June- 2011

BOOKLET-C

PART - B

21. According to crystal field theory, Ni^{2+} can have two unpaired electrons in
(a) Octahedral geometry only
(b) Square-planar geometry only
(c) Tetrahedral geometry only
(d) Both octahedral and tetrahedral geometry.

22. $\left[Ni\left(CN\right)_4\right]^{2-}$ and $\left[NiCl_4\right]^{2-}$ complex ions are
(a) Both diamagnetic
(b) Both paramagnetic
(c) Diamagnetic and paramagnetic respectively
(d) Antiferromagnetic and diamagnetic respectively

23. Which of the following spectroscopic techniques will be useful to distinguish between M-SCN and M-NCS binding modes?
(a) NMR
(b) IR
(c) EPR
(d) Mass

24. Which of the following compound show a charge-transfer band?
(a) Lanthanum nitrate
(b) Ceric ammonium nitrate
(c) Manganese (II) acetate
(d) Copper (II) sulphate pentahydrate

25. Among SF_4, BF_4^-, XeF_4 and ICl_4^- the number of species having two lone pair of electrons on the central atom according to VSEPR theory is:
(a) 2
(b) 3
(c) 4
(d) 0

26. The **FALSE** statement for a polarographic measurement procedure is:
(a) O_2 is removed
(b) Dropping mercury electrode is working electrode.
(c) I_d is proportionaal to concentation of electroactive species.
(d) Residual current is made zero by adding supporting electrolyte.

27. The ligand system present in vitamin B_{12} is:
(a) Porphyrin
(b) Corrin
(c) Phthalocyanine
(d) Crown ether

28. Which one of the following exhibits rotational spectra?
(a) H_2
(b) N_2
(c) CO
(d) CO_2

29. In Ziegler-Natta catalysis the commonly used catalyst system is:
(a) $TiCl_4, Al\left(C_2H_5\right)_3$
(b) $\left(\eta^5-Cp\right)_2 TiCl_2, Al\left(OEt\right)_3$
(c) $VO\left(acac\right)_2, Al_2\left(CH_3\right)_6$
(d) $TiCl_4, BF_3$

30. Oxidation occurs very easily in case of
(a) $\left(\eta^5-C_5H_5\right)_2 Fe$
(b) $\left(\eta^5-C_5H_5\right)_2 Co$
(c) $\left(\eta^5-C_5H_5\right)_2 Ru$
(d) $\left(\eta^5-C_5H_5\right)_2 Co^+$

31. Complex in which organic ligand is having only $\sigma-$bond with metal is:
(a) $W\left(CH_3\right)_6$
(b) $\left(\eta^5-C_5H_5\right)_2 Fe$
(c) $K\left[PtCl_3\left(C_2H_4\right)\right]$
(d) $\left(\eta^6-C_6H_6\right)_2 Ru$

32. In the molecules H_2O, NH_3 and CH_4.

(a) The bond angles are same
(b) The bond distances are same.
(c) The hybridizations are same
(d) The shapes are same.

33. The correct order of stability of difluorides is:

(a) $GeF_2 > SiF_2 > CF_2$
(b) $CF_2 > SiF_2 > GeF_2$
(c) $SiF_2 > GeF_2 > CF_2$
(d) $CF_2 > GeF_2 > SiF_2$

34. The number of possible isomers for $\left[Ru\left(bpy\right)_2 Cl_2\right]$ is (bpy = $2,2'-$bipyridine)

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

35. The species ^{19}Ne and ^{14}C emit a positron and $\beta-$particle respectively. The resulting species formed are respectively

(a) ^{19}Na and ^{14}B
(b) ^{19}F and ^{14}N
(c) ^{19}Na and ^{14}N
(d) ^{19}F and ^{14}B

36. Cis and trans complexes of the type $[PtA_2X_2]$ are distinguished by

(a) Chromyl chloride test
(b) Carbylamine test
(c) Kurnakov test
(d) Ring test

37. The term symbol of a molecule with electronic configuration

$$\left(1\sigma_g\right)^2\left(1\sigma_u\right)^2\left(2\sigma_g\right)^2\left(2\sigma_u\right)^2\left(1\pi_u\right)^1\left(1\pi_u\right)^1 \text{ is:}$$

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

38. A process is carried out at constant volume and at constant entropy. It will be spontaneous if:

(a) $\Delta G < 0$
(b) $\Delta H < 0$
(c) $\Delta U < 0$
(d) $\Delta A < 0$

39. The half life of a zero order reaction $\left(A \rightarrow P\right)$ is given by (k = rate constant):

(a) $t_{1/2} = \dfrac{[A]_0}{2k}$
(b) $t_{1/2} = \dfrac{2.303}{k}$
(c) $t_{1/2} = \dfrac{[A]_0}{k}$
(d) $t_{1/2} = \dfrac{1}{k[A]_0}$

40. For an aqueous solution at 25°C, the Debye-Huckel limiting law is given by

(a) $\log\gamma_{\pm} = 0.509\left|Z_+Z_-\right|\sqrt{\mu}$
(b) $\log\gamma_{\pm} = 0.509\left|Z_+Z_-\right|\mu$
(c) $\log\gamma_{\pm} = -0.509\left|Z_+Z_-\right|\sqrt{\mu}$
(d) $\log\gamma_{\pm} = -0.509\left|Z_+Z_-\right|\mu^2$

41. The microwave spectrum of a molecule yields three rotational constants. The molecule is

(a) Prolate symmetric top
(b) Spherical top
(c) Asymmetric top
(d) Oblate symmetric top

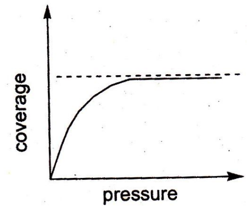
42. The Q band in the vibrational spectrum of acetylene is observed in the

(a) C–C stretching mode
(b) C-H symmetric stretching mode
(c) Bending mode
(d) C-H antisymmetric stretching mode.

43. The Stark splitting for a given field is larger for a molecule AX as compared to BX. Which one of the following is true? (μ is the dipole moment)

(a) $\mu_{AX} = \mu_{BX}$
(b) $\mu_{AX} > \mu_{BX}$
(c) $\mu_{AX} < \mu_{BX}$
(d) $\mu_{BX} = 2\mu_{AX}$

44. The adsoprtion of a gas on a solid surface exhibits the following isotherm. Which one of the following statements is true?



(a) Heat of adsoprtion is independent of coverage
(b) Adsorption is multilayer
(c) Heat of adsorption varies monotonically with coverage
(d) Heat of adsorption varies exponentially with coverage.

