B =

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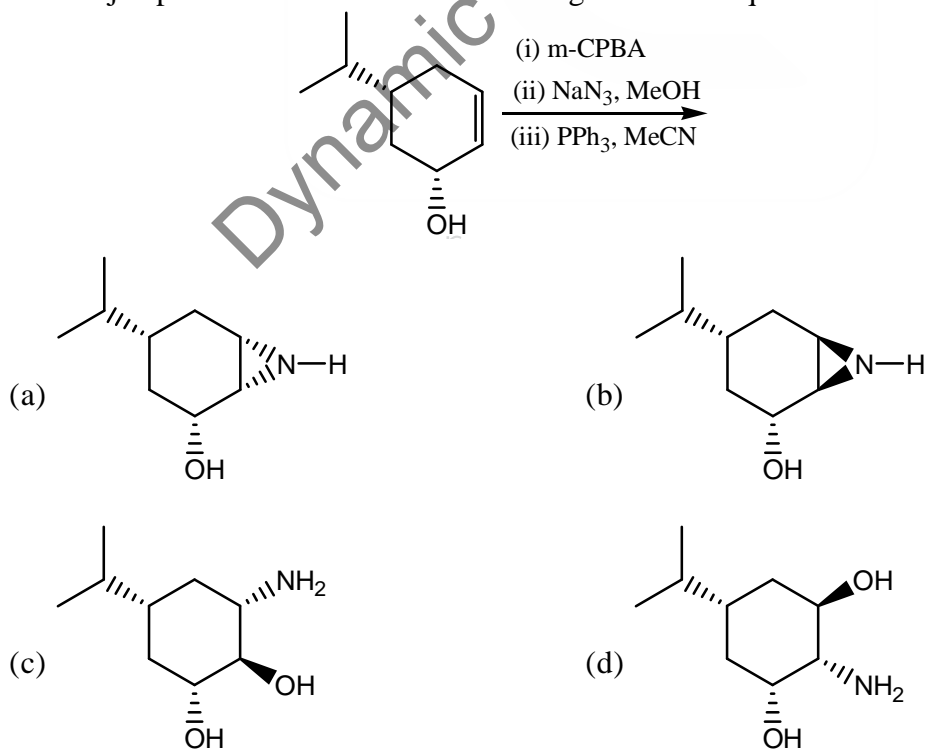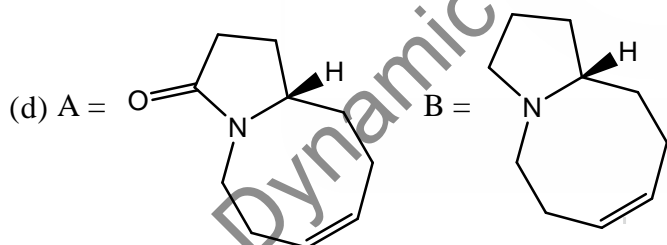
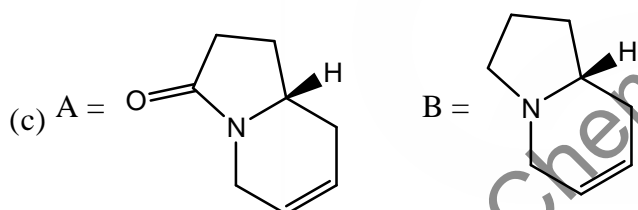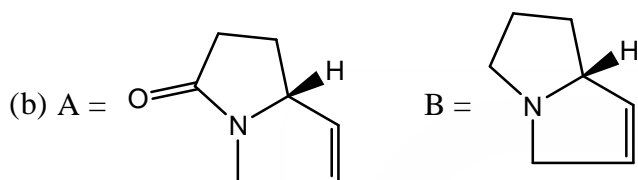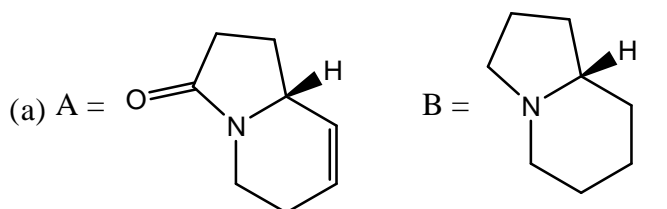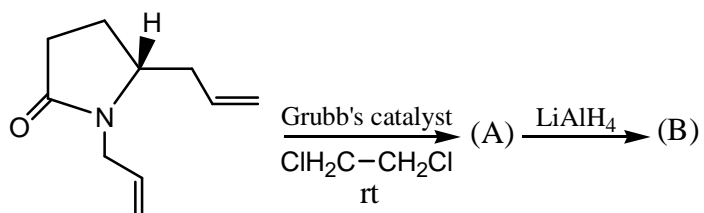100. The major product formed in the following reaction is

