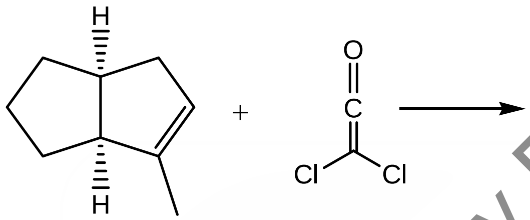
Section-A

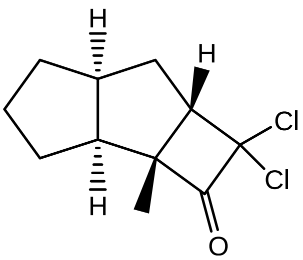
Q.1 – Q.25 : Carry ONE mark each.

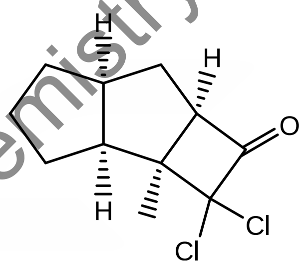
1. For low partial pressure of ozone (O_3), the adsorption of ozone on graphite surface is the fully dissociative in nature and follows Langmuir isotherm. Under these conditions, if the dependence of the surface coverage of graphite (θ) on partial pressure of ozone $\left(P_{O_3}\right)$ is given by $\theta \propto \left(P_{O_3}\right)^x$, the value of x is ______________(Upto two decimal places)

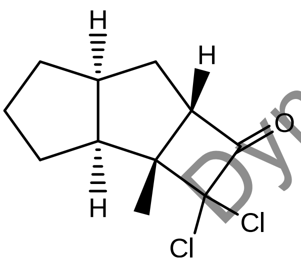
2. According to Eyring state theory for a bimolecular reaction, the activated complex has
(a) no vibrational degrees of freedom
(b) vibrational degrees of freedom but they never participate in product formation
(c) one high frequency vibration that leads to product formation
(d) one low frequency vibration that leads to product formation

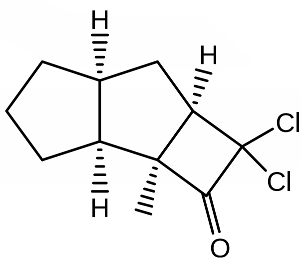
3. The major product formed in the following reaction is



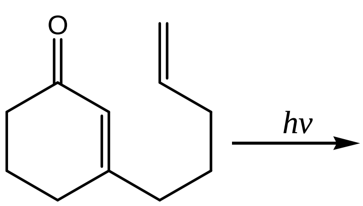
(a) 

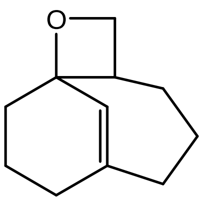
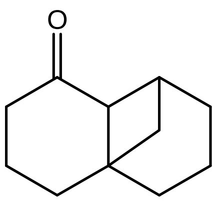
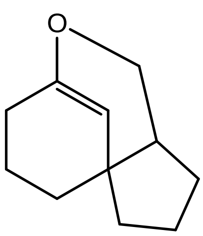
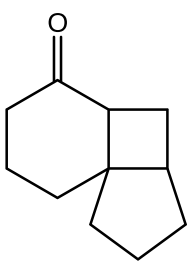
(b) 

(c) 

(d) 

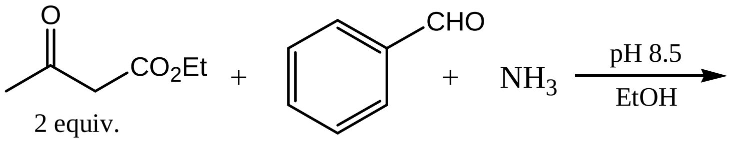
4. The major product of the following intramolecular cycloaddition reaction is

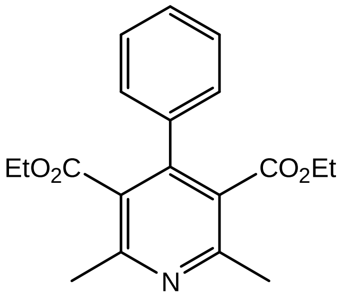


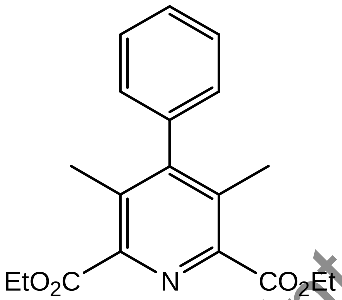
(a) 
(b) 
(c) 
(d) 