45. In a chemical reaction, $A(s)+B(g) \rightleftharpoons C(g)$, the total pressure at equilibrium is 6 atm. The value of equilibrium constant is:
(a) 1/2 (b) 9 (c) 1 (d) 36

46. A molecule, AX, has a vibrational energy of 1000 cm^{-1} and rotational energy of 10 cm^{-1}. Another molecule, BX, has a vibrational energy of 400 cm^{-1} and rotational energy of 40 cm^{-1}. Which one of the following statements about the coupling of vibrational and rotational motion is true?
(a) The coupling is stronger in BX.
(b) The coupling is stronger in AX.
(c) Magnitude of coupling is same in both AX and BX.
(d) There is no coupling in both AX and BX

47. At room temperature, which molecule has the maximum rotational entropy?
(a) H_2 (b) O_2 (c) D_2 (d) N_2.

48. The normalized hydrogen atom 1s wavefunction is given by $\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{\zeta}{a_0}\right)^{3/2} e^{-\zeta r/a_0}$ where $\zeta = 1$ and energy is – 0.5 au. If we use a normalized wavefunction of the above form with $\zeta \neq 1$, the average value of energy of the ground state of hydrogen atom is:
(a) Greater than – 0.5 au (b) Equal to – 0.5 au
(c) Less than – 0.5 au (d) Equal to ζ times – 0.5 au.

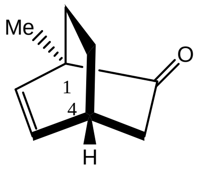
49. A constant of motion is defined by the equation:
(a) [H, A] = 0 (b) <[H, A] > =0 (c) A = f(H) (d) $A^\dagger = A$

50. The hermitian conjugate of operator d/dx, called $(d/dx)^\dagger$, is actually equal to
(a) $-d/dx$ (b) d/dx (c) i(d/dx) (d) –i(d/dx)

51. An ideal gas expands by following an equation PV^a = constant. In which case does one expect heating?
(a) $3 > a > 2$ (b) $2 > a > 1$ (c) $0 < a < 1$ (d) $-1 < a < 0$

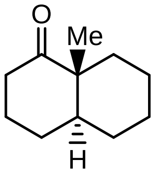
52. If $y^2 = 4x$ and 0.1% error is incurred for x, the percentage error involed in y will be
(a) 0.4 (b) 0.025 (c) 0.1 (d) 0.05

53. The configuration at the two stereocentres in the compound given below are

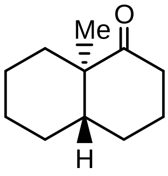


(a) 1R, 4R (b) 1R, 4S (c) 1S, 4R (d) 1S, 4S

54. The two compounds given below are

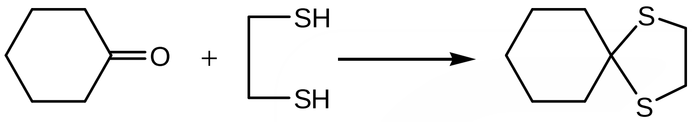


and



(a) Enantiomers (b) Identical (c) Diastereomers (d) Regioisomers.

55. A suitable catalyst for bringing out the transformation given below is:



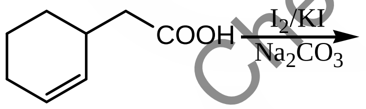
(a) $BF_3.Et_2O$ (b) NaOEt (c) Tungsten lamp (d) Dibenzoyl peroxide

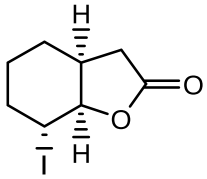
56. Thermolysis of allyl phenyl ether generates

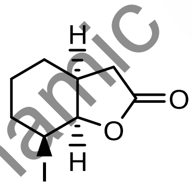
(a) o-allylphenol only (b) o- and p-allylphenols

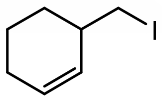
(c) o-, m- and p-allylphenols (d) m-allylphenol only

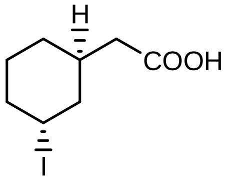
57. The major product formed in the reaction given below is:



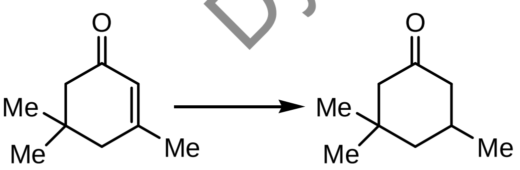
(a) 

(b) 

(c) 

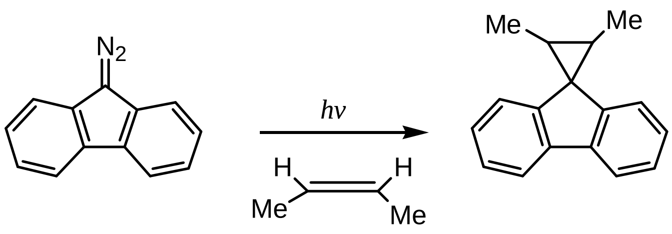
(d) 

58. The most suitable reagent for the following transformation is:



(a) $LiAlH_4$ (b) NH_2NH_2/KOH (c) $NaBH_4/CeCl_3$ (d) Li/liq. NH_3

59. The intermediate involved in the reaction given below is:



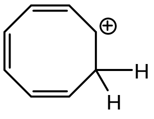
(a) Free radical (b) Carbocation (c) Carbanion (d) Carbene

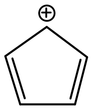
60. In the most stable conformation of trans-1-t-butyl-3-methylcyclohexane, the substituents at C–1 and C–3, respectively, are

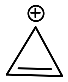
(a) Axial and equatorial (b) Equatorial and equatorial

(c) Equatorial and axial (d) Axial and axial.

61. Among the carbocations given below


(A)

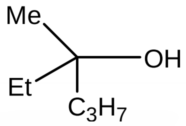

(B)


(C)

(a) A is homoaromatic, B is antiaromatic and C is aromatic.
(b) A is aromatic, B is antiaromatic and C is homoaromatic.
(c) A is antiaromatic, B is aromatic and C is harmoaromatic.
(d) A is homoaromatic, B is aromatic and C is antiaromatic.

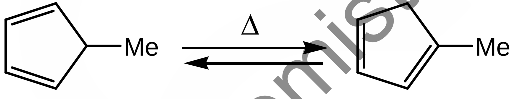
62. The order of carbonyl stretching frequency in the IR spectra of ketone, amide and anhydride is:
(a) Anhydride > amide > ketone
(b) Ketone > amide > anhydride
(c) Amide > anhydride > ketone
(d) Anhydride > ketone > amide

63. In the mass spectrum of the compound given below, during the $\alpha-$cleavage, the order of preferential loss of groups is:



(a) Me > C_3H_7 > Et (b) C_3H_7 > Et > Me (c) Et > Me > C_3H_7 (d) Et > C_3H_7 > Me

64. The reaction given below is an example of



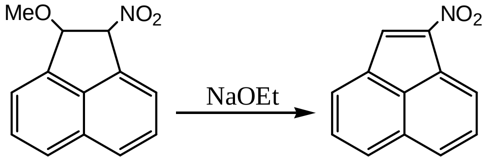
(a) 1, 3-sigmatropic hydrogen shift
(b) 1, 3-sigmatropic methyl shift
(c) 1, 5-sigmatropic hydrogen shift
(d) 1, 5-sigmatropic methyl shift.