$$\xrightarrow[\text{CH}_3\text{CN, }-40^\circ\text{C}]{\text{TMSOTf}}$$

(a)   (b)   (c)   (d)
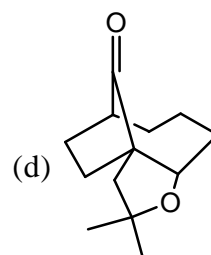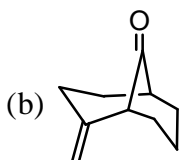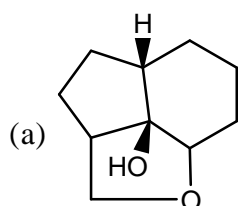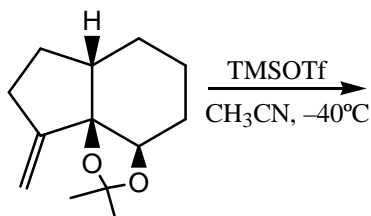
101. The major products A and B in the following reaction sequences are

A ←(i) Br₂, H₂O; (ii) Ca(OH)₂; (iii) H₂O₂, Fe₂(SO₄)₃— [sugar: CHO, HO—H, H—OH, H—OH, CH₂OH] —(i) KCN, HCN; (ii) H₂, Pd/BaSO₄; (iii) H⁺/H₂O→ (B)
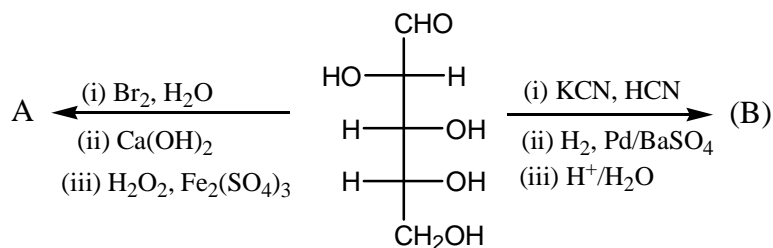
(a) A = D-threose; B = D-glucose
(b) A = D-etythrose; B = D-glucose + D-mannose
(c) A = D-threose; B = D-glucose + D-mannose
(d) A = D-tartaric acid; B = D-glucose

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

Br—CH₂CH₂—Br →(i) PPh₃; (ii) NaH→ (A) →[salicylaldehyde: CHO, OH] NaH→ (B)

(a) A = $Br^{\ominus}$ $Ph_3P^{\oplus}$—CH=CH₂   B = [2-hydroxyphenyl allene with OH]

(b) A = Ph_3P=CH—CH=PPh₃   B = [bis(2-hydroxyphenyl) diene, trans, OH groups]

(c) A = Ph_3P=CH—CH=PPh₃   B = [bis(2-hydroxyphenyl) diene, cis, OH groups]
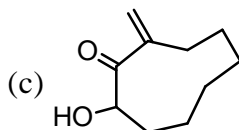
(d) A = $Br^{\ominus}$ $Ph_3P^{\oplus}$—CH=CH₂   B = [2H-chromene]

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

[2-cyclohexenone with Me] →$Me_3\overset{\oplus}{S}=O\ I^{\ominus}$ / NaH, DMSO→ (A) →Li / Liq. NH₃→ (B)

(a) A = [bicyclic cyclopropane ketone with Me]   B = [3-methyl-5-methylcyclohexanone with Me]   (b) A = [spiro epoxide cyclohexene with Me]   B = [cyclohexenyl methanol with OH, Me]

(c) A = [structure: cyclohexanone with methyl groups] B = [structure: cyclohexanone with Me groups]

(d) A = [structure: epoxide with Me] B = [structure: cyclohexenol with OH and Me]

104. The major products A and B in the following reactions sequence are

[reaction scheme: 1,5-cyclooctadiene with B₂H₆ (1 equiv.) at 25°C → (A); then (i) vinylcyclohexene, (ii) methyl (Z)-3-iodoacrylate, Pd(dppl)Cl₂, AsPh₃, Cs₂CO₃, DMF, H₂O → (B)]

B_2H_6 (1 equiv.)