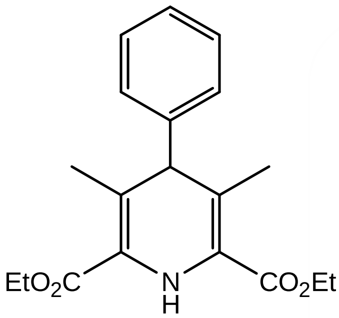
5. The coordination geometries around the copper ion of plastocyanin (a blue-copper protein) in oxidized and reduced form, respectively are
(a) tetrahedral and square-planar (b) square-planar and tetrahedral
(c) distorted tetrahedral for both (d) ideal tetrahedral for both

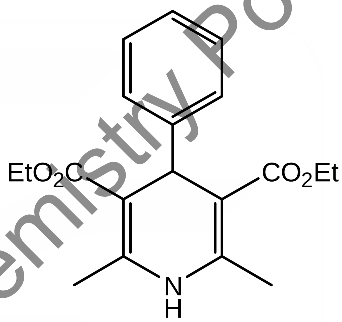
6. The major product formed in the following reaction is



(a) 

(b) 

(c) 

(d) 

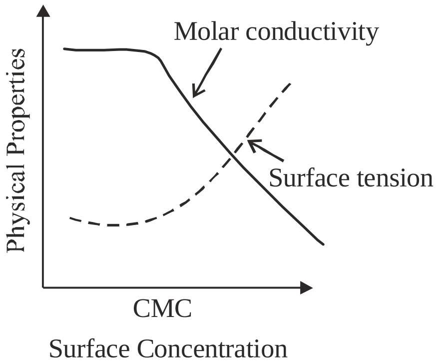
7. The spherical harmonic function $Y_{\ell,m}(\theta,\phi)$, with appropriate values of ℓ and m, is an eigenfunction of $\hat{L}_x^2 + \hat{L}_y^2$ operator. The corresponding eigenvalue is
(a) $\left(\ell(\ell+1) - m^2\right)\hbar^2$ (b) $\left(\ell(\ell+1) + m^2\right)\hbar^2$
(c) $\ell(\ell+1)\hbar^2$ (d) $m^2\hbar^2$

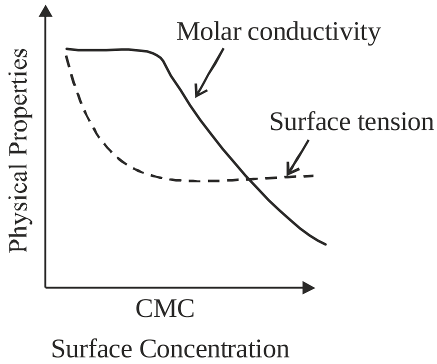
8. The temperature derivative of electrochemical potential E at constant pressure, $\left(\frac{\partial E}{\partial T}\right)_P$ is given by

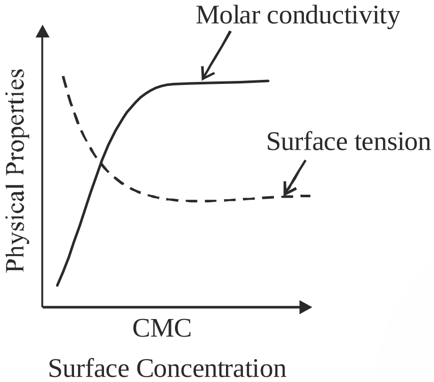
(a) $-\frac{\Delta S}{nF}$ (b) $\frac{\Delta S}{nF}$ (c) $\frac{\Delta S}{nFT}$ (d) $-\frac{\Delta S}{nFT}$