65. The concerted photochemical reaction between two olefins leading to a cyclobutane ring is:
(a) ${}_{\pi}2_s + {}_{\pi}2_a$ cycloaddition
(b) ${}_{\pi}2_s + {}_{\pi}2_s$ cycloaddition
(c) ${}_{\sigma}2_s + {}_{\sigma}2_s$ cycloaddition
(d) ${}_{\pi}2_s + {}_{\sigma}2_a$ cycloaddition

66. Addition of BH_3 to a carbon-carbon double bond is:
(a) anti-Markovinikov syn addition
(b) anti-Markovnikov anti addition
(c) Markovnikov syn addition
(d) Markovnikov anti addition.

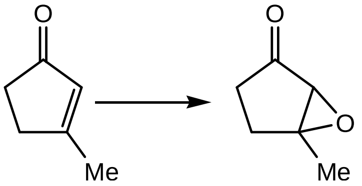
67. The absorption at λ_{max} 279 nm $(\varepsilon = 15)$ in the UV spectrum of acetone is due to
(a) $\pi-\pi^*$ transition (b) $n-\pi^*$ transition (c) $\sigma-\sigma^*$ transition (d) $\pi-\sigma^*$ transition

68. The reaction given below is an example of



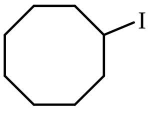
(a) E_2-elimination
(b) E_1-elimination
(c) syn-elimination
(d) E_1CB-elimination

69. The suitable reagent for the following conversion is:

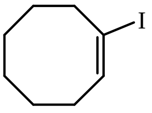


(a) m–CPBA (b) H_2O_2/AcOH (c) ${}^tBuOH/HCl$ (d) H_2O_2/NaOH

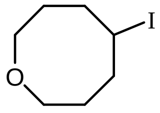
70. The relative rates of solvolysis of iodides A-C are



A



B



C

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

PART -C

71. Alkali metal superoxides are obtained by the reaction of
(a) Oxygen with alkali metals in liquid ammonia.
(b) Water with alkali metals in liquid ammonia
(c) H_2O_2 with alkali metals.
(d) H_2O_2 with alkali metals in liquid ammonia.

72. H_2O_2 reduces

(A) $\left[Fe(CN)_6\right]^{3-}$ (B) KIO_4 (C) $Ce(SO_4)_2$ (D) SO_3^{2-}

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

73. Match **List-I** (compounds) with **List-II** (application) and select the correct answer using the codes given below the lists.

List-I	**List-II**
(A) Trisodium phosphate	(i) Plasticizer
(B) Triarylphosphates	Water softener
(C) Triethylphosphate	(iii) Toothpaste
(D) Calcium hydrogen phosphate	(iv) Insecticides

(a) (A)-ii (B)-i (C)-iv (D)-iii (b) (A)-i (B)-ii (C)-iv (D)-iii
(c) (A)-ii (B)-iii (C)-iv (D)-i (d) (A)-iii (B)-i (C)-ii (D)-iv

74. Among the following statements, identify the correct ones for complexes of lanthanide(III) ion.
(A) Metal-ligand bond is significantly ionic.
(B) Complexes rarely show isomerism.
(C) The coordination number is not more than 8.
(D) The magnetic moments are not accounted even approximately by spin only value for majority of lanthanides.
(a) A, B and D only (b) A, B and C only (c) B and C only (d) A and D only.

75. According to VSEPR theory, the molecule/ion having ideal tetrahedral shape is:

(a) SF_4 (b) SO_4^{2-} (c) S_2Cl_2 (d) SO_2Cl_2

76. The complex $\left[Mn\left(H_2O\right)_6\right]^{2+}$ has very light pink colour. The best reason for it is

(a) The complex does not have a charge transfer transition.
(b) d-d transitions here are orbital forbidden but spin allowed.
(c) d-d transitions here are orbital allowed but spin forbidden.
(d) d-d transitions here are both orbital forbidden and spin forbidden.

77. The highest occupied MO in N_2 and O_2^+ respectively are (take x-axis as internuclear axis)

(a) $\sigma 2p_x, \pi^* 2p_y$ (b) $\pi 2p_y, \pi 2p_z$ (c) $\sigma^* 2p_x, \sigma 2p_x$ (d) $\pi^* 2p_y, \pi^* 2p_z$

78. The correct order of LMCT energies is:

(a) $MnO_4^- < CrO_4^{2-} < VO_4^{3-}$ (b) $MnO_4^- > CrO_4^{2-} > VO_4^{3-}$

(c) $MnO_4^- > CrO_4^{2-} < VO_4^{3-}$ (d) $MnO_4^- < CrO_4^{2-} > VO_4^{3-}$

79. Carboxypeptidase contains:
(a) Zn(II) and hydrolyses CO_2. (b) Zn(II) and hydrolyses peptide bonds.
(c) Mg(II) and hydrolyses CO_2. (d) Mg(II) and hydrolyses peptide bonds.

80. In the EPR spectrum of tetragonal Cu(II) complex, when $g\| > g\perp > g_e$ the unpaired electron resides in the orbital.

(a) d_{xy} (b) $d_{x^2-y^2}$ (c) d_{z^2} (d) d_{xz}

81. The oxidative addition and reductive elimination steps are favoured by
(a) Electron rich metal centres.
(b) Electron deficient metal centers
(c) Electron deficient and electron rich metal centers respectively.
(d) Electron rich and electron deficient metal centers respectively.