25ºC

(i)

(ii) CO_2Me

Pd(dppl)Cl$_2$

AsPh$_3$, Cs$_2$CO$_3$

DMF, H$_2$O

(a) A = [9-BBN structure] B = [cyclohexenyl-propyl-CO$_2$Me structure]

(b) A = [9-BBN structure] B = [cyclohexenyl chain with CO$_2$Me, E-alkene]

(c) A = [bicyclic borane structure] B = [cyclohexenyl chain with Z-CO$_2$Me]

(d) A = [bicyclic borane structure] B = [cyclohexenyl chain with methyl branch and CO$_2$Me]

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

(i) t-BuOK(2.2 equiv.)
MeI(2.5 equival.), THF

(ii) NaBH$_4$, MeOH
(iii|) AcCl, pyridine
(iv) CF$_3$CO$_2$H, Et$_3$SiH
CH$_2$Cl$_2$

(A) $\xrightarrow[\text{liq. NH}_3, \text{THF}, -40^\circ\text{C}]{\text{Li, t-BuOH}}$ (B)

(a) A =   B =

(b) A =   B =

(c) A =   B =

(d) A =   B =

106. The major product formed in the following reaction is

(i) PhSeCl
AcOH, NaOAc

(ii) H$_2$O$_2$, MeOH

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

107. The major product formed in the following reaction is

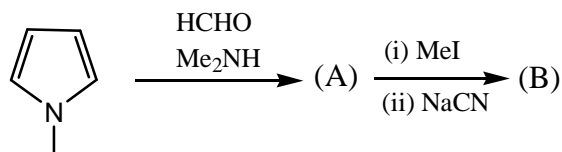$\xrightarrow[\text{PPh}_3, \text{Ag}_2\text{CO}_3]{\text{Pd(OAc)}_2}$

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

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

(a) A = [structure: 1-methylpyrrole with CH2NMe2 at position 2]   B = [structure: 1-methylpyrrole with CN at position 3, CH3 at position 2]

(b) A = [structure: 1-methylpyrrole with CH2NMe2 at position 2]   B = [structure: 1-methylpyrrole with CH2CN at position 2]

(c) A = [structure: 1-methylpyrrole with CH2NMe2 at position 3]   B = [structure: 1-methylpyrrole with CH3 at position 3, CN at position 2]
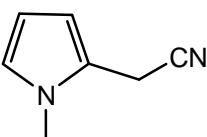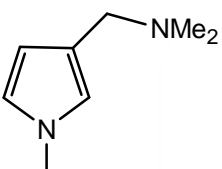
(d) A = [structure: 1-methylpyrrole with CH2NMe2 at position 3]   B = [structure: 1-methylpyrrole with CH2CN at position 3]
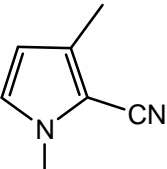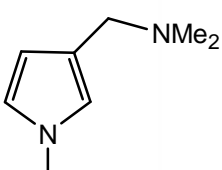
109. The major products A and B in the following reaction sequence are

E = CO$_2$Me

(a) A = [structure with azo group and two E substituents]   B = [structure with N=N azo group]

(b) A = [structure with H-N-Cl]   B = HO—[chain]—with NH$_2$ and E

(c) A =   B =

(d) A =   B =

110.   The correct reagent combination to effect the following transformation is

(a) A = NaBH$_4$, BF.OEt$_2$; B = MeMgBr (2.5 equiv.), THF then H$_3$O$^+$
(b) A = BH$_3$.THF; B = MeLi (2.5 equiv.), THF then H$_3$O$^+$
(c) A = BH$_3$.THF; B = (i) aq. NaOH then H$_3$O$^+$, (ii) MeLi (2.5 equiv,), THF then H$_3$O$^+$
(d) A = (i) Me$_3$Al, MeNHOMe; (ii) MeMgBr, THF then H$_3$O$^+$; B = LiAlH$_4$, THF

