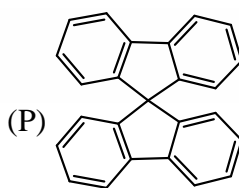


Q.21 – Q.85 : Carry TWO marks each.

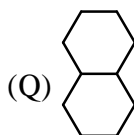
21. The spectroscopic ground state symbol and the total number of electronic transitions of $[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$ are
(a) ${}^3\text{T}_{1g}$ and 2 (b) ${}^3\text{A}_{2g}$ and 3 (c) ${}^3\text{T}_{1g}$ and 3 (d) ${}^3\text{A}_{2g}$ and 2
22. The structures of the complexes $[\text{Cu}(\text{NH}_3)_4](\text{ClO}_4)_2$ and $[\text{Cu}(\text{NH}_3)_4](\text{ClO})_4$ in solution respectively
(a) square planar and tetrahedral (b) octahedral and square pyramidal
(c) octahedral and trigonal bipyramidal (d) tetrahedral and square planar
23. In biological systems, the metal ions involved in electron transport are
(a) Na^+ and K^+ (b) Zn^{2+} and Mg^{2+}
(c) Ca^{2+} and Mg^{2+} (d) Cu^{2+} and Fe^{3+}
24. In a homogeneous catalytic reaction, 1.0 M of a substrate and 1.0 μM of a catalyst yields 1.0 mM of a product in 10 seconds. The turnover frequency (TOF) of the reaction (s^{-1}) is
(a) 10^{-2} (b) 10^2 (c) 10^{-3} (d) 10^3
25. The expected magnetic moments of the first-row transition metal complexes and those of the lanthanide metal complexes are usually calculated using
(a) $\mu_{s.o.}$ equation (s.o. = spin only) for both lanthanide and transition metal complexes
(b) $\mu_{s.o.}$ equation for lanthanide metal complexes and μ_j equation for transition metal complexes
(c) $\mu_{s.o.}$ equation for transition metal complexes and μ_j equation for lanthanide metal complexes
(d) μ_{L+S} equation for transition metal complexes and $\mu_{s.o.}$ equation for lanthanide metal complexes
26. The Bronsted acidity of boron hydrides follows the order
(a) $\text{B}_2\text{H}_6 > \text{B}_4\text{H}_{10} > \text{B}_5\text{H}_9 > \text{B}_{10}\text{H}_{14}$ (b) $\text{B}_2\text{H}_6 = \text{B}_4\text{H}_{10} > \text{B}_5\text{H}_9 = \text{B}_{10}\text{H}_{14}$
(c) $\text{B}_{10}\text{H}_{14} > \text{B}_5\text{H}_9 > \text{B}_4\text{H}_{10} > \text{B}_2\text{H}_6$ (d) $\text{B}_5\text{H}_9 > \text{B}_4\text{H}_{10} > \text{B}_2\text{H}_6 > \text{B}_{10}\text{H}_{14}$
27. NaCl is crystallised by slow evaporation of its aqueous solution at room temperature. The correct statement is
(a) The crystals will be non-stoichiometric
(b) The crystals should have Frenkel defects
(c) The percentage of defects in the crystals will depend on the concentration of the solution and its rate of evaporation
(d) The nature of defects will depend upon the concentration of the solution and its rate of evaporation
28. CaTiO_3 has a perovskite crystal structure. The coordination number of titanium in CaTiO_3 is :
(a) 9 (b) 6 (c) 3 (d) 12
29. If ClF_3 were to be stereochemically rigid, its ${}^{19}\text{F}$ NMR spectrum (I for ${}^{19}\text{F} = \frac{1}{2}$) would be (assume that Cl is not NMR active)
(a) a doublet and a triplet (b) a singlet
(c) a doublet and a singlet (d) two singlets.
30. The point group of NSF_3 is:
(a) D_{3d} (b) C_{3h} (c) D_{3h} (d) C_{3v}