82. Identify the order according to increasing stability of the following organometallic compounds, $TiMe_4$, $Ti(CH_2Ph)_4$, $Ti(i\text{-}Pr)_4$ and $TiEt_4$.
(Me = methyl, Ph = phenyl, i-Pr = isopropyl, Et = ethyl)

(a) $Ti\left(CH_2Ph\right)_4 < Ti\left(i-Pr\right)_4 < TiEt_4 < TiMe_4$

(b) $_4$ $_4$ $)_4$

(c) $Ti\left(i-Pr\right)_4 < TiEt_4 < TiMe_4 < Ti\left(CH_2Ph\right)_4$

(d) $TiMe_4 < TiEt_4 < Ti\left(i-Pr\right)_4 < Ti\left(CH_2Ph\right)_4$

83. Among the metals, Mn, Fe, Co and Ni, the ones those would react in its native form directly with CO giving metal carbonyl compounds are:
(a) Co and Mn (b) Mn and Fe (c) Fe and Ni (d) Ni and Co

84. The molecule with highest number of lone-pairs and has a linear shape based on VSEPR theory is:

(a) CO_2 (b) I_3^- (c) NO_2^- (d) NO_2^+

85. Given, $Ag^+ + e \rightarrow Ag, \quad E_0 = 0.50\ V$

$Cu^{2+} + 2e \rightarrow Cu, \quad E_0 = 0.34\ V$

A 100 ml solution is 1080 mg with respect to Ag^+ and 635 mg with respect to Cu^{2+}. If 0.1mg Ag^+ left in the solution is considered to be the complete deposition of Ag^+, the cathode potential, so that no copper is deposited during the process, is:
(a) 0.16 V (b) 0.84 V (c) 0.31 V (d) – 0.16 V

86. In the $H_2Ru_6(CO)_{18}$ cluster, containing 8-coordinated Ru centers, the hydrogen atoms are

(a) Both terminal
(b) One terminal and the other bridging
(c) Both bridging between two Ru centers
(d) Both bridging between three Ru centers.

87. In the hydroformylation reaction, the intermediate $CH_3CH_2CH_2Co(CO)_4$:

(a) Forms are acyl intermediate $CH_3CH_2CH_2COCo(CO)_3$
(b) Forms an adduct with an olefin reactant.
(c) Reacts with H_2.
(d) Eliminates propane.

88. **Statement I:** The sizes of Zr and Hf are similar
Statement II: Size of Hf is affected by lanthanide contraction.
(a) Statement I and II are correct and II is correct explanation of I.
(b) Statement I and II are correct but II is not a correct explanation of I.
(c) Statement I is correct and II is incorrect
(d) Statements I and II both are incorrect.

89. Consider the compounds, (A) SnF_4, (B) $SnCl_4$ and (C) R_3SnCl. The nuclaer quadrupole splitting are observed for.

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

90. Consider two redox pairs
(1) Cr(II)/Ru(III)
(2) Cr(II)/Co(III)
The rate of acceleration in going from a outer-sphere to a inner-sphere mechanism is lower for (1) relative to (2). Its correct explanation is:

(a) HOMO/LUMO are σ^* and σ^* respectively.
(b) HOMO/LUMO are σ^* and π^* respectively.
(c) HOMO/LUMO are π^* and σ^* respectively.
(d) HOMO/LUMO are π^* and π^* respectively.

91. The correct value of isomer shift (in Mossbauer spectra) and its explanation for Fe(II)–TPP and Fe(III)–TPP respectively from the following are:
(TPP = tetraphenylporphyrinate)

(A) 0.52 mms^{-1}
(B) 0.45mms^{-1}
(C) Increase in s electron density
(D) Decrease in s electron density.

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

92. In IR spectrum of $\left[Co(CN)_5H\right]^{3-}$ the Co–H stretch is observed at 1840 cm^{-1}. The (Co–D) stretch in $\left[Co(CN)_5D\right]^{3-}$ will appear at nearly

(a) 1300 cm^{-1}
(b) 1400 cm^{-1}
(c) 1500 cm^{-1}
(d) 1600 cm^{-1}.

93. For the complexes
(A) $\left[Ni(H_2O)_6\right]^{2+}$ (B) $\left[Mn(H_2O)_6\right]^{2+}$ (C) $\left[Cr(H_2O)_6\right]^{3+}$ (D) $\left[Ti(H_2O)_6\right]^{3+}$, the ideal octahedral geometry will not be observed in

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

94. Among the following, the number of anhydrides of acids are
CO, No, N_2O, B_2O_3, N_2O_5, SO_3 and P_4O_{10}.

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

95. For a given nuclear fission reaction of ^{235}U

$${}^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{142}_{56}Ba + {}^{91}_{36}Kr + 3{}^{1}_{0}n$$

the amount of energy (in kJ/mol) released during this process is (given ^{235}U = 235.0439 amu, ^{142}Ba = 141.9164 amu, ^{91}Kr = 90.9234 amu, neutron = 1.00866 amu)

(a) 3.12×10^{12} (b) 2.8×10^{11} (c) 1.0×10^{9} (d) 1.68×10^{10}.

96. The decomposition of gaseous acetaldehyde at T(K) follows second order kinetics. The half-life of this reaction is 400 s when the initial pressure is 250 Torr. What will be the rate constant (in $Torr^{-1}\ s^{-1}$) and half-life (in s) respectively, if the initial pressure of the acetaldehyde is 200 Torr at the same temperature?

(a) 10^{5} and 500 (b) 10^{-5} and 400 (c) 10^{-4} and 400 (d) 10^{-5} and 500

97. For an enzyme catalyzed reaction, a Lineweaver-Burk plot gave the following data:
slope = 40 s
intercept = 4 $(\text{mmol dm}^{-3}\ s^{-1})^{-1}$.
If the initial concentration of enzyme is 2.5×10^{-9} mol dm^{-3}, what is the catalytic efficiency (in $dm^{-3}\ mol^{-1}\ s^{-1}$) of the reaction?

(a) 10^{5} (b) 10^{6} (c) 10^{7} (d) 10^{4}.

98. A hydrogenic orbital with radial function of the form $r^{\alpha}\exp[-\beta r]$ and $\phi-$part as $\exp[-3i\phi]$ corresponds to

(a) $n > 4, \ell > 3, m = 3$ (b) $n = 4, \ell = 3, m = -3$

(c) $n = 4, \ell > 3, m = 3$ (d) $n > 4, \ell = 3, m = -3$

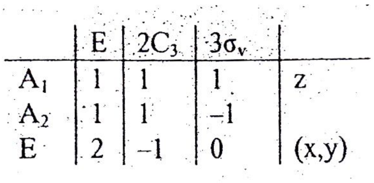
99. For an assembly of molecules (molar mass = M) at temperature T, the standard deviation of Maxweller's speed is approximately

(a) $0.7\sqrt{\frac{RT}{M}}$ (b) $1.4\sqrt{\frac{RT}{M}}$ (c) $0.7\sqrt{\frac{M}{RT}}$ (d) $1.4\sqrt{\frac{M}{RT}}$

100. The unperturbed energy levels of a system are $\in_0 = 0, \in_1 = 2$ and $\in_2 = 4$. The second order correction to energy for the ground state in pressure of the perturbation V for which $V_{10} = 2, V_{20} = 4$ and $V_{12} = 6$ has been found to be

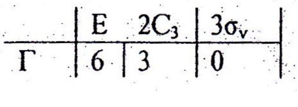
(a) –6 (b) 0 (c) +6 (d) –8

101. Given the character table of the point group C_{3V}.



	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	–1	
E	2	–1	0	(x,y)

