PART A

1. Oxidation of alcohols to acids involves formation and cleavage of bonds. Which of the following possibilities is valid in the process?

   1. Formation of C=O bond and cleavage of O–H and C–H bonds.
   2. Formation of C=O bonds and cleavage of O–H bond.
   3. Formation of C=O bonds and cleavage of C–H bonds.
   4. Formation of C≡O bond and cleavage of O–H and C–H bonds.

2. Suppose the Sun somehow becomes a black hole without change in its mass. Then this black hole will pull into itself

   1. all the planets
   2. only Mercury.
   3. all planets from Mercury to Mars
   4. none of the planets

3. Which of the following animals does not have modified legs used for flight?

   (1) Sparrow   (2) Bat
   (3) Flying squirrel   (4) Butterfly

4. Droplets of a herbicide solution form various shapes on a leaf as shown.
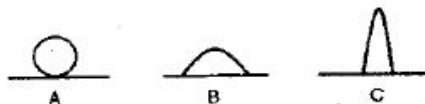
   Assuming that the droplets have the same volume, the trend in the rates of herbicide uptake would be

   1. A > B > C
   2. B > A > C

3. B > C > A
4. C > A > B

5. What is the minimum number of cards you need to uncover from the top of a well-shuffled deck of 52 playing cards, to ensure that you have two cards of a suit?

   (1) 41   (2) 15
   (3) 7   (4) 5

6. A long cylinder has an axially placed two-bladed fan spinning inside it. Bullets are shot through the cylinder at a constant rate. If the number of blades is increased to four, the number of bullets

   1. missing the blades is halved.
   2. missing the blades is reduced by one-fourth.
   3. hitting the blades is doubled.
   4. hitting the blades remains the same.

7. A jar containing an iron block B was floating on water in a bigger container. The block was taken out and put into water. As a result, the level of water in the container will
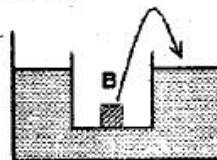
   1. rise
   2. fall
   3. remain the same
   4. rise or fall depending upon the mass of the block

8. A room has a west-facing window with glass panes. Which of the following is the most effective way to prevent the room from getting hot in summer?

1. Cover the inside of the glass pane by a black paper.

2. Cover the outside of the glass pane by an aluminum foil.

3. Cover the outside of the glass pane by a white thermocol sheet.

4. Cover the inside of the glass pane by a white thermocol sheet.

9. A polypeptide of 300 amino acids has tyrosine at the 157th position. If the tyrosine codon mutates to a nonsense codon, what would be the size of the polypeptide in this mutated organism?

(1) 157   (2) 156

(3) 299   (4) 144

10. After bubbling air through pure water (pH = 7.0), its pH decreased. Which of the following is responsible for the pH change?

(1) Nitrogen   (2) Carbon dioxide

(3) Oxygen   (4) Helium

11. Which of the following caused disruption of air-traffic in Europe after the volcanic eruption in Iceland in the year 2010?

1. Risk of engine damage by volcanic ash.
2. Increased local temperature.
3. Reduced visibility due to volcanic gases.
4. Presence of toxic gases.

12. A segment of a circle (slightly greater than a semicircle, whose centre is O) is given below. Identify the correct statement regarding the three angles A, B and C.
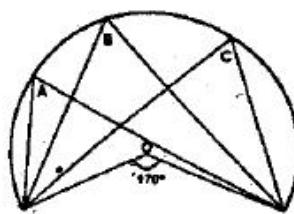
1. A is equal to B but not equal to C.
2. A, B and C are equal and have a value of 85°.
3. A, B and C are unequal.
4. A, B and C are each equal to 95°.

13. Three boys A, B and C kicked three balls horizontally from the edge of the roof of a building. The horizontal distances traversed by these balls before hitting the ground are d_A, d_B, d_C respectively, with $d_A > d_B > d_C$. If t_A, t_B and t_C are the times taken to hit the ground respectively, then

(1) $t_A > t_B > t_C$ (2) $t_A < t_B < t_C$

(3) $t_A > t_B < t_C$ (4) $t_A = t_B = t_C$

14. A swinging door is to be stopped by driving a wedge between the floor and the door. The most favourable position of the wedge is close to the

1. outer edge of the door because even a small frictional force can provide adequate torque to stop the door swing.
2. outer edge of the door because the frictional force is the largest at the outer edge.
3. hinged edge of the door because the moment of force is smallest near the hinge.
4. hinged edge of the door because there is friction in the hinge.

15. The most abundant element by mass in the human body is

   (1) carbon   (2) hydrogen
   (3) calcium   (4) oxygen

16. The figure shows cumulative weight percent curves for different types of sediments. Which type of sediment has the narrowest size distribution?
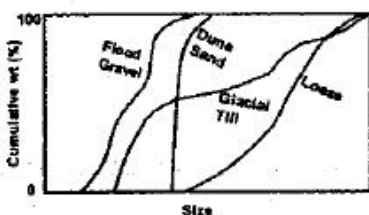
   1. Dune sand
   2. Glacial till
   3. Flood gravel
   4. Loess

17. A number system consists of digits 0, 1, 2, 3, 4 and 5. What is the decimal equivalent of 15 in this number system?

   (1) 15   (2) 13
   (3) 11   (4) 12

18. Absolute water content in the air in the equatorial region is measured to be 18 g m^{-3} and the same is 4 g m^{-3} in the polar region. However, the values of relative humidity reported are 60% and 78%, respectively. This could be because

   1. equatorial region is warmer and therefore the atmosphere has a higher water holding capacity.
   2. winds are stronger in the polar region.
   3. polar region is ice-covered and therefore its atmosphere has a higher water content.

   4. of higher snowfall in the polar region.

19. The simple representation of a detergent molecule is given below:

   Which one of the following representations describes the interaction of the detergent molecule in a system composed of grease and water?
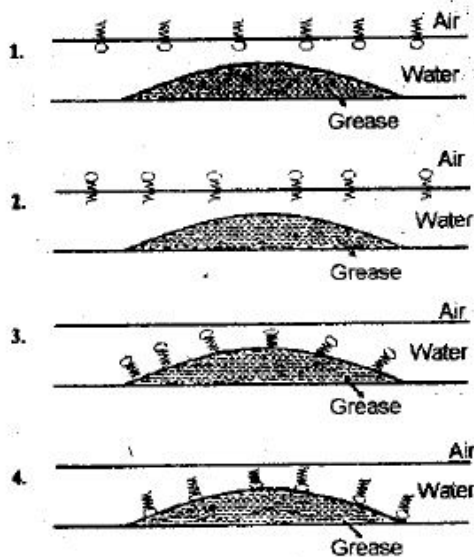
20. Parents with blood groups A and AB have two children. Which of the following cannot be the blood groups of their children?

   1. A and AB
   2. B and AB
   3. A and B
   4. O and B

PART B

21. Identify which of the following operators is **_not_** hermitian?

1. $\dfrac{\hbar}{i}\dfrac{d}{dx}$

2. $i\dfrac{d^2}{dx^2}$

3. $\dfrac{d^2}{dx^2}$

4. x^2

22. The term symbol for the ground state of nitrogen atom is

1. $^3P_0$
2. $^4P_{3/2}$
3. $^1P_1$
4. $^4S_{3/2}$

23. P_A and P_B denote the populations of two energy states E_A and E_B, and $E_A > E_B$. The correct statement when the temperature $T_1 > T_2$ is

1. $P_A(T_1) > P_B(T_1)$, $P_A(T_2) < P_B(T_2)$ and $(P_A/P_B)_{T_1} > (P_A/P_B)_{T_2}$

2. $P_A(T_1) \ngtr P_B(T_1)$, $P_A(T_2) > P_B(T_2)$ and $(P_A/P_B)_{T_1} < (P_A/P_B)_{T_2}$

3. $P_A(T_1) < P_B(T_1)$, $P_A(T_2) < P_B(T_2)$ and $(P_A/P_B)_{T_1} > (P_A/P_B)_{T_2}$

4. $P_A(T_1) < P_B(T_1)$, $P_A(T_2) < P_B(T_2)$ and $(P_A/P_B)_{T_1} < (P_A/P_B)_{T_2}$

24. The uncertainty in the NMR frequency of a compound in liquid state (relaxation time = 1 s) is 0.1 Hz. The uncertainty in the frequency (in Hz) of same compound in solid state (relaxation time = 10^{-4} s) is

1. 10^{-4}
2. 100
3. 1000
4. 10^{-3}

25. Which one of the following conductometric titrations will show a linear increase of the conductance with volume of the titrant added up to the break point and an almost constant conductance afterwards.

1. A strong acid with a strong base
2. A strong acid with a weak base
3. A weak acid with a strong base
4. A weak acid with a weak base.

26. Flocculation value of K_2SO_4 is much less than that of KBr for Sol A. Flocculation value of $CaCl_2$ is much less than that of NaCl for Sol B. Which of the following statements is correct?

1. Sol A is negatively charged and Sol B is positively charged.
2. Both the sols are negatively charged.
3. Sol A is positively charged and Sol B is negatively charged.
4. Both the sols are positively charged.