111.   The mechanism and the product formed in the following reaction, respectively, are

(a) S$_N$2

(b) S$_N$1

(c) S$_N$2

(d) S$_N$1

112. A concerted [1, 3]-sigmatropic rearrangement took place in the reaction shown below. The structure of the resulting product is
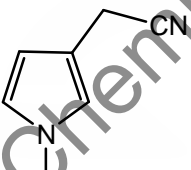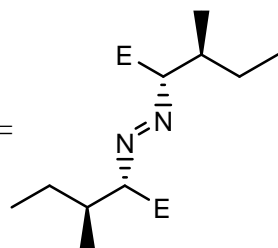

(a)   (b)   (c)   (d)

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

$$\xrightarrow[\text{DMAP, CH}_2\text{Cl}_2]{\text{PhCO}_2\text{H, DCC}} \text{(A)} \xrightarrow[\text{then alumina}]{\text{PDC, CH}_2\text{Cl}_2}} \text{(B)}$$

(a) A =   B =

(b) A =   B =

(c) A =   B =

(d) A = [structure: decalin system with OH (CH₂OH) and OCOPh substituents]   B = [structure: decalin system with CHO and OH substituents]
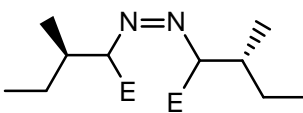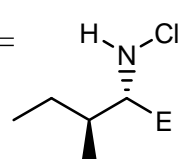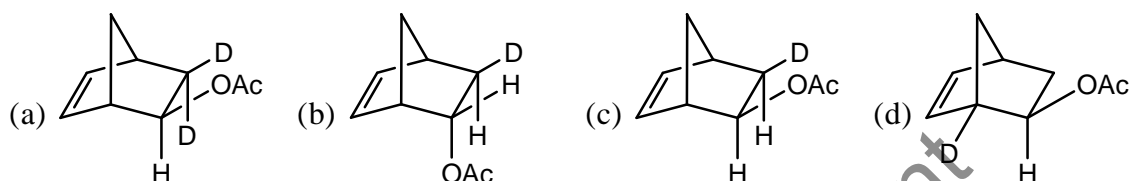
114. The major product formed in the following reaction sequence is

[structure: cyclopentane with boronate ester (1,3,2-dioxaborinane) and methyl group]

$$\xrightarrow[\text{(iii) H}_2\text{O}_2/\text{NaOH}]{\begin{array}{l}\text{(i) LiCH(OMe)SPh}\\ \text{(ii) HgCl}_2\end{array}}$$

(a) [cyclopentane with Ph]   (b) [cyclopentane with CH₂OH]   (c) [cyclopentane with CH₂OH]   (d) [cyclopentane with CHO]

115. The major product formed in the following reaction is

[structure: di-tert-butyl substituted benzene with additional tert-butyl groups]

$$\xrightarrow{h\nu}$$

(a) [1,3,5-tri-tert-butylbenzene]   (b) [bicyclic structure with tert-butyl groups]

(c) [1,2,3-tri-tert-butylbenzene]   (d) [cyclobutane fused ring with tert-butyl groups]

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

[structure: 1-naphthol (OH on naphthalene)] + [epichlorohydrin: epoxide with CH₂Cl] $\xrightarrow{\text{NaH}}$ (A) $\xrightarrow{\text{isopropylamine (NH}_2\text{)}}$ (B)

(a) A =   B =

(b) A =   B =

(c) A =   B =

(d) A =   B =

117. The major product of the following reaction is

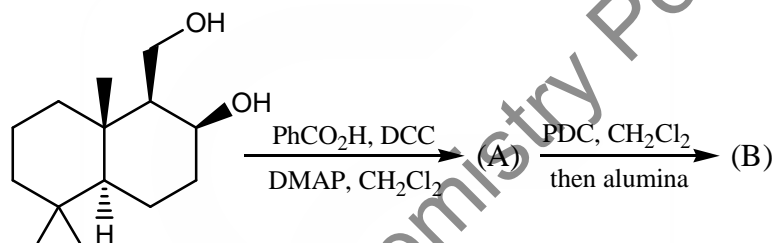$$\xrightarrow[\text{MeOH, }-78°C]{\text{NaBH}_4,\ \text{CeCl}_3}$$