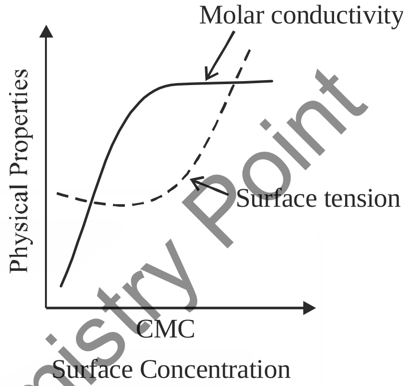
9. The water exchange rates for the complex ions follow the order
(a) $\left[V(H_2O)_6\right]^{2+} > \left[Co(H_2O)_6\right]^{2+} > \left[Cr(H_2O)_6\right]^{3+}$
(b) $\left[Cr(H_2O)_6\right]^{3+} > \left[Co(H_2O)_6\right]^{2+} > \left[V(H_2O)_6\right]^{2+}$
(c) $\left[Co(H_2O)_6\right]^{2+} > \left[Cr(H_2O)_6\right]^{3+} > \left[V(H_2O)_6\right]^{3+}$
(d) $\left[Co(H_2O)_6\right]^{2+} > \left[V(H_2O)_6\right]^{2+} > \left[Cr(H_2O)_6\right]^{3+}$

10. For an ionic micelle-forming surfactant near its critical micelle concentration (CMC), the dependence of molar conductivity and surface tension on surfactant concentration is best represented by

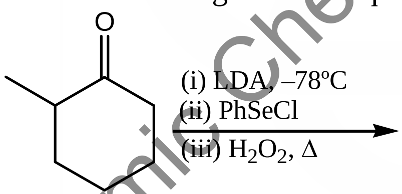
(a)


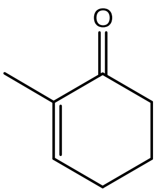
(b)


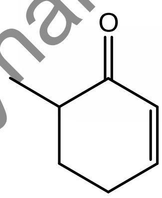
(c)


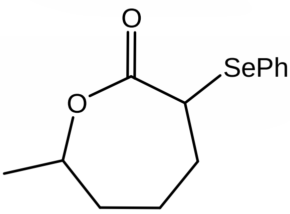
(d)


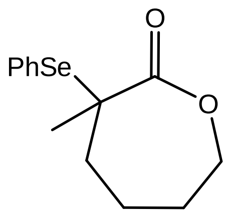
11. The major product formed in the following reaction sequence is



(a)


(b)


(c)


(d)


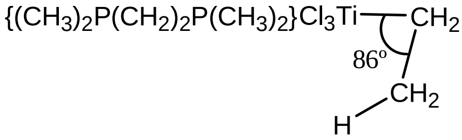
12. Two moles of an ideal gas X and two moles of an ideal gas Y, initially at the same temperature and pressure, are mixed under isothermal-isobaric condition. The entropy change on mixing is ____________________ JK^{-1}. (Upto one decimal place, Use R = 8.31 $JK^{-1}\ mol^{-1}$)

13. Consider the operators, $\hat{a}_{+} = \frac{1}{\sqrt{2}}\left(\hat{x} + \hat{i}p_{x}\right)$ and $\hat{a}_{-} = \frac{1}{\sqrt{2}}\left(\hat{x} - \hat{i}p_{x}\right)$, where $\hat{x}$ and $\hat{p}_{x}$ are the position and linear momentum operators, respectively. The commutator, $\left[\hat{a}_{+}, \hat{a}_{-}\right]$ is equal to

(a) $i\hbar$ (b) $-i\hbar$ (c) $\hbar$ (d) $-\hbar$

14. In the ^{1}H NMR spectrum of an organic compound recorded on a 300 MHz instrument, a proton resonates as a quartet at 4.20 ppm. The individual signals of quartet appear at δ 4.17, 4.19, 4.21 and 4.23 ppm . The coupling constant J in Hz is ____________

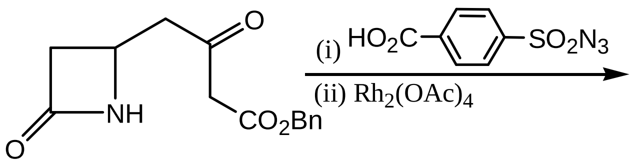
15. The bond angle (Ti–C–C) in the crystal structure of

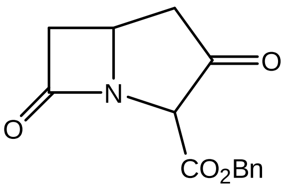


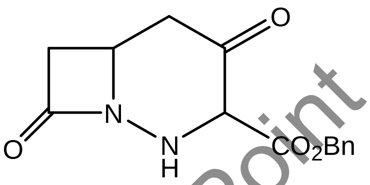
is severely distorted due to

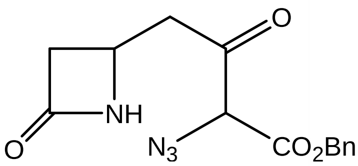
(a) hydrogen-bonding interaction
(b) agostic interaction
(c) steric bulk of the phosphine ligand
(d) higher formal charge on metal.