27. For a system of constant composition, the pressure (P) is given by

1. $-\left(\dfrac{\partial U}{\partial S}\right)_V$

2. $-\left(\dfrac{\partial U}{\partial V}\right)_S$

3. $\left(\dfrac{\partial V}{\partial S}\right)_T$

4. $\left(\dfrac{\partial U}{\partial V}\right)_T$

28. The value of d_{111} in a cubic crystal is 325.6 pm. The value of d_{333} is

1. 325.6 pm
2. 976.8 pm
3. 108.5 pm
4. 625.6 pm

29. The symmetry point group of ethane in its staggered conformation is

1. C_{3v}
2. D_{3d}
3. D_{3h}
4. S_6

30. For the reaction $C_2H_4 (g) + 3O_2 (g) \rightarrow 2CO_2 (g) + 2H_2O (l)$, the value of $\Delta H - \Delta U$ (in kJ) at 300 K and 1 bar is

1. -5.0
2. 0.0
3. 2.5
4. 5.0

31. The sodium D lines are due to $^2P_{1/2} \rightarrow {}^2S_{1/2}$ (ΔE_1) and $^2P_{3/2} \rightarrow {}^2S_{1/2}$ (ΔE_2) transitions. The splitting due to spin-orbit coupling in ^2P state of the sodium atom is

1. $\Delta E_2 + \Delta E_1$
2. $\Delta E_2 - \Delta E_1$
3. $\dfrac{\Delta E_2 + \Delta E_1}{2}$
4. $\dfrac{\Delta E_2 - \Delta E_1}{2}$

32. The rate constant of a unimolecular reaction was $2.66 \times 10^{-3} \text{ s}^{-1}$ and $2.2 \times 10^{-1} \text{s}^{-1}$ at T = 120 K and 360 K respectively. The rate constant (in s^{-1} units) at 240 K would be

1. 2.4×10^{-2}
2. 2.4×10^{-1}
3. 4.8×10^{-2}
4. 1.8×10^{-3}

33. For a potentiometric titration, in the curve of emf (E) vs volume (V) of the titrant added, the equivalence point is indicated by

1. $|dE / dV| = 0, |d^2E / dV^2| = 0$
2. $|dE / dV| = 0, |d^2E / dV^2| > 0$
3. $|dE / dV| > 0, |d^2E / dV^2| = 0$
4. $|dE / dV| > 0, |d^2E / dV^2| > 0$

34. The osmotic pressure (π) of a polymer sample at different concentrations (c) was measured at $T(K)$. A plot of (π/c) versus c gave a straight line with slope (m) and intercept (c'). The number average molecular weight of the polymer is (R = gas constant)

1. $\dfrac{RT}{c'}$
2. $\dfrac{c'}{RT}$
3. RT
4. mRT

35. The concentration of a reactant undergoing decomposition was 0.1, 0.08 and 0.067 mol L^{-1} after 1.0, 2.0 and 3.0 hr respectively. The order of the reaction is

1. 0
2. 1
3. 2
4. 3

36. A particle is constrained in a one-dimensional box of length $2a$ with potential $V(x) = \infty$; $x < -a$, $x > a$ and $V(x) = 0$; $-a \leq x \leq a$. Energy difference between levels n = 3 and n = 2 is

1. $\dfrac{5h^2}{8ma^2}$
2. $\dfrac{9h^2}{8ma^2}$
3. $\dfrac{9h^2}{32ma^2}$
4. $\dfrac{5h^2}{32ma^2}$

37. In the ^{19}F NMR spectrum of PF_5, the number of signals and multiplicity, at room temperature are

   1. one, singlet
   2. one, doublet
   3. two, doublet
   4. two, singlet

38. The correct statement regarding closo-$\{B_nH_n\}$ species is:

   1. it always has –2 charge
   2. it always has +2 charge
   3. it is a neutral species
   4. it is more reactive than nido-, arachno-, and hypo-boranes

39. Lewis acidity of BCl_3, BPh_3 and BMe_3 with respect to pyridine follows the order

   1. $BCl_3 > BPh_3 > BMe_3$
   2. $BMe_3 > BPh_3 > BCl_3$
   3. $BPh_3 > BMe_3 > BCl_3$
   4. $BCl_3 > BMe_3 > BPh_3$

40. Superoxide dismutase contains the metal ions

   1. Zn(II) and Ni(II)
   2. Cu(II) and Zn(II)
   3. Ni(II) and Co(III)
   4. Cu(II) and Fe(III)

41. The number of antibonding electrons in NO and CO according to MO theory are respectively:

   1. 1, 0
   2. 2, 2
   3. 3, 2
   4. 2, 3

42. The correct combination of metal, number of carbonyl ligands and the charge for a metal carbonyl complex $[M(CO)_x]^{z-}$ that satisfies the 18 electron rule is

   1. $M = Ti$, $x = 6$, $z = 1$
   2. $M = V$, $x = 6$, $z = 1$
   3. $M = Co$, $x = 4$, $z = 2$
   4. $M = Mo$, $x = 5$, $z = 1$

43. Among the following pairs,

   (A) oxygen-sulfur
   (B) nitrogen-phosphorus
   (C) phosphorus-arsenic
   (D) chlorine-iodine

those in which the first ionization energies differ by more than 300 kJ $mole^{-1}$ are:

   1. (A) and (C) only
   2. (A) and (B) only
   3. (B) and (C) only
   4. (C) and (D) only

44. The stable cyclopentadienyl complex of beryllium is

   1. $[Be(\eta^5-C_5H_5)_2]$
   2. $[Be(\eta^5-C_5H_5)(\eta^3-C_5H_5)]$
   3. $[Be(\eta^1-C_5H_5)(\eta^3-C_5H_5)]$
   4. $[Be(\eta^1-C_5H_5)(\eta^5-C_5H_5)]$

45. The reaction between NH_4Br and Na metal in liquid ammonia (solvent) results in the products

   1. NaBr, HBr
   2. NaBr, H_2
   3. H_2, HBr
   4. NBr_3, H_2

46. The material that exhibits the highest electrical conductivity among the following sulfur-nitrogen compounds is

   1. S_4N_4
   2. S_7NH
   3. S_2N_2
   4. $(SN)_x$

47. Uranium fluorides co-precipitate with

   1. CaF_2
   2. AgF
   3. LiF
   4. MgF_2

48. The acid-base indicator (HIn) shows a colour change at pH 6.40 when 20% of it is ionized. The dissociation constant of the indicator is

1. 9.95×10^{-8}
2. 3.95×10^{-6}
3. 4.5×10^{-8}
4. 6.0×10^{-8}

49. The actual magnetic moment shows a large deviation from the spin-only formula in the case of

1. Ti^{3+}
2. V^{3+}
3. Gd^{3+}
4. Sm^{3+}

50. The complex that absorbs light of shortest wavelength is

1. $[CoF_6]^{3-}$
2. $[Co(H_2O)_6]^{3+}$
3. $[Co(NH_3)_6]^{3+}$
4. $[Co(ox)_3]^{3-}$ $(ox = C_2O_4^{2-})$

51. Two α particles having speeds S_1 and S_2 have kinetic energies 1 and 2 MeV respectively; the relationship between S_1 and S_2 is:

1. $S_1 = 2S_2$
2. $S_2 = 2S_1$
3. $S_2 = \sqrt{2}S_1$
4. $S_1 = \sqrt{2}S_2$

52. Green coloured $Ni(PPh_2Et)_2Br_2$, has a magnetic moment of 3.20 B.M. The geometry and the number of isomers possible for the complex respectively, are

1. square planar and one
2. tetrahedral and one
3. square planar and two
4. tetrahedral and two

53. The chemiluminescence method for determining NO in environmental samples is based on formation of NO_2^* (excited) which is generally generated by reacting NO with

1. O_2
2. O_2^-
3. O_3
4. O_2^{2-}

54. In the IR spectrum, carbonyl absorption band for the following compound appear at
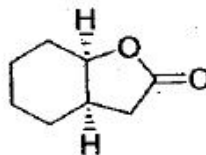
1. 1810 cm^{-1}
2. 1770 cm^{-1}
3. 1730 cm^{-1}
4. 1690 cm^{-1}.

55. Among the following compounds, the formyl anion equivalent is

1. acetylene
2. nitromethane
3. ethyl chloroformate
4. 1, 4-dithiane

56. In the following concerted reaction, the product is formed by a
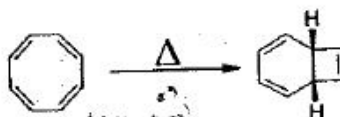
1. 6π-disrotatory electrocyclisation
2. 4π-disrotatory electrocyclisation
3. 6π-conrotatory electrocyclisation
4. 4π-conrotatory electrocyclisation

57. A suitable reagent combination for carrying out the following conversion is

1. trimethyl orthoacetate and p-toluenesulfonic acid
2. trimethyl orthoacetate and sodium hydroxide
3. 2-methoxypropene and p-toluenesulfonic acid
4. 2-methoxypropene and sodium hydroxide

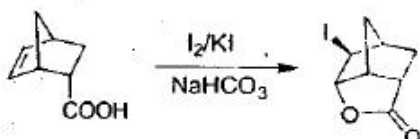**58.** The IUPAC name of the following compound is
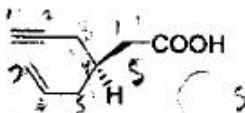
1. (R)-3-(prop-2-enyl)hex-5-ynoic acid
2. (S)-3-(prop-2-enyl)hex-5-ynoic acid
3. (R)-3-(prop-2-ynyl)hex-5-enoic acid
4. (S)-3-(prop-2-ynyl)hex-5-enoic acid

59. In the mass spectrum of dodecahedrane ($C_{20}H_{20}$), approximate ratio of the peaks at m/z 260 and 261 is

1. 1 : 1
2. 5 : 1
3. 10 : 1
4. 20 : 1

60. The reaction given below proceeds through

1.

2.

3.