31. When NiO is heated with a small amount of Li_2O in air at 1200°C , a non-stoichiometric compound $\text{Li}_x\text{Ni}_{(1-x)}\text{O}$ is formed. This compound is
- an n-type semiconductor containing only Ni^{1+}
 - an n-type semiconductor containing Ni^{1+} and Ni^{2+}
 - a p-type semiconductor containing Ni^{2+} and Ni^{3+}
 - a p-type semiconductor containing only Ni^{3+}
32. White phosphorus, P_4 , belongs to the
- cluso system
 - nodo system
 - arachno system
 - hypho system
33. Among the compounds Fe_3O_4 , NiFe_2O_4 and Mn_3O_4
- NiFe_2O_4 and Mn_3O_4 are normal spinels
 - Fe_3O_4 and Mn_3O_4 are normal spinels
 - Fe_3O_4 and Mn_3O_4 are inverse spinels
 - Fe_3O_4 and NiFe_2O_4 are inverse spinels
34. The number of M-M bonds in $\text{Ir}_4(\text{CO})_{12}$ are
- four
 - six
 - eight
 - zero
35. Schrock carbenes are
- Triplets and nucleophilic
 - Triplets and electrophilic
 - Singlets and nucleophilic
 - Singlets and electrophilic.
36. The INCORRECT statement about linear dimethylpolysiloxane, $[(\text{CH}_3)_2\text{SiO}]_n$, is
- it is extremely hydrophilic
 - it is prepared by a KOH catalysed ring-opening reaction of $[\text{Me}_2\text{SiO}]_4$
 - it has a very low glass transition temperature
 - it can be reinforced to give silicon elastomers
37. Match the entries a-d with their corresponding structures P-S

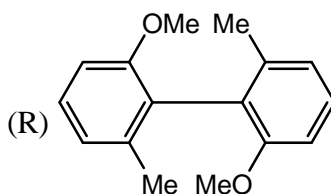
(A) bridged system



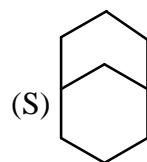
(B) atropisometric system



(C) spiro system



(D) Fused system



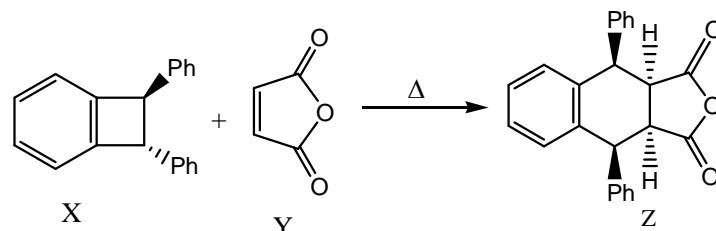
(a) A-S, B-R, C-Q, D-P

(b) A-P, B-S, C-Q, D-R

(c) A-Q B-P, C-S, D-R

(d) A-S, B-R, C-P, D-Q

38. The reaction between X and Y to give Z proceeds via



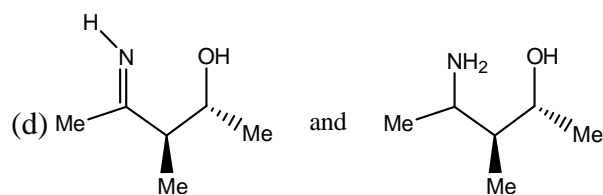
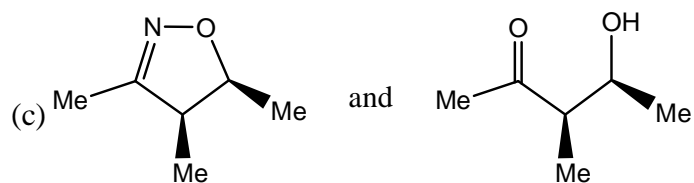
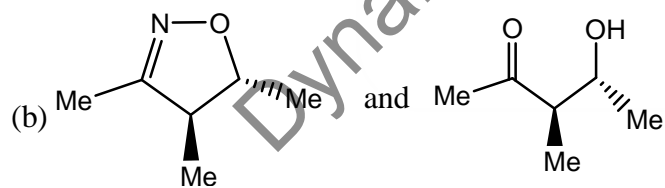
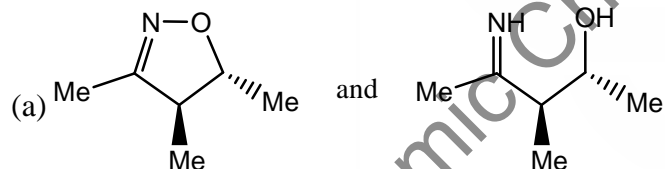
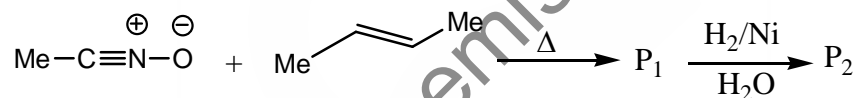
(a) 4π – conrotatory opening of X followed by endo Diels-Alder cycloaddition.