Consider the reducible representation, Γ



	E	$2C_3$	$3\sigma_v$
Γ	6	3	0

Its irreducible components are

(a) $E + 2A_1 + 2A_2$ (b) $2E + A_1 + A_2$ (c) $3A_1 + 3A_2$ (d) $E^2 + 2A_1$

102. Refer to the character table of the point group C_{3V} given above. Find which of the following transition is forbidden

(a) $a_1 \longleftrightarrow a_1$ (b) $a_1 \longleftrightarrow e$ (c) $a_2 \longleftrightarrow e$ (d) $a_1 \longleftrightarrow a_2$

103. The electronic configuration for gadalonium (Gd) is $[Xe]4f^7 5d^1 6s^2$, where as that of Gd^{2+} is:

(a) $[Xe]4f^5 5d6s^2$ (b) $[Xe]4f^6 6s^2$ (c) $[Xe]f^6 5d^1 6s^1$ (d) $[Xe]4f^7 5d^1$

104. The possible J values for ^3D term symbol are

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

105. The energy levels for cyclobutadiene are $\alpha+2\beta, \alpha, \alpha$ and α-2β. The delocalization energy in this molecule is:

(a) 0 (b) -4β (c) -8β (d) 4α

106. The variation of equilibrium constant (K) of a certain reaction with temperature (T) is $\ln k = 3.0 + \frac{2.0\times10^4}{T}$ given $R = 8.3\ Jk^{-1}mol^{-1}$, the values of ΔH^0 and ΔS^0 are.

(a) 166 kJ mol^{-1} and 24.9 Jk^{-1} mol^{-1}. (b) 166 kJ mol^{-1} and –24.9 Jk^{-1} mol^{-1}

(c) -166 kJ mol^{-1} and 24.9 Jk^{-1} mol^{-1} (d) -166 kJ mol^{-1} and 24.9 Jk^{-1} mol^{-1}

107. The chemical potential of component 1 in a solution of binary mixture is $\mu_1 = \mu_1^0 + RT\ln p_1$, when p_1 is the partial pressure of component 1 vapour phase. The standard state $\mu_1{}^0$ is:

(a) Independent of temperature and pressure

(b) Depends on temperature and pressure both

(c) Depends on temperature only

(d) Depends on pressure only

108. Debey-Hückel screening length $\left(\kappa^{-1}\right)$ is a measure of size of diffuse ion cloud around an ion, provided $\sqrt{\frac{2e^2N_A}{\in_0 k_B T}} \approx 30\left(nm\sqrt{molkg^{-1}}\right)^{-1}$ at 298K, which of the following values of κ^{-1} is true for a 0.03 molal solution for Na_2SO_4 in water $\left(\in_r \approx 100\right)$?

(a) $\frac{10}{9}$nm (b) $\frac{9}{10}$nm (c) $\frac{10\sqrt{2}}{9}$nm (d) $\frac{9}{10\sqrt{2}}$nm

109. If the ratio of composition of oxidized and reduced species in electrochemical cell, is given as $\frac{[O]}{[R]} = e^2$, the correct potential difference will be

(a) $E - E^{0'} = +\frac{2RT}{nF}$ (b) $E - E^{0'} = -\frac{2RT}{nF}$

(c) $E - E^{0'} = \frac{RT}{nF}$ (d) $E - E^{0'} = -\frac{RT}{nF}$

110. If the equilibrium constants for the reactions 1 and 2

(1) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ (2) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

are k_1 and k_2, the equilibrium constant for the reaction

$CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$ is:

(a) $k_1 + k_2$ (b) $k_1 - k_2$ (c) k_1k_2 (d) k_1 / k_2

111. The virial expansion for a real gas can be written in either of the following forms:

$$\frac{P\overline{V}}{RT} = 1 + B_P P + C_P P^2 + ...$$
$$= 1 + B_V V + C_V V^2 + ...$$

If $B_V = \alpha B_P$, the value of α would be

(a) PV/RT (b) RT/PV (c) PV (d) RT

112. A certain system of noninteracting particles has the single-particle patition has the single-particle partition function $f = A\frac{T^m}{V}$ where A is some constant. The average energy per particle will be

(a) $m\kappa T$ (b) $A\kappa T$ (c) $\kappa T / m$ (d) $\kappa T / A$

113. Observe the following aqueous solutions of same compound. All the measurements are made at same wavelength and same temperature.

Solution A: The transmittance of 0.1 mol dm^{-3} using 1 cm cell is 0.5.

Solution B: The optical density 0.5 mol dm^{-3} is measured using 1 mm cell.

Solution C: The transmittance of this solution is 0.1.

The optical density of these solutions follow the order.

(log 20 = 1.3010; log 30 = 1.4771, log 50 = 1.6990

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

114. The rotational constant of $^{14}N_2$ is 2 cm^{-1}. The wave number of incident radiation in a Raman spectrometer is 20487 cm^{-1}. What is the wave number of first scattered Stokes line (in cm^{-1}) of $^{14}N_2$?

(a) 20479 (b) 20475 (c) 20499 (d) 20495

115. For a certain particle encountering a barrier, the tunneling probability is approximately e^{-10}. If the mass is halved and width of the barrier (rectangular) doubled, approximate value of the tunneling probability will be

(a) $e^{-10/\sqrt{2}}$ (b) $e^{-10\sqrt{2}}$ (c) $e^{-20\sqrt{2}}$ (d) e^{-10}

116. An operator A is defined as $A = -\frac{d}{dx} + x$. Which one of the following statements is true?

(a) A is a Hermitian operator. (b) $A^\dagger$ is an antihermitian operator.

(c) Both $AA^\dagger$ and $A^\dagger A$ are Hermitian. (d) $AA^\dagger$ is Hermitian, but $A^\dagger A$ is antihermitian.

117. Isothermal which has fractional coverage, linearly, dependent on pressure at low pressures but almost indepenent at high pressure is called

(a) BET isotherm (b) Langmuir isotherm

(c) Freundlich isotherm (d) Temkin isotherm

118. A one-dimensional crystal of lattice dimension 'a' is metallic. If the structure is distorted in such a way that the lattice dimension is enhanced to '2a'.

(a) The electronic structure remains unchagned.

(b) The width of conduction band decreases and a band gap is generated.

(c) The width of conduction band increases

(d) The width of the conduction band remains unchanged.