4.
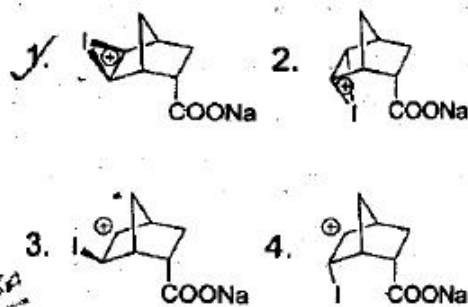
61. Among the following drugs, the anti-cancer agent is

1. captopril
2. chloroquin
3. camptothecin
4. ranitidine

62. The reaction that involves the formation of both C-C and C-O bonds is

1. Diels-Alder reaction
2. Darzen's glycidic ester condensation
3. aldol reaction
4. Beckmann rearrangement

63. Among A-C, the aromatic compounds are
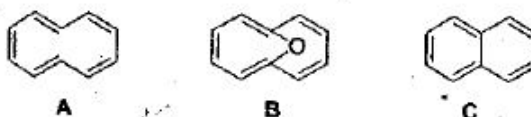
1. A, B and C
2. A and B only
3. B and C only
4. A and C only

64. In the following Markonikov addition reaction, the products A and B are
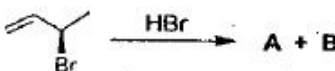
1. homomers
2. enantiomers
3. diastereomers
4. regioisomers

65. The major product formed in the following reaction is

$\xrightarrow[\text{liq. NH}_3]{\text{NaNH}_2}$

1.

2.

3.

4.
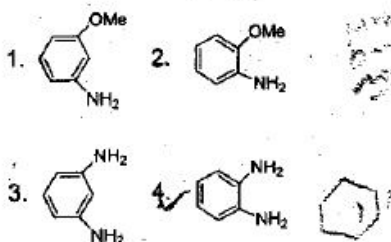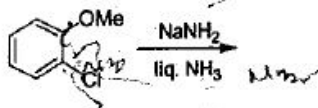
66. Among A-C, the compounds which can exhibit optical activity are

A   B   C
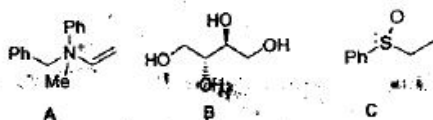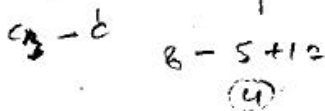
1. A, B and C
2. A and B only
3. A and C only
4. B and C only

67. The major product formed in the following reaction is

$\xrightarrow[-70\,°C]{\text{LiAlH}_4}$

1.

2.

3.

4.
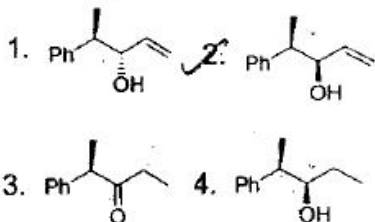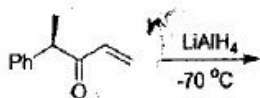
68. An organic compound (MF: $C_8H_{10}O$) exhibited the following ^1H NMR spectral data: δ 2.5 (3 H, s), 3.8 (3 H, s), 6.8 (2 H, d, J 8 Hz), 7.2 (2 H, d, J 8 Hz) ppm. The compound, among the choices, is

1. 4-ethylphenol
2. 2-ethylphenol
3. 4-methylanisole
4. 4-methylbenzyl alcohol

69. With respect to electrophilic aromatic substitution, reactivity order of pyrrole, pyridine and indole is

1. indole > pyrrole > pyridine
2. pyrrole > pyridine > indole
3. pyrrole > indole > pyridine
4. indole > pyridine > pyrrole

70. The most appropriate reagent suitable for the conversion of 2-octyne into trans-2-octene is

1. zinc and acetic acid
2. 10% Pd/C
3. lithium in liquid ammonia
4. hydrazine hydrate

PART C

71. Consider a n-type semiconductor whose $E_v = 0$, $E_c = 2.0$ eV and $E_d = 1.98$ eV. The correct statement among the following is

   1. $E_f = 1$ eV and is independent of T
   2. $E_f = 1.99$ eV and remains independent of T
   3. $E_f = 1.99$ eV and increases towards 2.0 eV with increase of T
   4. $E_f = 1.99$ eV and decreases with increase of T

72. Reaction of $Fe(CO)_5$ with OH^- leads to complex **A** which on oxidation with MnO_2 gives **B**. Compounds **A** and **B** respectively are

   (1) $[HFe(CO)_4]^-$ and $Fe_3(CO)_{12}$ (2) $[Fe(CO)_5(OH)]^-$ and $Fe_2(CO)_9$

   (3) $[Fe(CO)_4]^{2-}$ and $Mn_2(CO)_{10}$ (4) $[HFe(CO)_4]^-$ and Fe_2O_3

73. For the reaction $H_2O(g) + C$ (graphite) $\rightleftharpoons CO(g) + H_2O(g)$, the variation of energy parameter ΔG°, ΔH° and $T\Delta S^\circ$ of the reaction over a large temperature range is shown below. The correct identification of the curves is given by
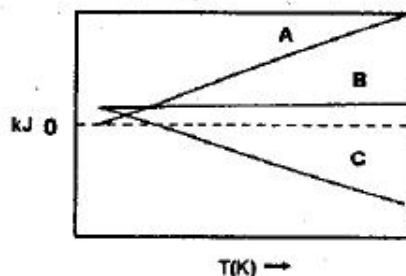
   (1) $A \rightarrow \Delta G^\circ$, $B \rightarrow \Delta H^\circ$, $C \rightarrow T\Delta S^\circ$ (2) $A \rightarrow \Delta H^\circ$, $B \rightarrow \Delta G^\circ$, $C \rightarrow T\Delta S^\circ$

   (3) $A \rightarrow \Delta G^\circ$, $B \rightarrow T\Delta S^\circ$, $C \rightarrow \Delta H^\circ$ (4) $A \rightarrow T\Delta S^\circ$, $B \rightarrow \Delta H^\circ$, $C \rightarrow \Delta G^\circ$

74. A sodalite cage in zeolites is

   (1) a truncated tetrahedron   (2) an icosahedron

   (3) a truncated octahedron   (4) a dodecahedron

75. Two moles of a nonvolatile solute is dissolved in 48 mol of water and the resultant solution has a vapour pressure of 0.0392 bar at 300 K. If the vapour pressure of pure water at 300 K is 0.0400 bar, the activity coefficient of water in the solution is

   (1) 0.96   (2) 0.98   (3) 1.00   (4) 1.02
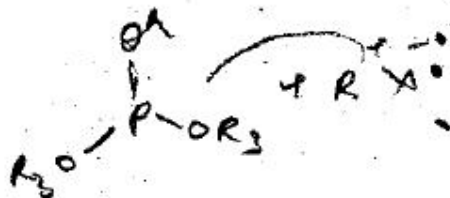
76. The final product(s) of the reaction

$P(OR)_3 + R'X$ is/are
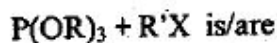
(1) $R'PO(OR)_2$ and RX
(2) $[R'PO(OR)_2]X$
(3) $[R'RPO_2(OR)]X$
(4) ROR' and $P(OR)_2X$

77. 1 mol of CO_2, 1 mol of N_2 and 2 mol of O_2 were mixed at 300 K. The entropy of mixing is

(1) $6 R \ln2$
(2) $8 R \ln2$
(3) $\dfrac{8R \ln2}{300}$
(4) $16R \ln2$

78. For the eigenstates of the hydrogen atom, which of the following relations between the expectation value of kinetic energy (T) and potential (V) holds true?

(1) $\langle T \rangle = \langle V \rangle$
(2) $2\langle T \rangle = -\langle V \rangle$
(3) $2\langle T \rangle = \langle V \rangle$
(4) $\langle T \rangle = -2\langle V \rangle$

79. For the liquid $\rightleftharpoons$ vapour equilibrium of a substance, $\dfrac{dP}{dT}$ at 1 bar and 400 K is 8×10^{-3} bar K^{-1}. If the molar volume in the vapour form is 200 L mol^{-1} and the molar volume in the liquid form is negligible, the molar enthalpy of vapourisation is (1.0 bar L = 100 J)

(1) 640 kJ mol^{-1}
(2) 100 kJ mol^{-1}
(3) 80 kJ mol^{-1}
(4) 64 kJ mol^{-1}

80. The correct order of acidity among the following species is

1. $[Na(H_2O)_6]^+ > [Ni(H_2O)_6]^{2+} > [Mn(H_2O)_6]^{2+} > [Sc(H_2O)_6]^{3+}$
2. $[Sc(H_2O)_6]^{3+} > [Ni(H_2O)_6]^{2+} > [Mn(H_2O)_6]^{2+} > [Na(H_2O)_6]^+$
3. $[Mn(H_2O)_6]^{2+} > [Ni(H_2O)_6]^{2+} > [Sc(H_2O)_6]^{3+} > [Na(H_2O)_6]^+$
4. $[Sc(H_2O)_6]^{3+} > [Na(H_2O)_6]^+ > [Ni(H_2O)_6]^{2+} > [Mn(H_2O)_6]^{2+}$

81. The Langmuir adsorption isotherm is given by $\theta = \dfrac{Kp}{1+Kp}$, where p is the pressure of the adsorbate gas. The Langmuir adsorption isotherm for a diatomic gas A_2 undergoing dissociative adsorption is

(1) $\theta = \dfrac{Kp}{1+Kp}$
(2) $\theta = \dfrac{2Kp}{1+2Kp}$
(3) $\theta = \dfrac{(Kp)^2}{1+(Kp)^2}$
(4) $\theta = \dfrac{(Kp)^{1/2}}{1+(Kp)^{1/2}}$

82. The standard electrode potentials (E^o) of Fe^{3+}/Fe^{2+} and Fe^{2+}/Fe electrodes are +0.77 V and −0.44 V respectively at 300 K. The E^o of Fe^{3+}/Fe electrode at the same temperature is

(1) 1.21 V   (2) 0.33 V   (3) −0.11 V   (4) −0.04 V

83. Which of the following is true for the radial part of the hydrogen atom wavefunctions $R_{nl}(r)$ (n: principal quantum number) and the nodes associated with them?