(a)   (b)

(c)   (d)

118. The major product A and B in the following reaction sequence are

$$\xrightarrow{\ } (A) \xrightarrow[\text{t-BuOH, heat}]{\text{t-BuOK diglyme}} (B)$$

(a) A =   B =

(b) A =   B =

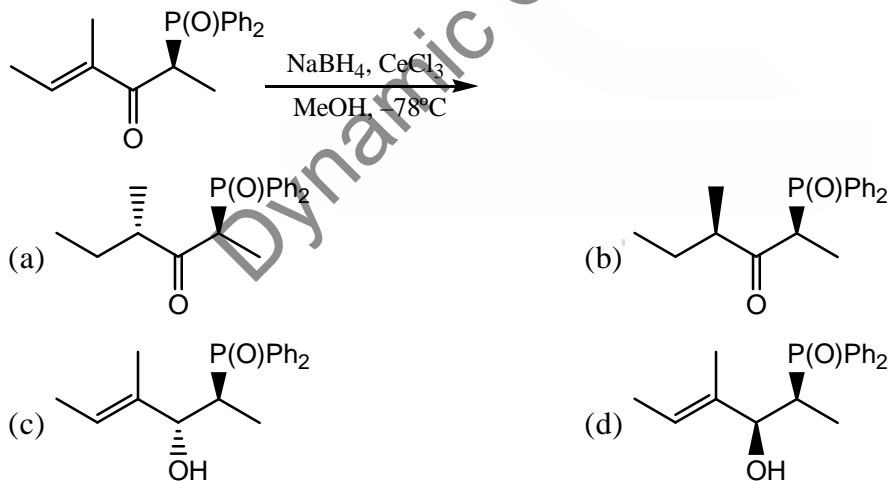(c) A =   B =

(d) A =   B =

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

(a) A =   B =

(b) A =   B =

(c) A =   B =

(d) A =

(structure: ethyl ester with ketone) B = (structure with NO group)