119. For a H_2 molecule, the ground state wavefunction is $\psi(1,2) = \phi(1,2)\sigma(1,2)$ where ϕ refers to the space part and σ to the spin part. Given that $\phi(1,2) = \phi(2,1)$, the form of $\sigma(1,2)$ would be

(a) $\alpha(1)\beta(2)$ (b) $\alpha(2)\beta(1)$

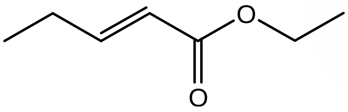
(c) $\alpha(1)\beta(2) - \alpha(2)\beta(1)$ (d) $\alpha(1)\beta(2) + \alpha(2)\beta(1)$

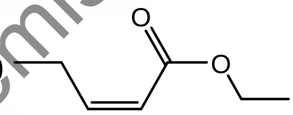
120. There are several types of mean molar masses for polymer and they are dependent on experimental methods like:
(1) Osmometry (2) Light scattering (3) Sedimentation.
Correct relation between mean molar masses and experimental method is:

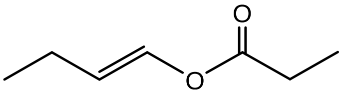
(a) $\bar{M}_n \Leftrightarrow (3), \bar{M}_w \Leftrightarrow (2), \bar{M}_z \Leftrightarrow (1)$ (b) $\bar{M}_n \Leftrightarrow (2), \bar{M}_w \Leftrightarrow (3), \bar{M}_z \Leftrightarrow (1)$

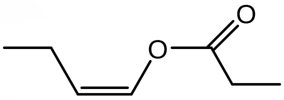
(c) $\bar{M}_n \Leftrightarrow (1), \bar{M}_w \Leftrightarrow (2), \bar{M}_z \Leftrightarrow (3)$ (d) $\bar{M}_n \Leftrightarrow (1), \bar{M}_w \Leftrightarrow (3), \bar{M}_z \Leftrightarrow (2)$

121. An organic compound ($C_7H_{12}O_2$) exhibited the following data in the ^{1}H NMR spectrum.
δ 7.10(1 H, d t, J = 16 and 7.2Hz), 5.90 (1H, d t, J = 16 and 2 Hz),
4.1(2H, q, J = 7.2Hz), 2.10(2H, m), 1.25(3H, t, J = 7.2Hz),
0.90 (3H, t, J = 7.2 Hz) ppm.
The compound, among the choices given below, is:

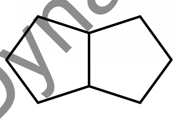
(a) 

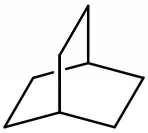
(b) 

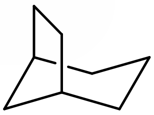
(c) 

(d) 

122. In the broad band decoupled ^{13}C NMR spectrum, the number of signals appearing for the bicyclooctane A–C, respectively, are


(A)

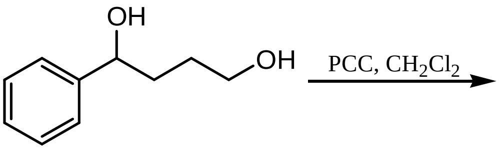

(B)

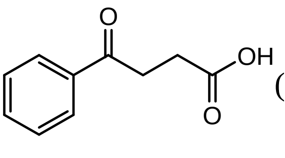

(C)

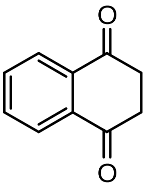
(a) Five, four and eight (b) Three, two and five
(c) Five, four and five (d) Three, two and eight

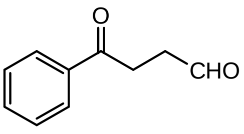
123. In the mass spectrum of dichlorobenzene the ratio of the peaks at m/z 146, 148 and 150, is:
(a) 1:1:1 (b) 3:3:1 (c) 1:2:1 (d) 9:6:1

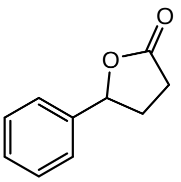
124. The major compound X formed in the following reaction exhibited a strong absorption at ν_{max} 1765 cm^{-1} in the IR spectrum. The structure of X is:



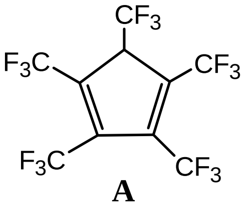
(a) 

(b) 

(c) 

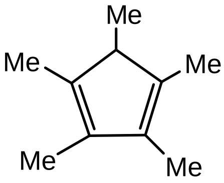
(d) 

125. The correct order of acidity of the following compound A–C is:



A

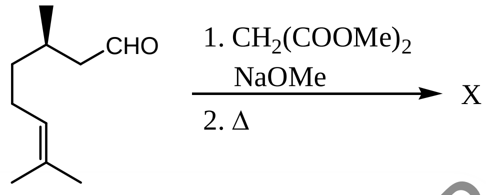
B



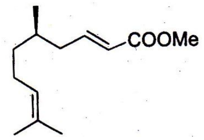
C

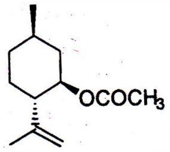
(a) B > C > A (b) C > B > A (c) A > C > B (d) A > B > C

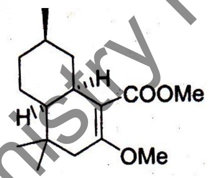
126. The major product formed in the reaction sequence is:

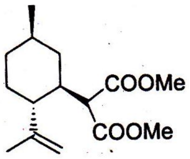


(citronellal)

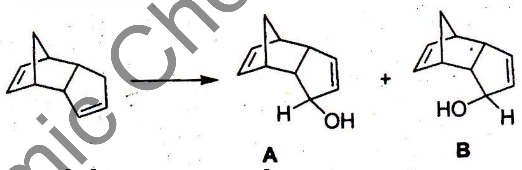
(a) 

(b) 

(c) 

(d) 

127. For the following allylic oxidation reaction, the appropriate statement, among the choices given below, is:



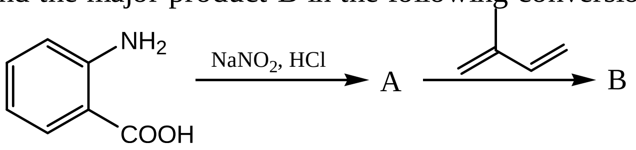
(a) Suitable reagent is $KMnO_4$ and the major product is A.

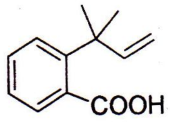
(b) Suitable reagent is $KMnO_4$ and the major product is B.

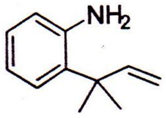
(c) Suitable reagent

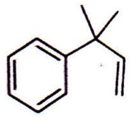
(d) Suitable reagent is SeO_2 and the major product is B.