1. The radial part of only s function is non-zero at the origin and has $(n-1)$ nodes.
2. The radial part of s function is zero at the origin and has n number of nodes.
3. All radial functions have values of zero at the origin and have $(n-1)$ nodes.
4. The radial parts of all s functions are zero at the origin and have no nodes.

84. For non-degenerate perturbation theory for ground state, with $E_0^{(0)}$ as zeroth order energy, $E_0^{(1)}$ as the first-order perturbation correction and E_0 as the exact energy, which of the following is true?

(1) $(E_0^{(0)} + E_0^{(1)})$ is always equal to E_0 (2) $(E_0^{(0)} + E_0^{(1)}) \leq E_0$

(3) $(E_0^{(0)} + E_0^{(1)}) \geq E_0$ (4) $E_0^{(0)} \leq (E_0 + E_0^{(1)})$

85. Observe the following electronic transitions of a diatomic molecule.

(A) $^1\Sigma_g^+ \to {}^3\Sigma_g^+$ (B) $^1\Sigma_u^+ \to {}^1\Sigma_g^+$

(C) $^1\Delta_u \to {}^1\Sigma_g^+$ (D) $^1\Pi_g \to {}^1\Sigma_u^+$

The allowed transitions are

(1) (A) and (C) only   (2) (B) and (D) only

(3) (A), (B) and (C) only   (4) (A), (C) and (D) only

86. An excited triplet state wavefunction of hydrogen molecule with the electronic configuration $\sigma_g^1 \sigma_u^1$ has the following space part

(1) $\sigma_g(1)\sigma_u(2)$ (2) $\sigma_g(1)\sigma_u(2) + \sigma_u(1)\sigma_g(2)$

(3) $\sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2)$ (4) $\sigma_g(1)\sigma_g(2) + \sigma_u(1)\sigma_u(2)$

87. The NMR spectrum of AX_3 exhibits lines at $\delta = 2.1$ and 2.3 ppm (for X type protons) and $\delta = 4.1, 4.3, 4.5$ and 4.7 ppm (for A type protons), measured from TMS with an instrument operating at 100 MHz. The chemical shift (in ppm) of A and X protons and coupling constant (in Hz) are respectively.

(1) 4.4, 2.2 and 20   (2) 2.2, 4.4 and 10

(3) 2.2, 4.4 and 5   (4) 4.3, 2.1 and 20

88. The character table of the C_{2v} point group is given below:

| C_{2v}	E	C_2	σ_v	σ'_v
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

The two functions $\phi_1 = p_1 + 2p_2 + 2p_3 + p_4$ and $\varphi_2 = 2p_1 - p_2 - p_3 + 2p_4$ (where p_k is the p-orbital on the kth atom of *cis*-butadiene and σ_v is the molecular plane) belong to

(1) A_1 and A_2 respectively   (2) Both A_2

(3) Both B_2 (4) B_1 and B_2 respectively

89. If θ_r denotes the characteristic temperature of rotation, then the magnitude of $[\theta_r(H_2) \cdot \theta_r(D_2)]/[\theta_r(HD)]^2$ (assume the bond lengths to be the same for all the molecules) is

(1) 2/3   (2) 3/2   (3) 8/9   (4) 9/8

90. The overall reaction for the passage of 1.0 Faraday of charge in the following cell

$$Ag(s)\text{-}AgCl(s)|KCl(a_1)|\ KCl(a_2)|\ AgCl(s)\text{-}Ag(s)$$
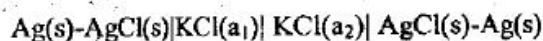
is given by (t denotes the transport numbers)

(1) $t_+ KCl(a_1) \to t_+ KCl(a_2)$ (2) $t_+ KCl(a_2) \to t_+ KCl(a_1)$

(3) $t_- KCl(a_1) \to t_- KCl(a_2)$ (4) $t_- KCl(a_2) \to t_- KCl(a_1)$

91. A system consisting of 4 identical and distinguishable particles, each possessing three available states of 1, 2 and 3 units, has 10 units of energy. The number of ways, W, in which these conditions are satisfied is

(1) 2   (2) 4   (3) 6   (4) 10

92. The molar conductivities at infinite dilution (Λ_m^0) for Na_2SO_4, K_2SO_4, KCl, HCl and HCOONa at 300 K are 260, 308, 150, 426 and 105 S cm^{-2} mol^{-1} respectively. Hence Λ_m^0 for formic acid in the same unit and at the same temperature is

(1) 381   (2) 405   (3) 429   (4) 531

93. If the displacement vectors of all atoms in *cis*-butadiene are taken as the basis vectors, the characters of the reducible representation of E, C_2, σ_v (molecular plane) and σ'_v are

1. 30, 10, 30, 0
2. 30,   0, 10, 0
3. 30, 20,   0, 0
4. 30,   0, 20, 0
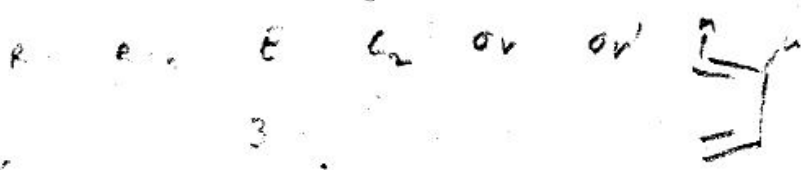
94. In least square fitting of a data set $\{X_i, Y_i\}$ to the equation $Y = A \cdot X$, the regression coefficient (A) is estimated by

(1) $\sum Y_i^2 / \sum X_i^2$

(2) $\sum X_i Y_i / \sum X_i^2$

(3) $\sum X_i Y_i / \sum Y_i^2$

(4) $\sum X_i^2 / \sum Y_i^2$

95. At any temperature for the following reaction (D and T are deuterium and tritium respectively) correct statement is

(A) $HCl + F \rightarrow HF + Cl$ (B) $DCl + F \rightarrow DF + Cl$ (C) $TCl + F \rightarrow TF + Cl$
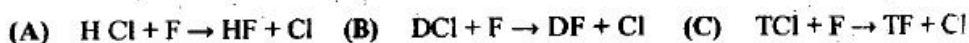
1. (A) is fastest
2. (B) is fastest
3. (C) is fastest
4. All the above reactions have the same rate constant

96. An example of a relaxation method of measuring rates is

1. spectroscopic monitoring of product concentration
2. stopped flow technique
3. temperature jump experiments
4. measurement of spectral line widths

97. The overall rate law of the following complex reaction,

$$2A \xrightleftharpoons{K_1} A_2 \qquad \text{(fast equilibrium)}$$

$$A + B \xrightleftharpoons{K_2} C \qquad \text{(fast equilibrium)}$$

$$A_2 + C \xrightarrow{k_3} P + 2A \qquad \text{(slow)}$$
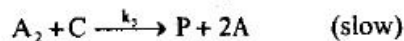
by steady state approximation would be

(1) $K_1 K_2 k_3 [A]^3 [B]$

(2) $K_2 K_1 k_3 [A] [B]^3$

(3) $K_1 K_2 k_3 [A] [B]^2$

(4) $K_1 K_2 k_3 [A] [B]$

98. The vibrational energy levels, $v'' = 0$ and $v' = 1$ of a diatomic molecule are separated by 2143 cm^{-1}. Its anharmonicity constant $(\omega_e x_e)$ is 14 cm^{-1}. The values of ω_e (in cm^{-1}) and first overtone (cm^{-1}) of this molecule are respectively.

(1) 2143 and 4286

(2) 2157 and 4286

(3) 2157 and 4314

(4) 2171 and 4258

99. The addition polymerization of M (monomer) involves the following stages:
(I = initiator; R = free radical)

$$I \xrightarrow{k_1} R \quad \text{(initiation)}$$
$$R + M \xrightarrow{k_2} RM$$
$$RM + M \xrightarrow{} RM_2 \text{ and so on}$$
$$RM_n + M_n R \xrightarrow{k_3} R - M_n - M_n - R$$
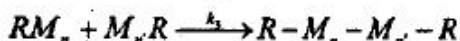
The rate constant for free radical formation is 2×10^{-3} s^{-1}. The initial concentration of initiator is 10^{-3} mol dm^{-3}. The overall rate of the reaction is 4×10^{-3} mol dm^{-3} s^{-1}. Assuming steady state approximation for free radical, the kinetic chain length is

(1) 2000   (2) 8×10^9 (3) 20   (4) 200

100. The electronic spectrum of $[CrF_6]^{3-}$ shows three bands at 14,900 cm^{-1}, 22400 cm^{-1} and 34,800 cm^{-1}. The value of Δ_0 in this case is

(1) 5,500 cm^{-1} (2) 14,900 cm^{-1} (3) 22,400 cm^{-1} (4) 34,800 cm^{-1}

101. Among the following pairs, those in which both species have similar structures are:

(A) N_3^-, XeF_2 (C) $[ClF_2]^+$, $[ICl_2]^-$
(B) $[ICl_4]^-$, $[PtCl_4]^{2-}$ (D) XeO_3, SO_3
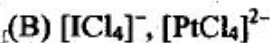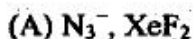
1. (A) and (B) only
2. (A) and (C) only
3. (A), (B) and (C) only
4. (B), (C) and (D) only
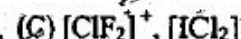
102. The number of metal-metal bonds in the dimers, $[CpFe(CO)(NO)]_2$ and $[CpMo(CO)_3]_2$ respectively, are