(b) 4π – disrotatory opening of X followed by endo Diels-Alder cycloaddition.

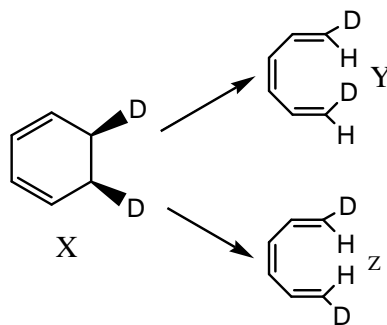
(c) 4π – conrotatory opening of X followed by exo Diels-Alder cycloaddition.

(d) 4π – disrotatory opening of X followed by exo Diels -Alder cycloaddition.

39. The Major products P_1 and P_2 , respectively, in the following reaction sequenc are



40. The products Y and Z are formed, respectively, from X via

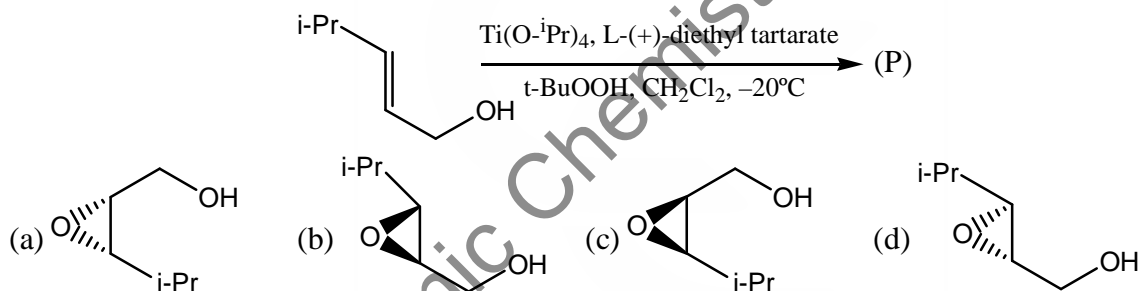


- (a) $h\nu$, conrotatory opening and Δ , disrotatory opening.
 (b) $h\nu$, disrotatory opening and Δ , conrotatory opening.
 (c) Δ , conrotatory opening and $h\nu$, disrotatory opening.
 (d) Δ , disrotatory opening and $h\nu$, conrotatory opening.

41. o-Bromophenol is readily prepared from phenol using the following conditions

- (a) (i) $(\text{CH}_3\text{CO})_2\text{O}$; (ii) Br_2 ; (iii) $\text{HCl-H}_2\text{O}, \Delta$
 (b) (i) $\text{H}_2\text{SO}_4, 100^\circ\text{C}$ (ii) Br_2 (iii) $\text{H}_3\text{O}^+, 100^\circ\text{C}$
 (c) N-Bromosuccinimide, dibenzoyl peroxide, CCl_4, Δ
 (d) $\text{Br}_2 / \text{FeBr}_3$

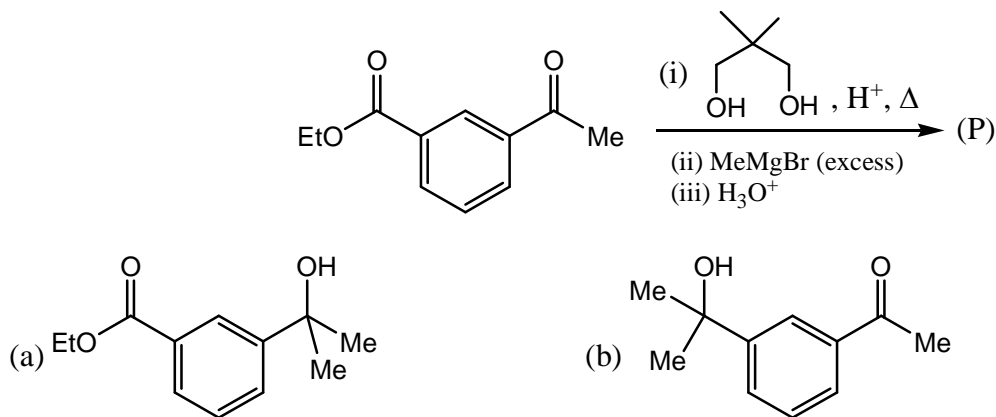
42. The major product of the following reaction is