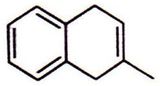
128. The intermediate A and the major product B in the following conversion are



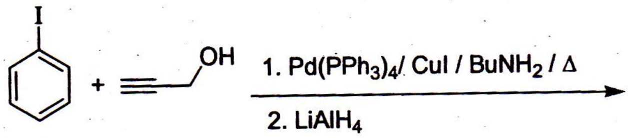
(a) A is carbocation and B is 

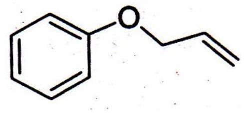
(b) A is a carbanion and B is 

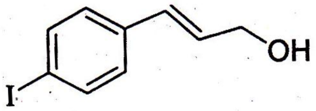
(c) A is a free radical and B is 

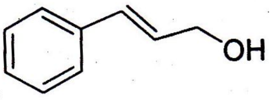
(d) A is a benzyne and B is 

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



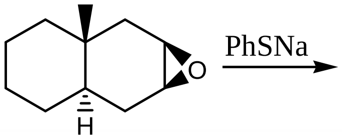
(a) 

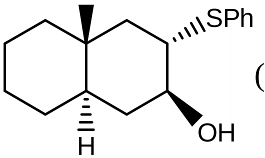
(b) 

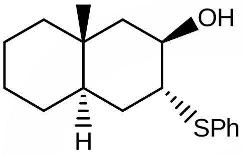
(c) 

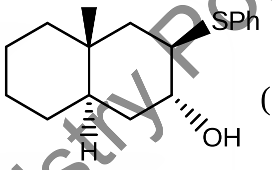
(d) 

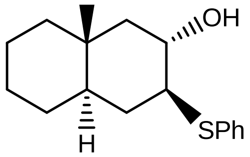
130. The major product formed in the following reaction is:



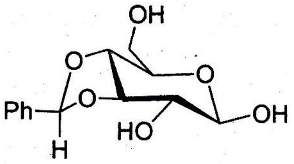
(a) 

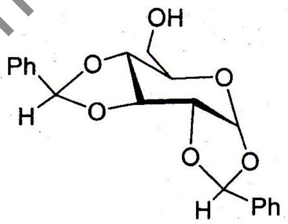
(b) 

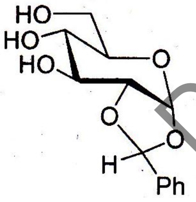
(c) 

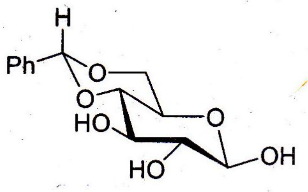
(d) 

131. The major product formed in the reaction of glucose with benzaldehyde and p-TSA is:

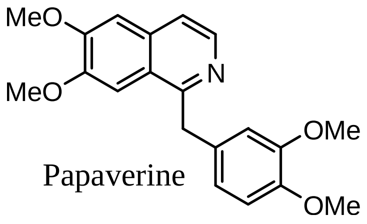
(a) 

(b) 

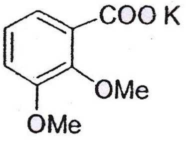
(c) 

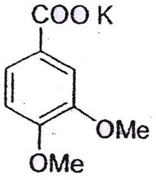
(d) 

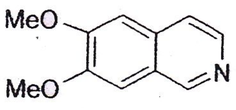
132. Papaverine on oxidation with potassium permanganate gives a ketone, which on fusion with potassium hydroxide gives

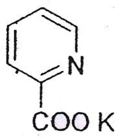


Papaverine

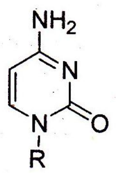
(a) 

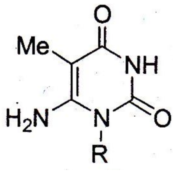
(b) 

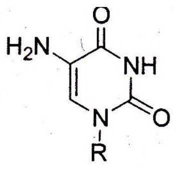
(c) 

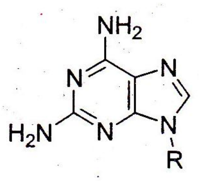
(d) 

133. The major product formed on nitration (HNO_3/H_2SO_4) of uridine followed by reduction with tin and HCl is:

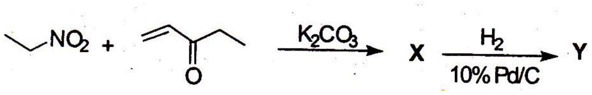
(a) 

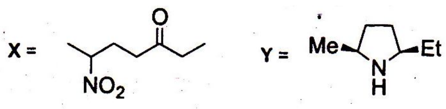
(b) 

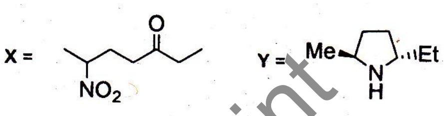
(c) 

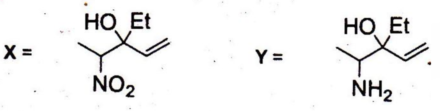
(d) 

134. In the following reaction sequence, the correct structures for the major products X and Y are



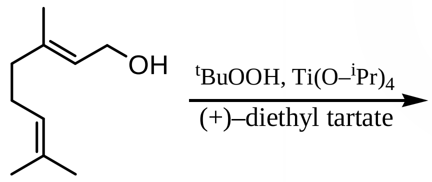
(a) 

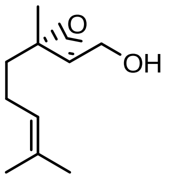
(b) 

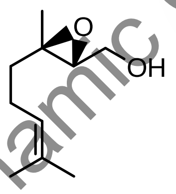
(c) 

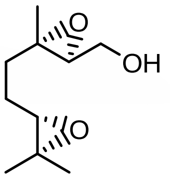
(d) 

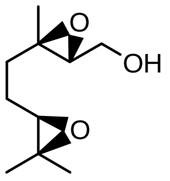
135. The major product formed in the following reaction is:



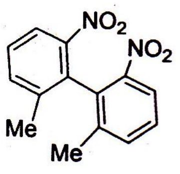
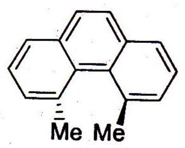
(a) 

(b) 

(c) 

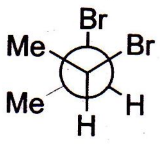
(d) 

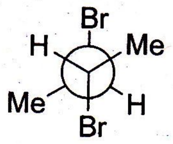
136. Match the following:

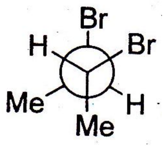
Column I	**Column II**
(A) 	(i) Chiral centre
(B) 	(ii) Chiral axis
(C) 	(iii) Chiral plane
	(iv) Helical chirality

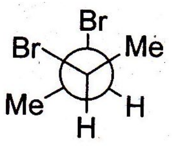
(a) (A)-iii (B)-ii (C)-iv
(b) (A)-iv (B)-iii (C)-ii
(c) (A)-ii (B)-iv (C)-iii
(d) (A)-ii (B)-iii (C)-iv