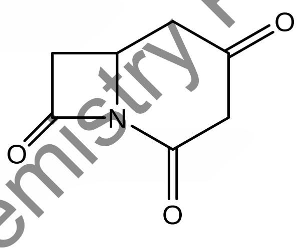
16. The major product formed in the following reaction sequence is



(a) 

(b) 

(c) 

(d) 

17. The lowest energy $d \rightarrow d$ transition of the complexes follow the order

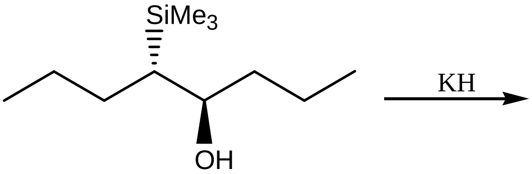
(a) $\left[\mathrm{Cr}\left(\mathrm{H_2O}\right)_6\right]^{3+} < \left[\mathrm{Cr}\left(\mathrm{NH_3}\right)_6\right]^{3+} < \left[\mathrm{Cr}\left(\mathrm{CN}\right)_6\right]^{3-}$

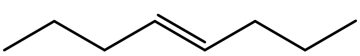
(b) $\left[\mathrm{Cr}\left(\mathrm{CN}\right)_6\right]^{3-} < \left[\mathrm{Cr}\left(\mathrm{NH_3}\right)_6\right]^{3+} < \left[\mathrm{Cr}\left(\mathrm{H_2O}\right)_6\right]^{3+}$

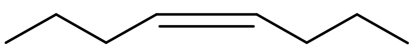
(c) $\left[\mathrm{Cr}\left(\mathrm{CN}\right)_6\right]^{3-} < \left[\mathrm{Cr}\left(\mathrm{H_2O}\right)_6\right]^{3+} < \left[\mathrm{Cr}\left(\mathrm{NH_3}\right)_6\right]^{3+}$

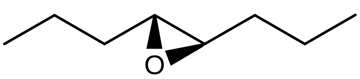
(d) $\left[\mathrm{Cr}\left(\mathrm{NH_3}\right)_6\right]^{3+} < \left[\mathrm{Cr}\left(\mathrm{CN}\right)_6\right]^{3-} < \left[\mathrm{Cr}\left(\mathrm{H_2O}\right)_6\right]^{3+}$

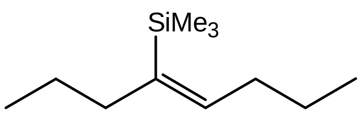
18. The major product of the following reaction is



(a) 

(b) 

(c) 

(d) 

19. The total number of valence electrons in $\mathrm{W}\left(\eta^3-\mathrm{Cp}\right)\left(\eta^5-\mathrm{Cp}\right)\left(\mathrm{CO}\right)_2$ is ____________(Atomic number of W = 74)

20. The energy of a hydrogen molecule in its ground state equilibrium configuration is –31.7 eV. Its dissociation energy is ________________eV. (Upto one decimal places)

21. The molar heat capacity of a substance is represented in the temperature range 298K to 400K by the empirical relation $C_{p,m} = 14 + bT\ JK^{-1}mol^{-1}$, where *b* is a constant. The molar enthalpy change when the substance is heated from 300K to 350K is 2 kJ mol^{-1}. The value of b is ________________J K^{-2} mol^{-1}. (Upto two decimal places)

22. In the electron ionization (EI) mass spectra, methyl hexanoate, methyl heptanoate and methyl octanoate give the same base peak. The m/z value of the base peak is ____________

23. For the radioactive isotope ^{131}I, the time required for 50% disintegration is 8 days. The time required for the 99.9% disintegration of 5.5g of ^{131}I is ________________ days. (Upto one decimal place)

24. The symmetry label of valence p orbitals of a metal ion in an octahedral ligand field is

(a) t_{1g} (b) t_{1u} (c) $e_g + a_{1g}$ (d) t_{2g}

25. Based on Wade's rule, the structure-type of $[B_5H_8]^-$ is

(a) closo (b) nido (c) arachno (d) hypho

Q.26 – Q.55 : Carry TWO marks each.