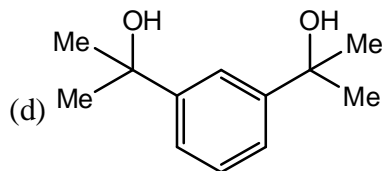
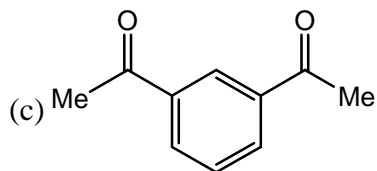


43. The photochemical reaction of 2-methylpropane with F_2 gives 2-fluoro-2-methylpropane and 1-fluoro-2-methylpropane in 14:86 ratio. The corresponding ratio of the bromo products in the above reaction using Br_2 is most likely to be

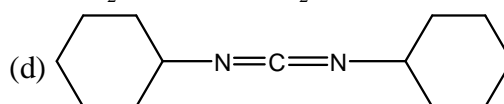
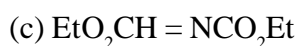
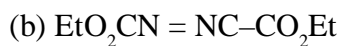
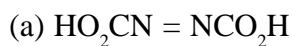
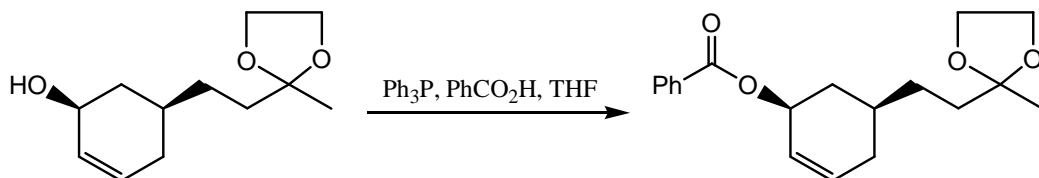
- (a) 14 : 86 (b) 50 : 50 (c) 1 : 9 (d) 99 : 1

44. The major product P of the following reactions is

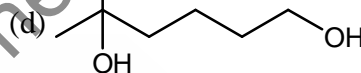
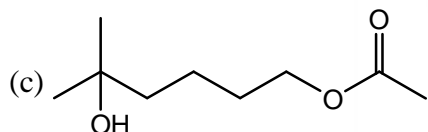
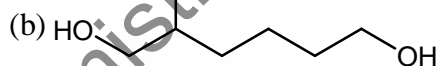
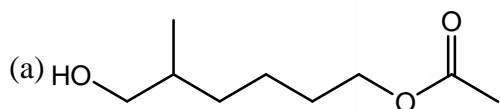
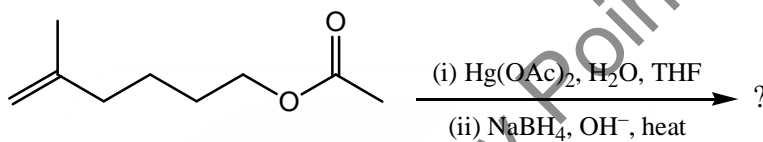




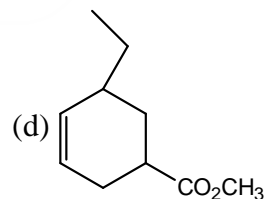
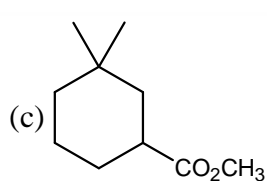
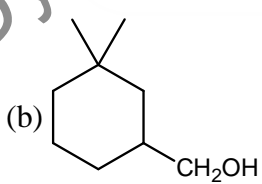
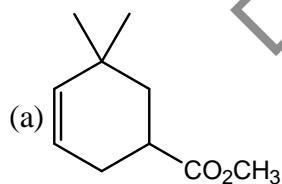
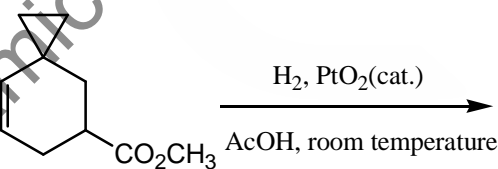
45. The reagent X in the following reaction is



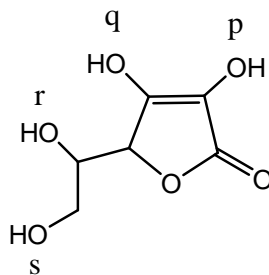
46. The major product of the following reactions is