120. The major product of the following reaction is
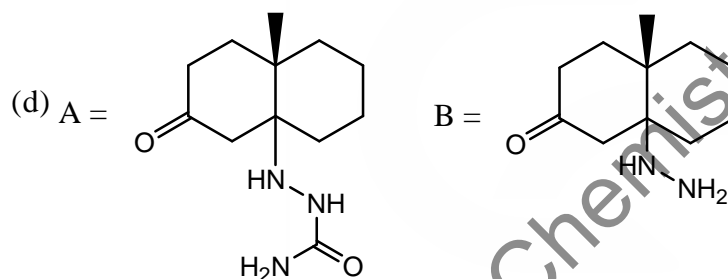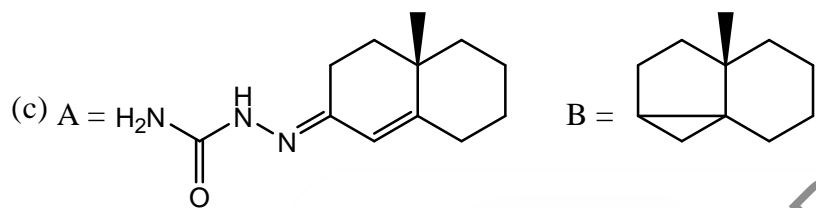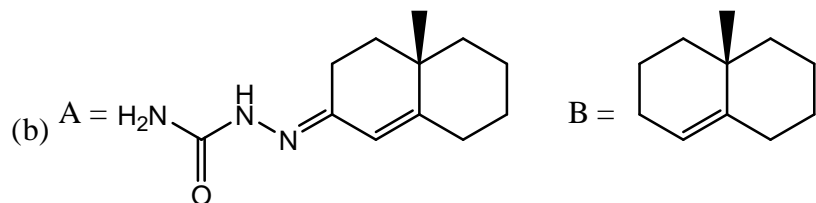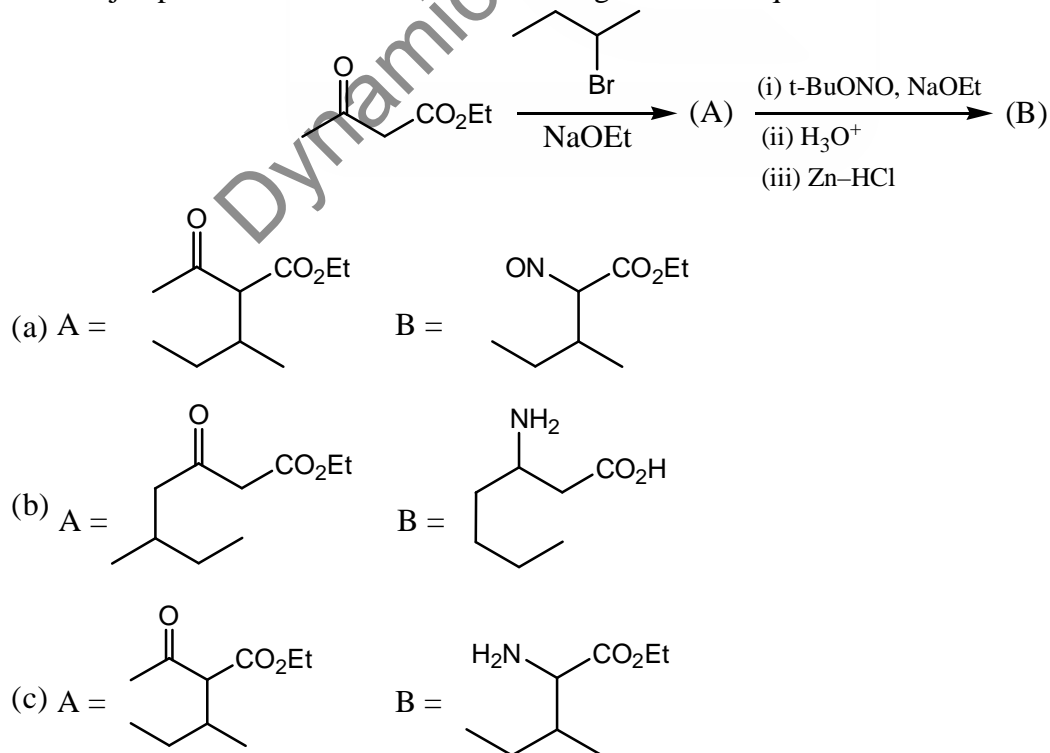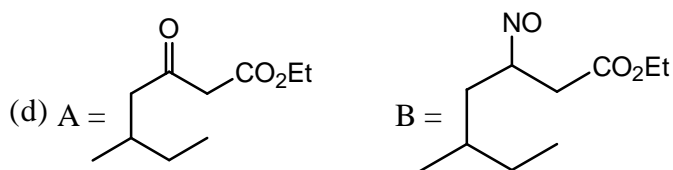

(i) THF, heat
(ii) CF_3CO_2H

(a) (structure with Me, CO_2Me)

(b) (structure with COMe, OMe)

(c) (structure with Me, CO_2Me)

(d) (structure with OMe, COMe)

121. According to the transition state theory, one of the vibrations in the activated complex is a loose vibration. The partition function for this loose vibration is equal to (k_B is the Boltzmann's constant and h is the Planck's constant)

(a) $\dfrac{k_B T}{h}$
(b) $\dfrac{h\nu}{k_B T}$
(c) $k_B T$
(d) $\dfrac{k_B T}{h\nu}$

122. Possible term symbol(s) of the excited states of Na atom with the electronic configuration $\left[1s^2 2s^2 2p^6 3p^1\right]$ is/are

(a) $^2S_{1/2}$
(b) $^2P_{3/2}$ and $^2P_{1/2}$
(c) $^1S_0$ and $^1P_1$
(d) $^3P_0$ and $^3P_1$