137. The gauche interaction values for Me/Me, Me/Br and Br/Br are 3.3, 0.8 and 3.0 kJ/mol, respectively. Among the following, the most stable conformation of 2, 3-dibromobutane is:

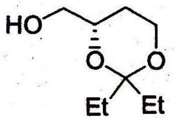
(a) 

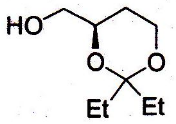
(b) 

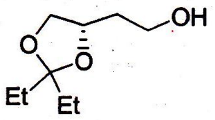
(c) 

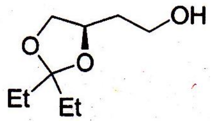
(d) 

138. The major product formed in the reaction of (S)-1, 2, 4-butanetriol with 3-pentanone in the presence of a catalytic amount of p-TSA is:

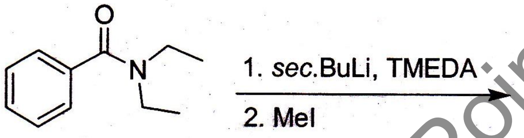
(a) 

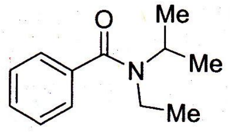
(b) 

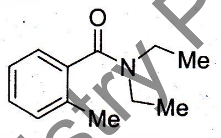
(c) 

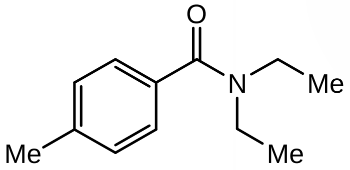
(d) 

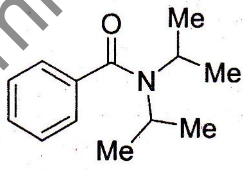
139. The major product formed in the following reaction is:



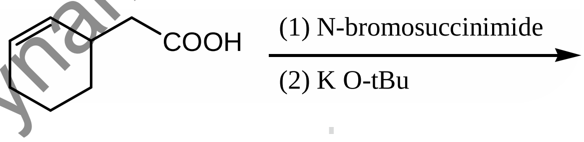
(a) 

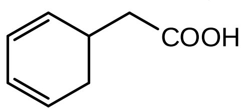
(b) 

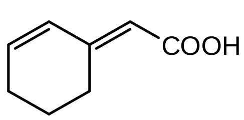
(c) 

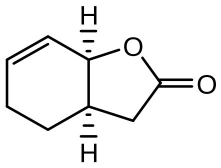
(d) 

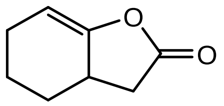
140. The major product formed in the following transformation is:



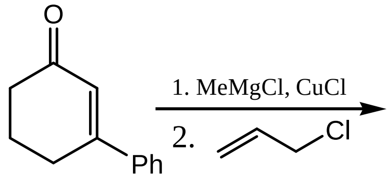
(a) 

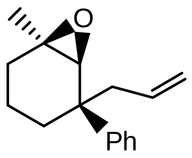
(b) 

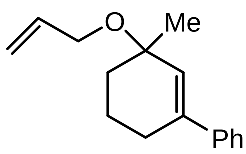
(c) 

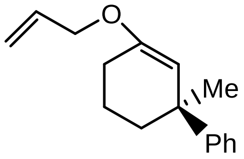
(d) 

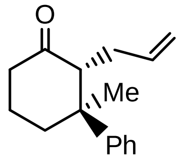
141. The major product formed in the following transformation is:



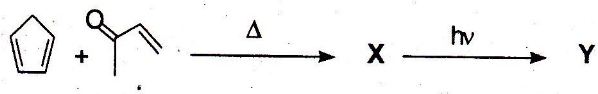
(a) 

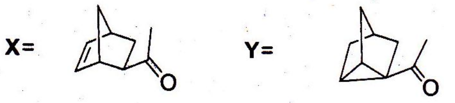
(b) 

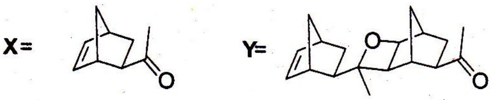
(c) 

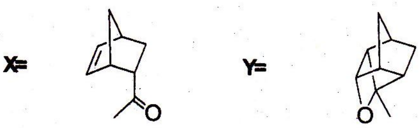
(d) 

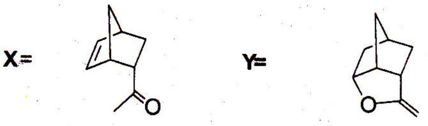
142. The structures of the major products X and Y in the following transformation are



(a) 

(b) 

(c) 

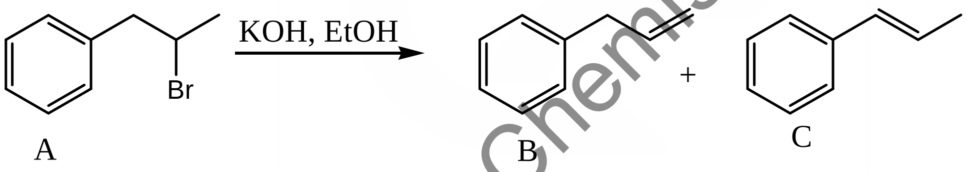
(d) 

143. Match the following:

Column I	**Column II**
A. Pyrrole	i. Pictet-Spengler
B. 1, 4-dihydropyridine	ii. Chichibabin
C. Isoquinoline	iii. Paal-Knorr
	iv. Hantzsch

(a) (A)-i (B)-ii (C)-iii
(b) (A)-ii (B)-iii (C)-iv
(c) (A)-iv (B)-i (C)-ii
(d) (A)-iii (B)-iv (C)-i

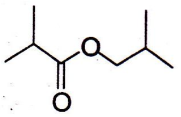
144. Consider the following reaction:

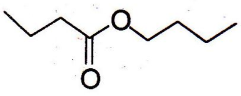


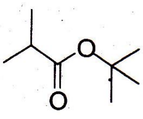
In an experiment, 1.99 g of bromide A on reaction with ethanolic potassium hydroxide gave 1.062 g of a mixture of the olefins B and C. If the ratio of olefins B:C formed is 2:1, the yields for their formation, respectively, are

(a) 60 and 30%
(b) 50 and 25%
(c) 66 and 33%
(d) 54 and 27%

145. An organic compound A ($C_8H_{16}O_2$) on treatment with an excess of methylmagnesium chloride generated two alcohols B and C, whereas reaction of A with lithium aluminium hydride generated only a single alcohol C. Compound B on treatment with an acid yielded an olefin (C_6H_{12}), which exhibited only a singlet at $\delta\,1.6$ ppm in the ^{1}H NMR spectrum. The compound A is:

(a) 

(b) 

(c) 

(d)