47. The major product of the following reaction is:



48. In the following compound, the hydroxy group that is most readily methylated with CH_3N_2 is:



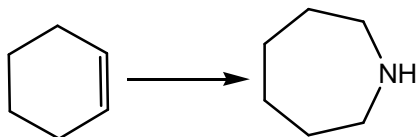
(a) p

(b) q

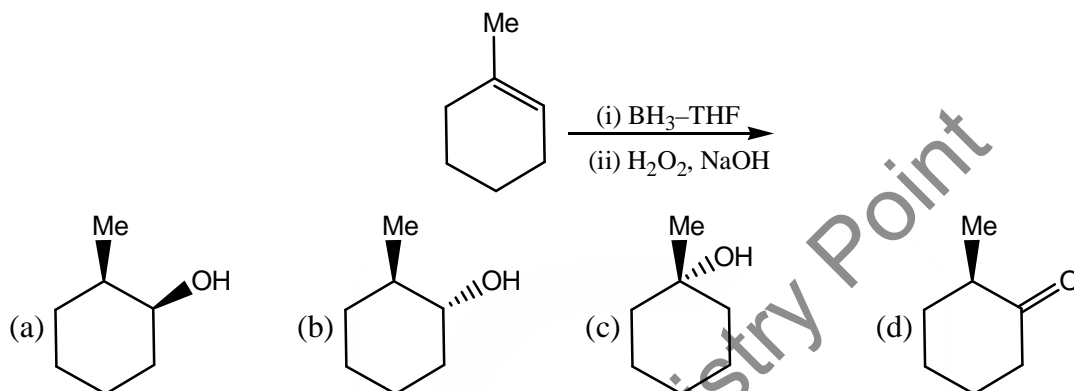
(c) r

(d) s

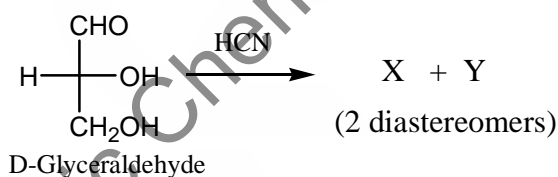
49. The most appropriate sequence of reactions for carrying out the following transformations.



- (a) (i) $\text{O}_3/\text{H}_2\text{O}_2$; (ii) excess $\text{SOCl}_2/\text{pyridine}$; (iii) excess NH_3 ; (iv) LiAlH_4
 (b) (i) $\text{O}_3/\text{Me}_2\text{S}$; (ii) excess $\text{SOCl}_2/\text{pyridine}$; (iii) LiAlH_4 ; (iv) excess NH_3
 (c) (i) $\text{O}_3/\text{H}_2\text{O}_2$; (ii) excess $\text{SOCl}_2/\text{pyridine}$; (iii) LiAlH_4 ; (iv) excess NH_3
 (d) (i) $\text{O}_3/\text{Me}_2\text{S}$; (ii) excess $\text{SOCl}_2/\text{pyridine}$; (iii) excess NH_3 ; (iv) LiAlH_4
50. The number of optically active stereoisomers possible for 1,3-cyclohexanediol in its chair conformation is
 (a) 4 (b) 3 (c) 2 (d) 1
51. The major product of the following reactions is

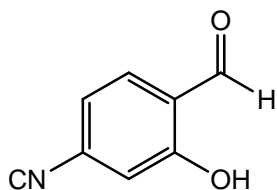


52. In the following reaction,



The absolute configurations of the chiral centres in X and Y are

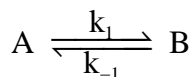
- (a) 2S, 3R and 2R, 3R (b) 2R, 3R and 2R, 3S
 (c) 2S, 3S and 2R, 3R (d) 2S, 3R and 2S, 3R
53. The IR stretching frequencies (cm^{-1}) for the compound X are as follows: 3300-3500 (s, br); 3000 (m); 2225 (s); 1680(s).



The correct assignment of the absorption bands is:

- (a) $\bar{\nu}_{(\text{OH})} = 3300 - 3500$; $\bar{\nu}_{(\text{CH})} = 3000$; $\bar{\nu}_{(\text{CN})} = 2225$; $\bar{\nu}_{(\text{CO})} = 1680$
 (b) $\bar{\nu}_{(\text{OH})} = 3000$; $\bar{\nu}_{(\text{CH})} = 3300 - 3500$; $\bar{\nu}_{(\text{CN})} = 2225$; $\bar{\nu}_{(\text{CO})} = 1680$
 (c) $\bar{\nu}_{(\text{OH})} = 3300 - 3500$; $\bar{\nu}_{(\text{CH})} = 3000$; $\bar{\nu}_{(\text{CN})} = 1680$; $\bar{\nu}_{(\text{CO})} = 2225$
 (d) $\bar{\nu}_{(\text{OH})} = 3000$; $\bar{\nu}_{(\text{CH})} = 3300 - 3500$; $\bar{\nu}_{(\text{CN})} = 1680$; $\bar{\nu}_{(\text{CO})} = 2225$