123. For a simple cubic crystal, X-ray diffraction shows intense reflections for angles θ_1 and θ_2 which are assigned to [1 0 1] and [1 1 1] planes, respectively. The ratio $\dfrac{\sin\theta_1}{\sin\theta_2}$ is
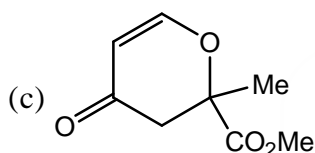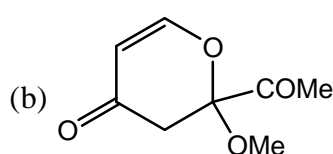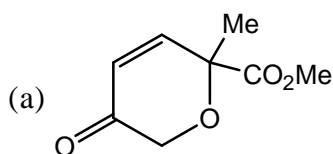
(a) 1.5
(b) 1.22
(c) 0.82
(d) 0.67

124. Stability of lyophobic dispersions is determined by
(a) inter-particle electric double layer repulsion and intra-particle van der waals attraction
(b) inter-particle electric double layer attraction and intra-particle van der waals repulsion
(c) inter-particle excluded volume repulsion and intra-particle van der waals attraction
(d) inter-particle excluded volume attraction and intra-particle van der waals repulsion.

125. A certain 2-level system has stationary state energies E_1 and E_2 ($E_1 < E_2$) with normalized wave functions φ_1 and φ_2 respectively. In the presence of a perturbation V, the second-order correction to the energy for the first state (φ_1) will be

(a) $\dfrac{\langle\varphi_1|V|\varphi_2\rangle}{E_1 - E_2}$
(b) $\dfrac{\langle\varphi_1|V|\varphi_2\rangle}{E_2 - E_1}$
(c) $\dfrac{\left|\langle\varphi_1|V|\varphi_2\rangle\right|^2}{E_1 - E_2}$
(d) $\dfrac{\left|\langle\varphi_1|V|\varphi_2\rangle\right|^2}{\left(E_1 - E_2\right)^2}$

126. The ^1H NMR frequency at 1.0 T is 42.4 MHz. If the gyromagnetic ratios of ^1H and ^{13}C are 27×10^7 and 6.75×10^7 T^{-1}S^{-1}, respectively, what will be the ^{13}C frequency at 1.0 T?

(a) 10.6 MHz   (b) 169.9 MHz   (c) 42.6 MHz   (d) 21.3 MHz

127. 10 mL aliquots of a mixture of HCl and HNO_3 are titrated are titrated conductometrically using a 0.1M NaOH and a 0.1M $AgNO_3$ separately. The titre volumes are V_1 and V_2 mL, respectively. The concentration of HNO_3 in the mixture is obtained from the combination.

(a) $V_1 - V_2$ (b) $2V_1 - V_2$ (c) $V_2 - V_1$ (d) $2V_2 - V_1$

128. Given that $E^0 \left(Cl_2 / Cl^- \right) = 1.35\,V$ and $K_{sp} \left(AgCl \right) = 10^{-10}$ at 25°C, E^0 corresponding to the electrode reaction

$$\frac{1}{2}Cl_2 \left(g \right) + Ag^+ \left(so\ln. \right) + e^- \rightarrow AgCl \left(s \right) \text{ is} \qquad \left[\frac{2.303RT}{F} = 0.06V \right]$$

(a) 0.75V   (b) 1.05V   (c) 1.65V   (d) 1.95V

129. The standard EMF of the cell $Pt, H_2 \left(g \right) | HCl \left(so\ln. \right) | AgCl \left(s \right), Ag \left(s \right)$

(a) increases with T   (d) decreases with T

(c) remains unchanged with T   (d) decreases with [HCl]

130. The molecule with the smalllest rotational constant (in the microwave spectrum) among the following is

(a) $N \equiv CH$ (b) $HC \equiv CCl$ (c) $CCl \equiv CF$ (d) $B \equiv CCl$

131. The spectroscopic technique that can distinghuish unambiguously between trans-1, 2-dichloroethylene and cis-1, 2-dichloroethylene without any numerical calculation is

(a) microwave spectroscopy   (b) UV-visible spectroscopy

(c) X-ray photoelectron spectroscopy   (d) γ-ray spectroscopy

132. The ground state electronic configuration of C_2 using all electron is

(a) $\sigma_{1s}^2 \, \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^2$ (b) $\sigma_{1s}^2 \, \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \sigma_{2p}^{*2}$