(1) two and two   (2) two and three   (3) one and two   (4) zero and one

103. The reduction of nitrogen to ammonia, carried out by the enzyme nitrogenase, needs

(1) 2 electrons   (2) 4 electrons   (3) 6 electrons   (4) 8 electrons

104. In the titration of 50 mL of 0.1 M HCl with 0.1 M NaOH using methyl orange as an indicator, the end point (color change) occurs as pH reaches 4.0. The titration error is

(1) −0.2%   (2) −84.7%   (3) +0.2%   (4) +84.7%

105. The *styx* code of B_4H_{10} is

(1) 4120   (2) 4220   (3) 4012   (4) 3203

106. Match list I (compounds) with list II (structures), and select the correct answer using the codes given below

List I

(A) XeO_4
(B) BrF_4
(C) $SeCl_4$

List II

(i) square planar
(ii) tetrahedral
(iii) distorted tetrahedral

1. (A – ii) (B – iii) (C – i)
2. (A – iii) (B – i) (C – ii)
3. (A – ii) (B – i) (C – iii)
4. (A – i) (B – ii) (C – iii)
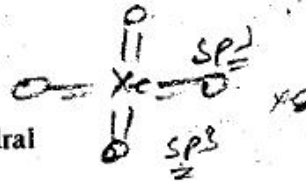
107. In the *trans*-$PtCl_2L(CO)$ complex, the CO stretching frequency for L = NH_3, pyridine, NMe_3 decreases in the order

1. pyridine > NH_3 > NMe_3
2. NH_3 > pyridine > NMe_3
3. NMe_3 > NH_3 > pyridine
4. pyridine > NMe_3 > NH_3

108. For the nuclear reactions

(A) $_4^8Be \rightarrow 2\,_2^4He$

(B) $_{36}^{80}Kr \rightarrow 2\,_{18}^{40}Ar$

(Given masses: ^8Be = 8.005300, ^4He = 4.002603 and $_{36}^{80}Kr$ = 79.81638, $_{18}^{40}Ar$ = 39.96238)
The correct statement is

1. (A) and (B) are both spontaneous fission processes
2. (A) is spontaneous fission but (B) is not
3. (B) is spontaneous fission but (A) is not
4. both (A) and (B) are not spontaneous fission processes

109. A metal ion that can replace manganese(II) ion in mangano-proteins without changing its function, is

(1) Fe(II)   (2) Zn(II)   (3) Mg(II)   (4) Cu(II)

110. In $^{57}Fe^*$ Mössbauer experiment, source of 14.4 keV (equivalent to 3.48×10^{12} MHz) is moved towards absorber at a velocity of 2.2 mm s^{-1}. The shift in frequency of the source for this sample is

(1) 35.5 MHz   (2) 25.5 MHz   (3) 20.2 MHz   (4) 15.5 MHz

111. Bayer's process involves

1. synthesis of B_2H_6 from $NaBH_4$
2. synthesis of $NaBH_4$ from borax
3. synthesis of $NaBH_4$ from B_2H_6
4. synthesis of $B_3N_3H_6$ from B_2H_6

112. A true statement about base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ is,

   1. it is a first order reaction
   2. the rate determining step involves the dissociation of chloride in $[Co(NH_3)_4(NH_2)Cl]^+$
   3. the rate is independent of the concentration of the base
   4. the rate determining step involves the abstraction of a proton from $[Co(NH_3)_5Cl]^{2+}$

113. The catalyst involved in carrying out the metathesis of 1-butene to give ethylene and 3-hexene is

   (1)
$$\begin{array}{c} Cl \quad PCy_3 \quad C_6H_5 \\ \backslash \ | \ / \\ Ru = \\ / \ | \\ Cl \quad PCy_3 \end{array}$$
   2) Na_2PdCl_4
   (3) $Co_2(CO)_8, H_2$
   (4) $RhCl(PPh_3)_3$
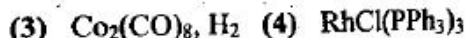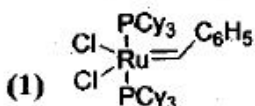
114. The correct order of d-orbital splitting in a trigonal bipyramidal geometry is

   (1) $d_z^2 > d_{xz}, d_{yz} > d_{x^2-y^2}, d_{xy}$

   (2) $d_{xz}, d_{yz} > d_{x^2-y^2}, d_{xy} > d_z^2$

   (3) $d_{x^2-y^2}, d_{xy} > d_z^2 > d_{xz}, d_{yz}$

   (4) $d_z^2 > d_{x^2-y^2}, d_{xy} > d_{xz}, d_{yz}$

115. For the following outer sphere electron transfer reactions,

   $$[Co(NH_3)_6]^{2+} + [Co^*(NH_3)_6]^{3+} \rightarrow [Co(NH_3)_6]^{3+} + [Co^*(NH_3)_6]^{2+}$$
   $$[Ru(NH_3)_6]^{2+} + [Ru^*(NH_3)_6]^{3+} \rightarrow [Ru(NH_3)_6]^{3+} + [Ru^*(NH_3)_6]^{2+}$$
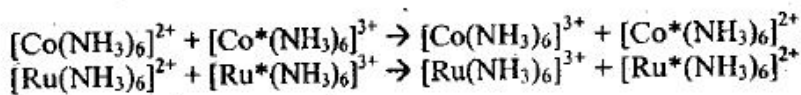
   the rate constants are 10^{-6} M^{-1} s^{-1} and 8.2×10^2 M^{-1} s^{-1} respectively. This difference in the rate constants is due to

   1. a change from high spin to low spin in Co* and high spin to low spin in Ru
   2. a change from high spin to low spin in Co* and low spin to high spin in Ru*
   3. a change from low spin to high spin in Co* and the low spin state remains unchanged in Ru
   4. a change from low spin to high spin in Co* and high spin to low spin in Ru*

116. The greater stability of $((CH_3)_3C-CH_2-)_4Ti$ (A) compared to that of $((CH_3)_2CH-CH_2-)_4Ti$ (B) is due to

   1. hyperconjugation present in complex (A)
   2. β-hydride elimination is not possible in complex (A)
   3. steric protection of titanium from reactive species in complex (A)
   4. the stronger nature of Ti–C bond in complex (A)

117. The coordination number and geometry of cerium in $[Ce(NO_3)_6]^{2-}$ are respectively,

   (1) 6 and octahedron
   (2) 6 and trigonal prism
   (3) 8 and cubic
   (4) 12 and icosahedron
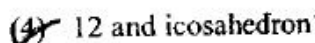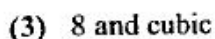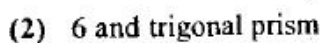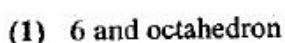
118. A compound A having the composition $FeC_9H_8O_3$ shows one signal at 2.5 ppm and another one around 5.0 ppm in its ^1H NMR spectrum. The IR spectrum of this compound shows two bands around 1900 and 1680 cm^{-1}. The compound follows the 18 electron rule. of the following statements for A, the correct one is/are

(A) It has η^5-Cp group   (B) It has a terminal CO ligand
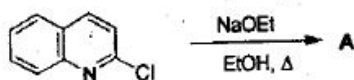(C) It has a CH_3 ligand   (D) It has Fe–H bond

(1) (A) and (B) only   (2) (C) only
(3) (A) and (C) only   (4) (B) and (D) only

119. In bacterial rubredoxin, the number of iron atoms, sulfur bridges and cysteine ligands are

	Fe atom	sulfur bridge	cysteine
1.	4	4	4
2.	2	2	4
3.	2	2	2
4.	1	0	4
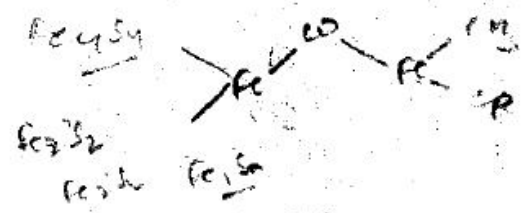
120. In the following reaction, the product formed and the mechanism involved are

NaOEt / EtOH, Δ → A
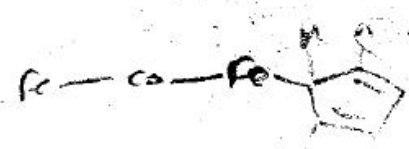
1. A is   [structure with OEt]   and is formed by addition-elimination mechanism

2. A is   [structure with OEt]   and is formed by benzyne mechanism

3. A is   [structure with OEt]   and is formed by benzyne mechanism

4. A is   [structure with OEt]   and is formed by S_N2 displacement

121. An optically active compound enriched with R-enantiomer (60% ee) exhibited $[\alpha]_D$ +90°. If the $[\alpha]_D$ value of the sample is –135°, the ratio of R and S enantiomers would be

(1) $R:S = 1:19$ (2) $R:S = 19:1$
(3) $R:S = 1:9$ (4) $R:S = 9:1$

122. Match the amino acids with their structures:

i.

ii.

iii.