54. The Td point group has 24 elements and 5 classes. Given that it has two 3-dimensional irreducible representation, the number of one dimensional irreducible representation is:
 (a) 1 (b) 2 (c) 0 (d) 3
55. The total number of ways in which two nonidentical spin-1/2 particles can be oriented relative to a constant magnetic field is;
 (a) 1 (b) 2 (c) 3 (d) 4
56. Approximately one hydrogen atom per cubic meter is present in interstellar space. Assuming that the H-atom has a diameter of 10^{-10} m, the mean free path (m) approximately is
 (a) 10^{10} (b) 10^{19} (c) 10^{24} (d) 10^{14} .
57. The wavefunction of a diatomic molecule has the form $\psi = 0.89 \phi_{\text{covalent}} + 0.45 \phi_{\text{ionic}}$. The chance that both electrons of the bond will be found on the same atom in 100 inspections of the molecule approximately is
 (a) 79 (b) 20 (c) 45 (d) 60
58. For the reaction given below, the relaxation time is 10^{-6} s. Given that 10% of A remains at equilibrium, the value of k_1 (s^{-1}) is



- (a) 9×10^5 (b) 10^{-5} (c) 10^5 (d) 9×10^{-5}
59. The minimum number of electrons needed to form a chemical bond between two atoms is
 (a) 1 (b) 2 (c) 3 (d) 4
60. The ground state electronic energy (Hartree) of a helium atom, neglecting the inter-electron repulsion, is
 (a) -1.0 (b) -0.5 (c) -2.0 (d) -4.0
61. A particle is confined to a one-dimensional box of length 1 mm. If the length is changed by 10^{-9} m, the % change in the ground state energy is
 (a) 2×10^{-4} (b) 2×10^{-7} (c) 2×10^{-2} (d) 0
62. A certain molecule can be treated as having only a doubly degenerate state lying at 360 cm^{-1} above the non-degenerate ground state. The approximate temperature (K) at which 15% of the molecules will be in the upper state is
 (a) 500 (b) 150 (c) 200 (d) 300
63. A box of volume V contains one mole of an ideal gas. The probability that all N particles will be found occupying one half of the volume leaving the other half empty is
 (a) 1/2 (b) 2/N (c) $(1/2)^N$ (d) $(1/2)^{6N}$
64. According to the Debye-Huckel limiting law, the mean activity coefficient of $5 \times 10^{-4} \text{ mol kg}^{-1}$ aqueous solution of CaCl_2 at 25°C is (the Debye-Huckel constant 'A' can be taken to be 0.509)
 (a) 0.63 (b) 0.72 (c) 0.80 (d) 0.91
65. The operation of the commutator $[x, d/dx]$ on a function f(x) is equal to
 (a) 0 (b) f(x) (c) -f(x) (d) x df/dx
66. If a gas obeys the equation of state $P(V - nb) = nRT$, the ratio $\frac{(C_P - C_V)}{(C_P - C_V)_{\text{ideal}}}$ is:
 (a) >1 (b) <1 (c) 1 (d) (1-b)

67. Physisorbed particles undergo desorption at 27 °C with an activation energy of 16.628 kJ mol⁻¹. Assuming first-order process and a frequency factor of 10¹² Hz, the average residence time (in seconds) of the particles on the surface is
 (a) 8 × 10⁻¹⁰ (b) 8 × 10⁻¹¹ (c) 2 × 10⁻⁹ (d) 1 × 10⁻¹²
68. The rotational constants for CO in the ground and the first excited vibrational states are 1.9 and 1.6 cm⁻¹, respectively. The % change in the internuclear distance due to vibrational excitation is
 (a) 9 (b) 30 (c) 16 (d) 0
69. The mechanism of enzyme (E) catalysed reaction of a substrate (S) to yield product (P) is:
- $$E + S \xrightleftharpoons[k_{-1}]{k_1} [ES] \xrightleftharpoons[k_{-2}]{k_2} E + P; \quad \frac{-d[S]}{dt} = \frac{k_1 k_2 [S]_0 + k_2 k_{-2} [P]}{k_1 [S]_0 + k_{-2} [P] + k_{-1} + k_2} [E]_0$$
- If a small amount of S is converted to P, the maximum rate for the reaction will be observed for
 (a) (k₁ + k₂) >> k₁[S]₀ (b) (k₋₁ + k₂) << k₁[S]₀
 (c) (k₁ + k₂) >> k₁(s)₁ (d) k₂ << k₁
70. The lowest energy state of the (1s)²(2s)¹(3s)¹ configuration of Be is:
 (a) ¹S₀ (b) ¹D₂ (c) ³S₁ (d) ³P₁