(c) $\sigma_{1s}^2 \, \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^2 \sigma_{2p}^1 \sigma_{2p}^{*1}$ (d) $\sigma_{1s}^2 \, \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4$

133. $v_{\max}$ and K_m for an enzyme catalyzed reaction are $2.0 \times 10^{-3}\,Ms^{-1}$ and $1.0 \times 10^{-6}M$, respectively. The rate of the reaction when the substrate concentration is $1.0 \times 10^{-6}M$ is

(a) $3.0 \times 10^{-3} s^{-1}$ (b) $1.0 \times 10^{-3} s^{-1}$ (c) $2.0 \times 10^{-3} s^{-1}$ (d) $0.5\ s^{-1}$

134. The first order rate constant for a unimolecular gas phase reaction $A \rightarrow$ products that follows Lindemann mechanism is 2.0 s^{-1} at p_A = 1 atm and 4.0 s^{-1} at p_A = 2 atm. The rate constant for the activation step is

(a) $1.0\ atm^{-1}s^{-1}$ (b) $2.0\ atm^{-1}s^{-1}$ (c) $4.0\ atm^{-1}s^{-1}$ (d) $8.0\ atm^{-1}s^{-1}$

135. The molecule diborane belongs to the symmetry point group

(a) C_{2v} (b) C_{2h} (c) D_{2d} (d) D_{2h}

136. Though a constant shift of energy levels of a system changes the partition function, the properties that do not change are

(a) average energy, entropy and heat capacity

(b) average energy and entropy

(c) average energy and heat capacity

(d) entropy and heat capacity.

137. The vibrational frequency of a homo-nuclear diatomic molecule is v. The temperature at which the population of the first excited state will be half that of the ground state is given by

(a) $hv \cdot \ln 2 / k_B$ (b) $hv / (\ln 2 \cdot k_B)$ (c) $\ln 2 / (hv \cdot k_B)$ (d) $hv \cdot \log 2 / k_B$

138. The irreducible representations of C_{2h} are A_g, B_g, A_u and B_u. The Raman active modes of trans-1, 3-butadiene belong to the irreducible representations

(a) A_g and B_g (b) A_g and A_u (c) A_u and B_g (d) B_g and B_u

139. The symmetry-allowed atomic transition among the following is

(a) $^3F \rightarrow {}^1D$ (b) $^3F \rightarrow {}^3D$ (c) $^3F \rightarrow {}^1P$ (d) $^3F \rightarrow {}^3P$

140. The average end-to-end distance of a random coil polymer 10^6 monomers (in units of segment length) is

(a) 10^6 (b) 10^5 (c) 10^4 (d) 10^3

141. A reversible expansion of 1.0 mol of an ideal gas is carried out from 1.0 L to 4.0 L under isothermal condition at 300K. ΔG for this process is

(a) $300R \cdot \ln 2$ (b) $600R \cdot \ln 2$ (c) $-600R \cdot \ln 2$ (d) $-300R \cdot \ln 2$

142. The temperature-dependence of the vapour pressurse of solid A can be represented by $\log p = 10.0 - \dfrac{1800}{T}$, and that of liquid A by $\log p = 8.0 - \dfrac{1400}{T}$. The temperature of the triple point of A is

(a) 200 K (b) 300 K (c) 400 K (d) 500 K

143. The non-spontaneous process among the following is
(a) vapourisation of superhead water at 105°C and 1 atm pressure
(b) expansion of a gas into vacuum freezing
(c) freezing of supercooled water at −10°C and 1 atm pressure
(d) freezing of water at 0°C and 1 atm pressure.

144. The radial part of a hydrogenic wave function is given as $r(\alpha - r)e^{-\beta r}$ $(\alpha, \beta$ are constants$)$. This function is then indentifiable as

(a) 2s (b) 3p (c) 4d (d) 5f

145. A normalised state ϕ is constructed as a linear combination of the ground state (ψ_0) and the first excited state (ψ_1) of some harmonic oscillator with energies 1/2 and 3/2 units, respectively. If the average energy of the state ϕ is 7/6, the probability of finding ψ_0 in ϕ will be

(a) 1/2 (b) 1/3 (c) 1/4 (d) 1/5