a. tryptophan

b. histidine

c. asparagine

d. serine

e. glutamic acid
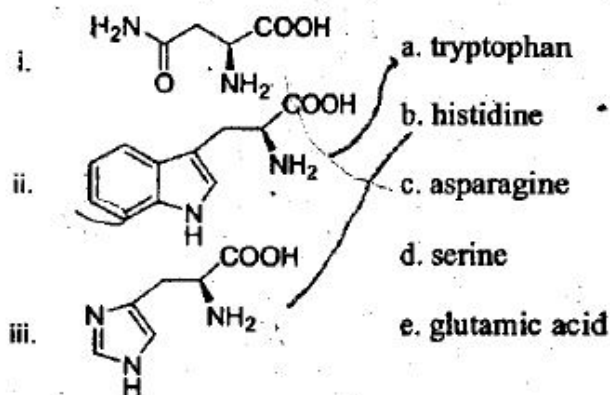
1. i-a   ii-e   iii-c
2. i-c   ii-d   iii-b
3. i-a   ii-b   iii-d
4. i-c   ii-a   iii-b
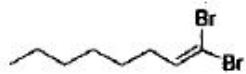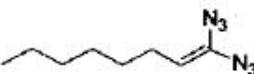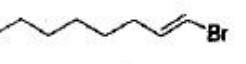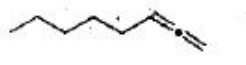
123. **Statement I.** U(VI) is more stable than Nd(VI).
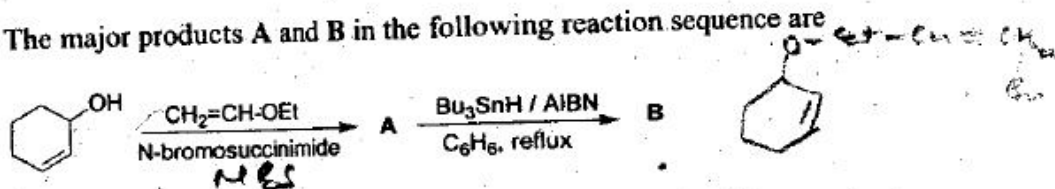**Statement II.** The valence electrons in U are in $5f$, $6d$ and $7s$ orbitals

1. Statements I and II are correct and Statement II is correct explanation of I
2. Statement I and II are correct but Statement II is not an explanation for Statement I
3. Statement I is correct and Statement II is incorrect
4. Statements I and II both are incorrect

124. The major products A and B in the following reaction sequence are
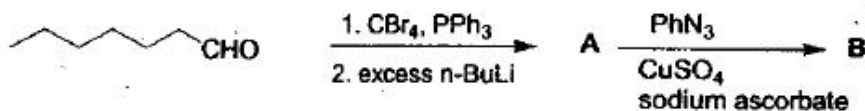
1. A =   B =

2. A =   B =

3. A =   B =

4. A =   B =

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

1. A = [structure] B = [structure]   2. A = [structure] B = [structure]

3. A = [structure] B = [structure]   4. A = [structure] B = [structure]

126. An organic compound having molecular formula $C_{15}H_{14}O$ exhibited the following ^1H and ^{13}C NMR spectral data.

^1H NMR: δ 2.4 (s), 7.2 (d, J=8 Hz), 7.7 (d, J=8 Hz).
^{13}C NMR: δ 21.0, 129.0, 130.0, 136.0, 141.0, 190.0.
The compound is

1. [structure]   2. [structure]

3. [structure]   4. [structure]

127. Identify appropriate reagents A and B in the following reactions.
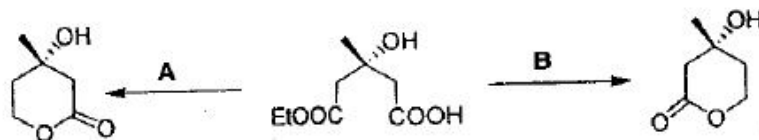
1. A = LiAlH₄   B = BH₃.Me₂S
2. A = BH₃.Me₂S   B = LiAlH₄
3. A = LiBH₄   B = BH₃.Me₂S
4. A = BH₃.Me₂S   B = LiBH₄

128. The correct sequence of the reagents to be employed in the following transformation is
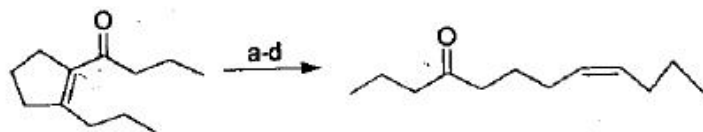
1. (a) m-CPBA; (b) TsNHNH₂; (c) AcOH; (d) H₂, Pd/BaSO₄
2. (a) H₂O₂, NaOH; (b) NH₂NH₂; (c) AcOH; (d) H₂, Pd/C
3. (a) m-CPBA; (b) TsNHNH₂; (c) NaOH; (d) H₂, Pd/C
4. (a) H₂O₂, NaOH; (b) TsNHNH₂; (c) AcOH; (d) H₂, Lindlar's catalyst

129. Reaction of 11.6 g of the aldehyde **A** with 462 mg of Wilkinson's catalyst provided 9.2 g of alkene **B**. The mol % of the catalyst used and the yield of the reaction, approximately, are
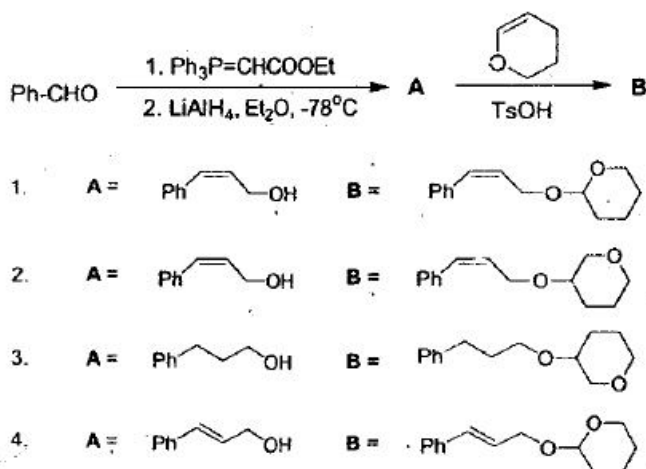

A (mol. wt. 232)   + (Ph$_3$P)$_3$RhCl (mol. wt. 923)
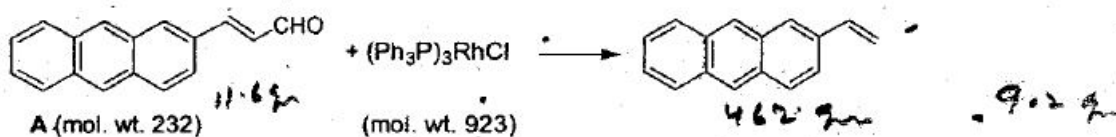
(1) 1.0 mol%; and 80%

(2) 1.0 mol%; and 90%
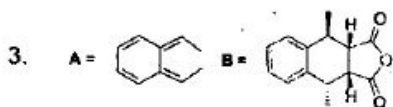
(3) 0.1 mol%; and 90%

(4) 0.2 mol%; and 80%

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

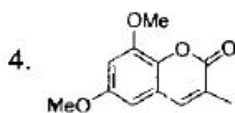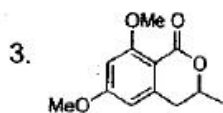**131.** The major products **A** and **B** in the following reaction sequence are

Ph-CHO $\xrightarrow[\text{2. LiAlH}_4, \text{Et}_2\text{O}, -78°\text{C}]{\text{1. Ph}_3\text{P=CHCOOEt}}$ **A** $\xrightarrow{\text{TsOH}}$ **B**

1. A = Ph—CH=CH—CH$_2$OH   B = ...

2. A = Ph—CH=CH—CH$_2$OH   B = ...

3. A = Ph—CH$_2$CH$_2$CH$_2$OH   B = ...

4. A = Ph—CH=CH—CH$_2$OH   B = ...
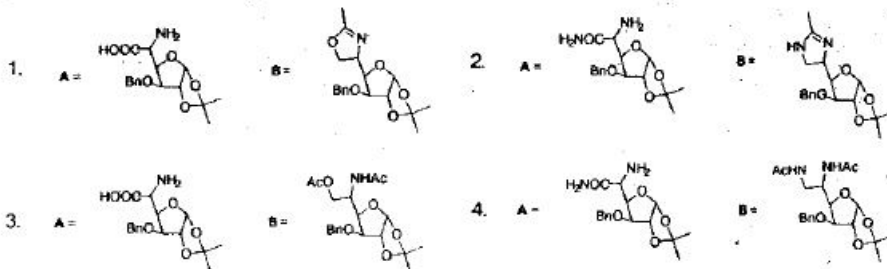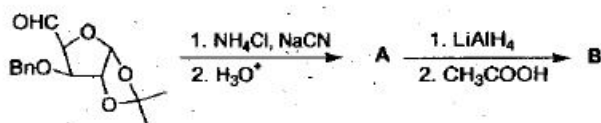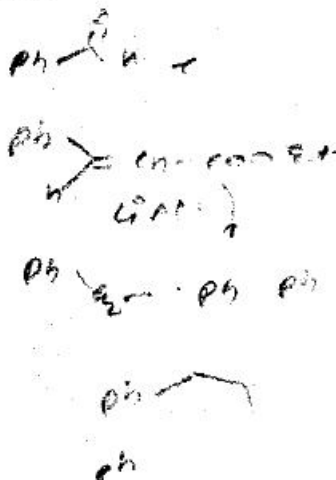
132. The major products A and B in the following reaction sequence are

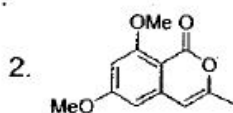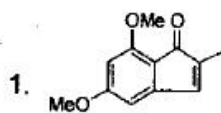1. A= ... B= ...
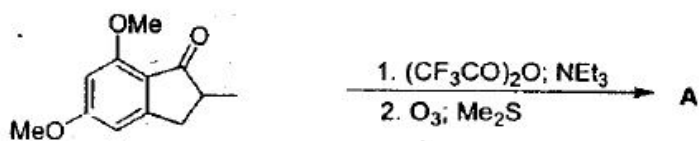
2. A= ... B= ...