Common Data for Q. 71 , Q.72 and Q.73

An electron accelerated through a potential difference of φ volts impinges on a nickel surface, whose (100) planes have a spacing d = 351.5 × 10⁻¹² m (351.5 pm)

71. The de-Broglie wavelength of the electron is $\frac{\lambda}{\text{pm}} = \left(\frac{a}{\phi}\right)^{1/2}$. The value of 'a' in volts is
 (a) 1.5 × 10⁻¹⁸ (b) 1.5 × 10⁶ (c) 6.63 × 10⁻⁵ (d) 2.5 × 10¹⁸
72. The condition for observing diffraction from the nickel surface is
 (a) λ >> 2d (b) λ ≤ 2d (c) λ ≤ ad (d) λ ≥ ad
73. The minimum value of φ (V) for the electron to diffract from the (100) planes is
 (a) 3000 (b) 300 (c) 30 (d) 3

Common Data for Q. 74 and Q.75

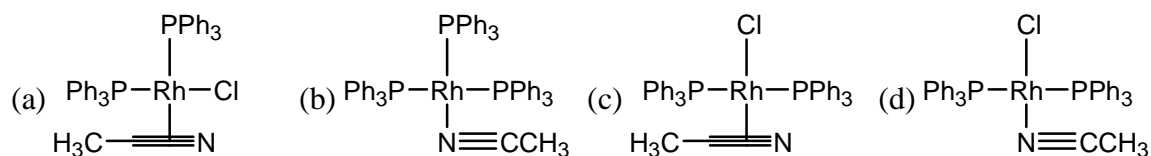
An iron complex [FeL₆]²⁺ (L = neutral monodentate ligand) catalyses the oxidation of (CH₃)₂S by perbenzoic acid.

74. The formation of the organic product in the above reaction can be monitored by
 (a) gas chromatography (b) cyclic voltammetry
 (c) electron spin resonance (d) fluorescence spectroscopy
75. The oxidation state of the metal ion in the catalyst can be deduced by
 (a) Atomic absorption spectroscopy (b) Mossbauer spectroscopy
 (c) HPLC (d) Gas Chromatography

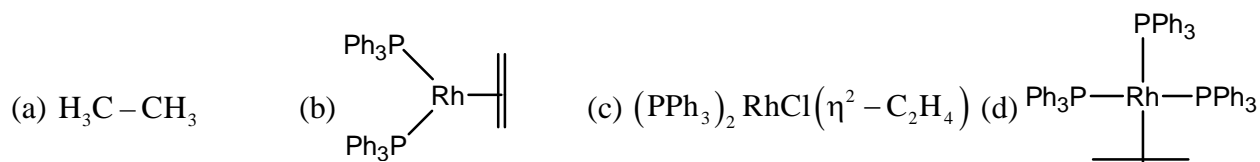
Linked Answer type Q. 76 and Q. 77:

In the reaction, $(\text{PPh}_3)_3 \text{RhCl} \xrightarrow{\text{CH}_3\text{CN}} \text{X} + \text{Y}$

76. Compound X is



77. $\text{Rh}(\text{PPh}_3)_3 \text{Cl}$ reacts very fast with a gaseous mixture of H_2 and C_2H_4 to immediately give Z. The structure of Z is

**Linked Answer Type for Q. 78 and Q. 79:**

The reaction of PCl_3 with methanol in the presence of triethylamine affords compound X. EI mass spectrum of X shows a parent ion peak at $m/z = 124$. Microanalysis of X shows that it contains C, H, O and P. The ^1H NMR spectrum of X shows a doublet at 4.0 ppm. The separation between the two lines of the doublet is approximately 15 Hz (I for ^1H and $^{31}\text{P} = \frac{1}{2}$).

78. Compound X is:

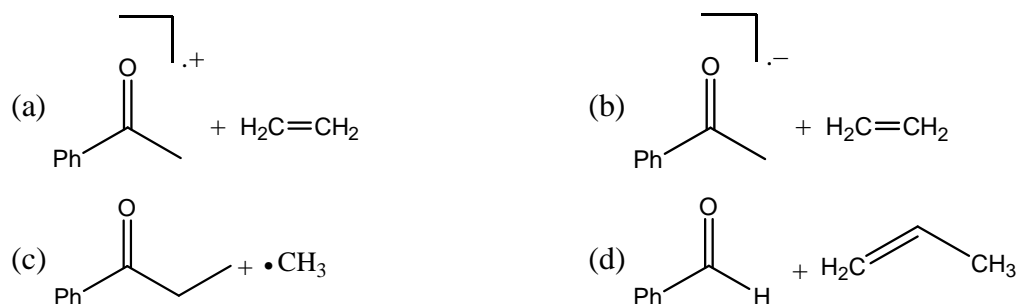


79. Upon heating, compound X is converted to Y, which has the same molecular formula as that of X. The ^1H NMR spectrum of Y shows two doublets centered at 3.0 ppm (separation of two lines ~ 20 Hz) and 4.0 ppm (separation of two lines ~ 15 Hz) respectively. Compound Y is:

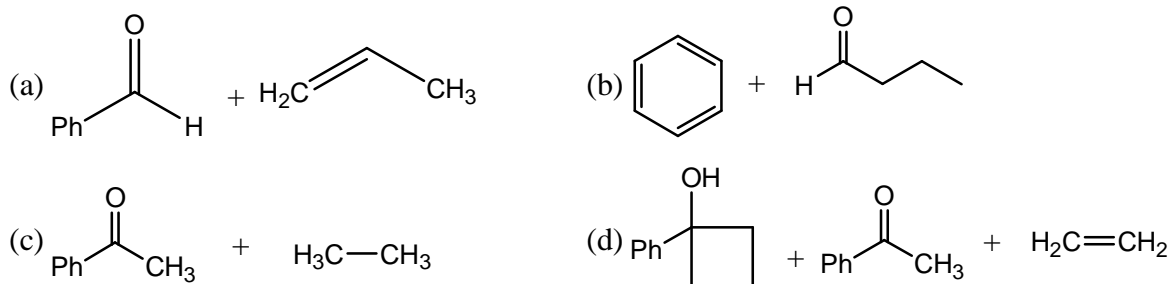
**Linked Answer Type Q.80 and Q. 81.**

For butyrophenone ($\text{PhCOCH}_2\text{CH}_2\text{CH}_3$),

80. The most probable fragmentation observed in the electron impact ionization (EI) mass spectrometry is:

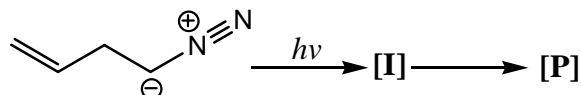


81. Photoirradiation leads to the following set of products:

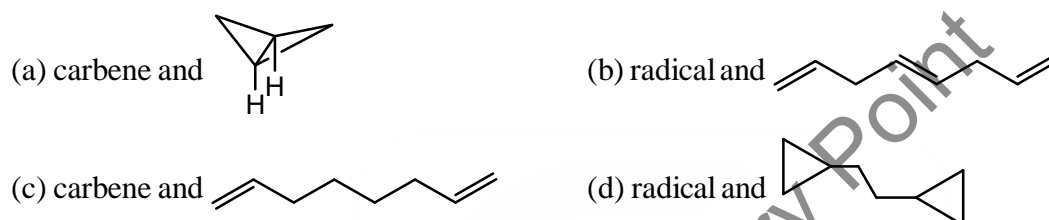


Linked Answer Q. 82 and Q. 83

In the following reaction,



82. The reactive intermediate I and the product P are



83. The product P shows 'm' and 'n' number of signals in ^1H and ^{13}C NMR spectra, respectively. The values of 'm' and 'n' are

- (a) $m = 3$ and $n = 2$ (b) $m = 2$ and $n = 3$ (c) $m = 2$ and $n = 2$ (d) $m = 4$ and $n = 3$

Linked Answer Type Q.84 and Q. 85:

The infrared spectrum of a diatomic molecule exhibits transitions at 2144, 4262 and 6354 cm^{-1} corresponding to excitations from the ground state to the first, second and, third vibration states respectively.

84. The fundamental transition (cm^{-1}) of the diatomic molecule is at:

- (a) 2157 (b) 2170 (c) 2183 (d) 2196

85. The anharmonicity constant (cm^{-1}) of the diatomic molecule is:

- (a) 0.018 (b) 0.012 (c) 0.006 (d) 0.003