3. A= ... B= ...

4. A= ... B= ...
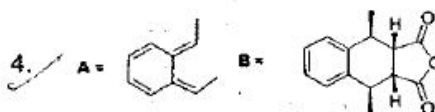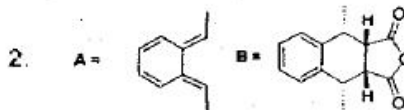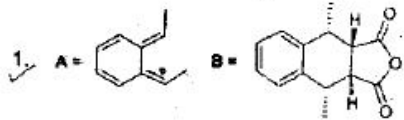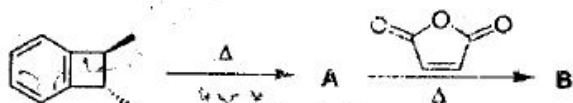
133. Appropriate ¹H NMR chemical shifts (δ) for the protons A-D for the following compound are
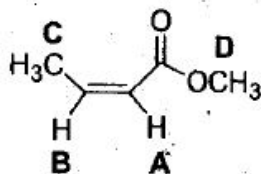

1. A – 6.8; B – 5.7; C – 3.9; D – 2.1 ppm
2. A – 6.8; B – 5.7; C – 2.1; D – 3.9 ppm
3. A – 5.7; B – 6.8; C – 3.9; D – 2.1 ppm
4. A – 5.7; B – 6.8; C – 2.1; D – 3.9 ppm

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

$$\text{1. (CF}_3\text{CO)}_2\text{O; NEt}_3$$
$$\text{2. O}_3\text{; Me}_2\text{S} \longrightarrow A$$

1.

2.

3.

4.

135. Citronellol A on oxidation with pyridinium chlorochromate (PCC) followed by treatment with aq. sodium hydroxide gives the product B (IR: 1680 cm⁻¹); whereas oxidation with PCC in the presence of sodium acetate gives product C (IR: 1720 cm⁻¹). Compounds B and C are
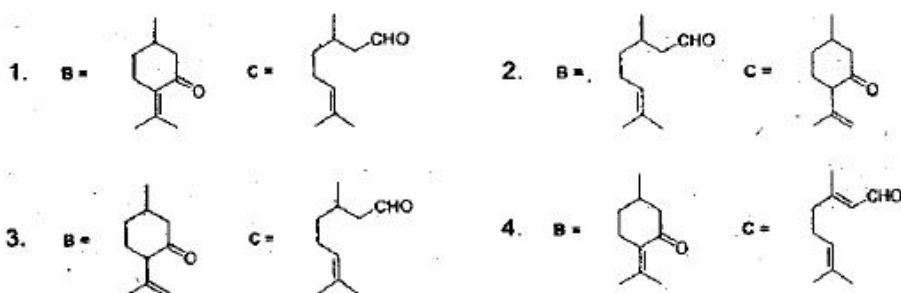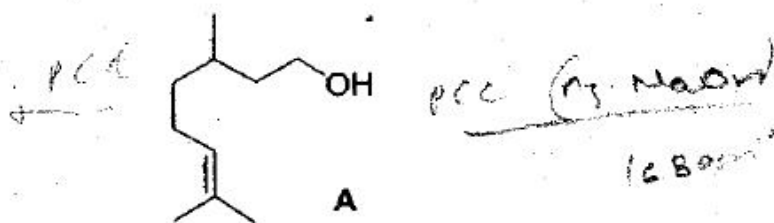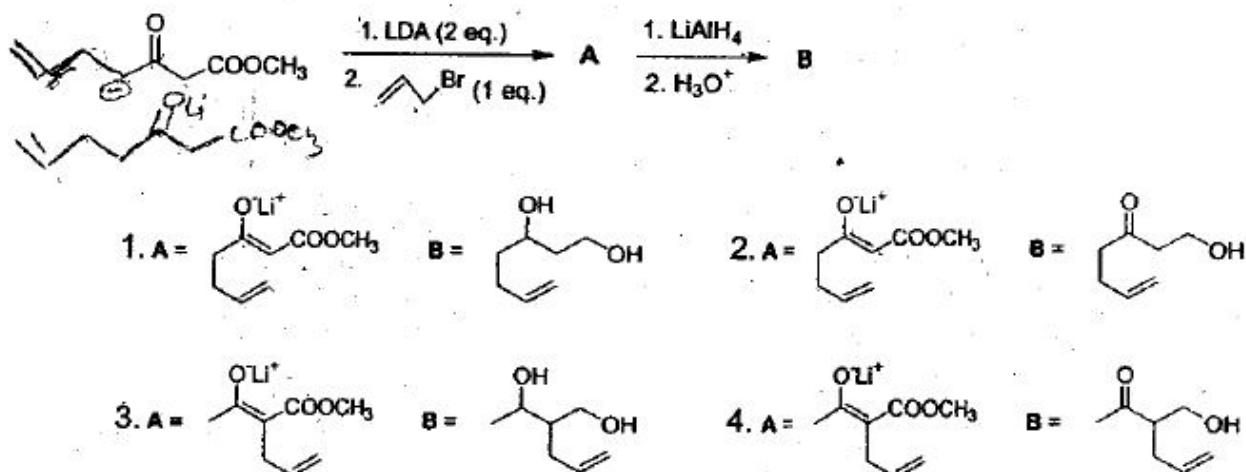

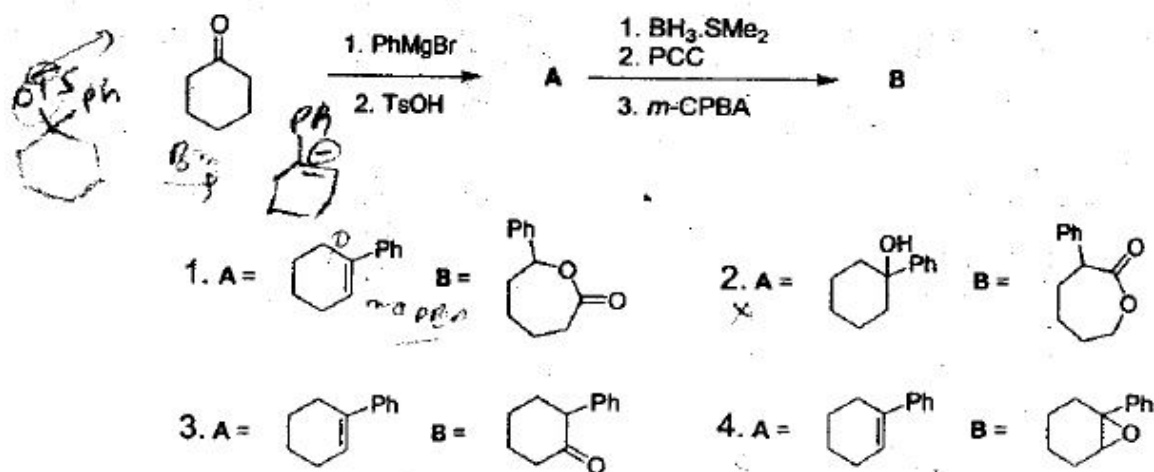136. Match the following starting compounds with corresponding products in **photochemical** reactions:
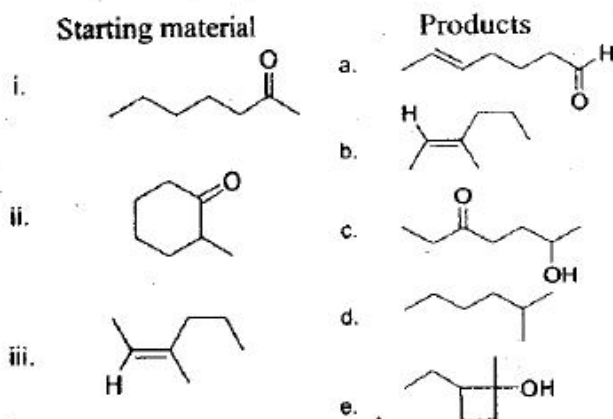
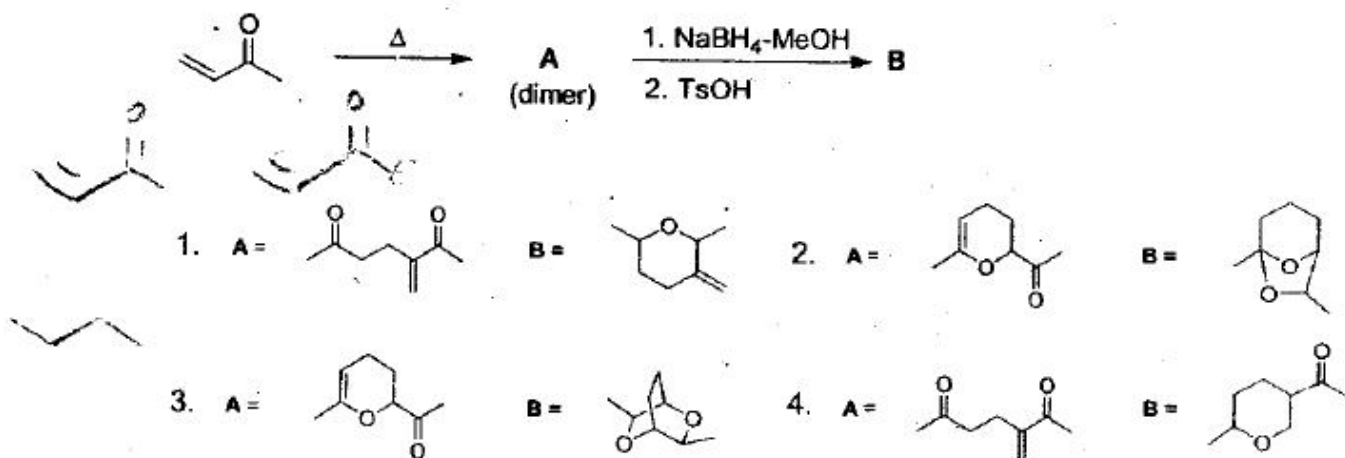|			
1.	i-e	ii-a	iii-b
2.	i-a	ii-c	iii-b
3.	i-d	ii-c	iii-a
4.	i-e	ii-a	iii-d

28

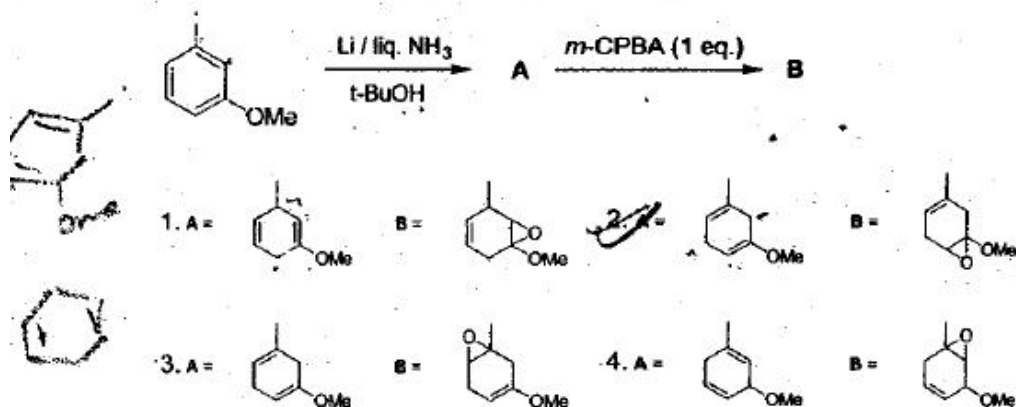137. The major products **A** and **B** in the following reaction sequence are

1. **A =** **B =**   2. **A =** **B =**

3. **A =** **B =**   4. **A =** **B =**

138. The major products **A** and **B** of the following reaction sequence are

1. **A =** **B =**   2. **A =** **B =**

3. **A =** **B =**   4. **A =** **B =**

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

1. **A =** **B =**   2. **A =** **B =**

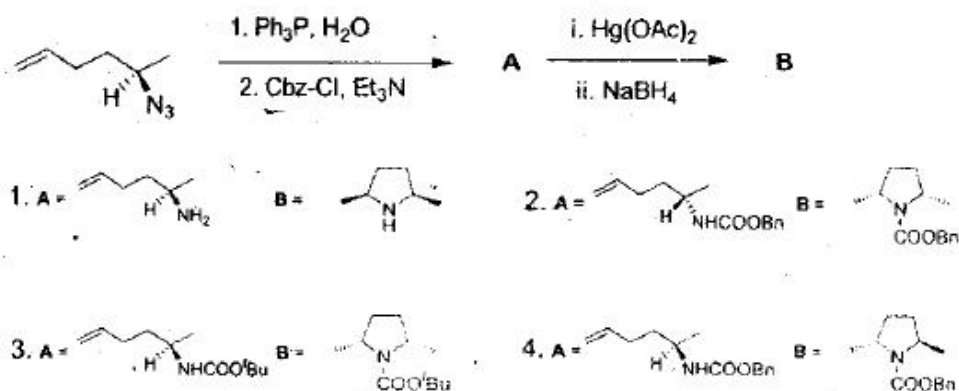3. **A =** **B =**   4. **A =** **B =**

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

141. The correct reagents for effecting the following reactions are

1. A = Me–S(=O)(Me)–CH₂ B = Me–S(Me)–CH₂ C = CH₂I₂, Zn-Cu

2. A = Me–S(Me)–CH₂ B = Me–S(=O)(Me)–CH₂ C = CH₂I₂, Zn-Cu

3. A = CH₂I₂, Zn-Cu B = Me–S(Me)–CH₂ C = Me–S(=O)(Me)–CH₂

4. A = Me–S(=O)(Me)–CH₂ B = Me–S(Me)–CH₂ C = Tebbe's reagent
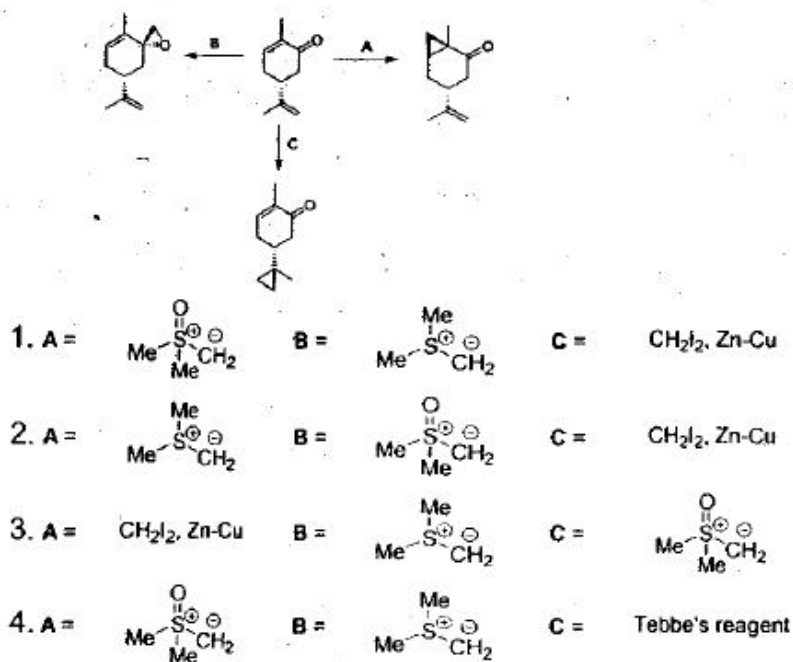
142. The major product **A** and **B** of the following reaction sequence are

1. A = ...NH₂ B = pyrrolidine
2. A = ...NHCOOBn B = ...COOBn
3. A = ...NHCOOtBu B = ...COOtBu
4. A = ...NHCOOBn B = ...COOBn

143. The major products **A** and **B** in the following synthetic sequence are
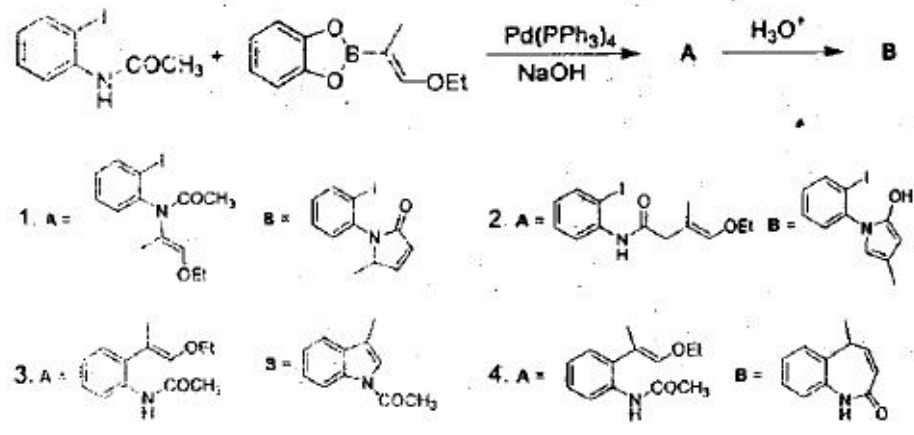
144. The major products **A** and **B** in the following synthetic strategy are
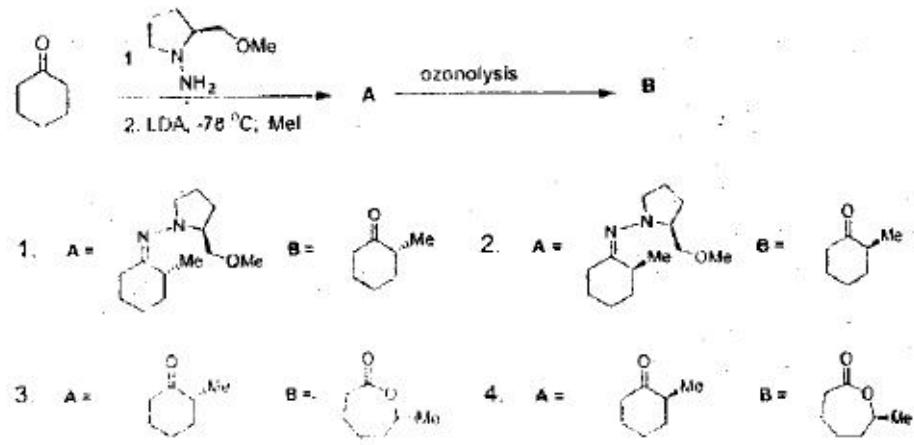
145. The product formed and the process involved in the following reaction are

1. [3,3]-sigmatropic rearrangement

2. [1,3]-sigmatropic rearrangement

3. [5,5]-sigmatropic rearrangement

4. [1,5]-sigmatropic rearrangement