26. Spectroscopic ground state term symbols of cobalt ions in $\left[Co\left(H_2O\right)_6\right]^{2+}$ and $\left[CoCl_4\right]^{2+}$ respectively are

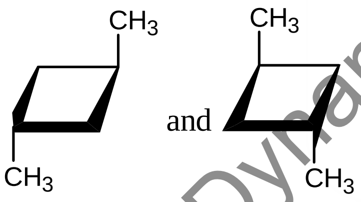
(a) $^2T_{1g}$ and $^4A_2$ (b) $^4T_{1g}$ and $^4A_2$ (c) $^2T_{2g}$ and $^4T_1$ (d) $^2T_1$ and $^4A_1$

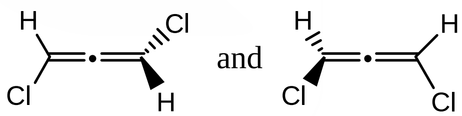
27. The reaction of equimolar quantities of $Fe(CO)_5$ and OH^- gives a complex species X which on further reaction with MnO_2 gives species Y. X and Y, respectively, are

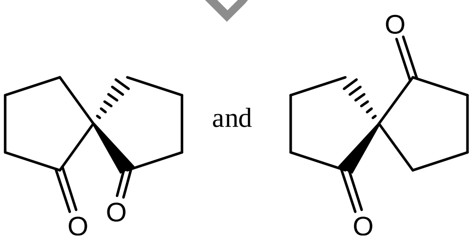
(a) $\left[Fe\left(CO\right)_5\left(OH\right)\right]^-$ and $Fe_2\left(CO\right)_9$ (b) $\left[Fe\left(CO\right)_4\right]^{2-}$ and $Mn_2\left(CO\right)_{10}$

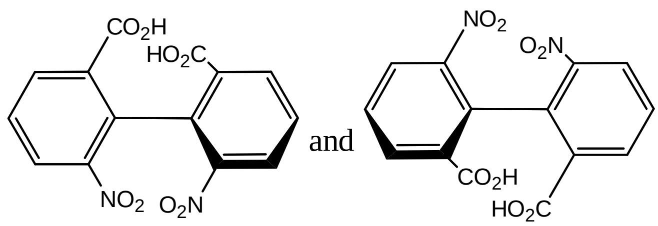
(c) $\left[HFe\left(CO\right)_4\right]^-$ and Fe_2O_3 (d) $\left[HFe\left(CO\right)_4\right]^-$ and $Fe_3\left(CO\right)_{12}$

28. The enantiomeric pair, among the following is

(a) 

(b) 

(c) 

(d) 

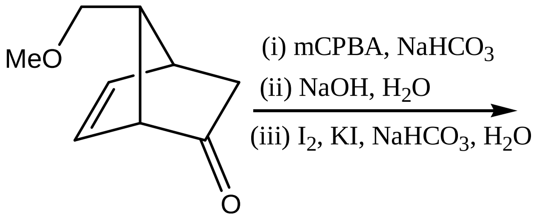
29. In a molecule XY, let ψ_X and ψ_Y denote normalized atomic orbitals of atoms X and Y, respectively. **A** normalized molecular orbital of XY is given by $\psi_+ = 0.56\left(\psi_X + \psi_Y\right)$. The value of the overlap integral of ψ_X and ψ_Y is ________________(Upto two decimal places)

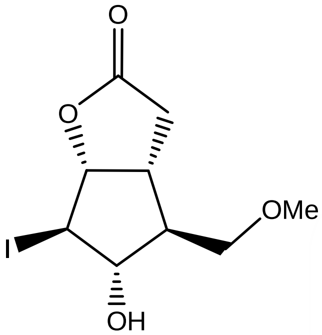
30. The absorption maxima of two dyes X and Y are 520 and 460 nm, respectively. The absorbance data of these measured in a 1cm path length cell are given in the table below.

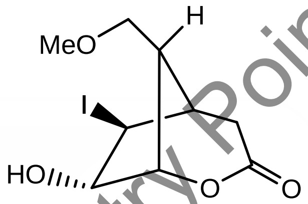
Dye solution	Absorbance at 460 nm	Absorbance at 520 nm
$X\,(9\ mM)$	0.144	0.765
$Y\,(12\ mM)$	0.912	0.168
Mixture of X and Y	0.700	0.680

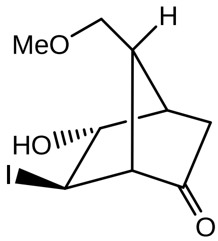
The concentration of Y in the mixture is ____________________mM. (Upto two decimal places)

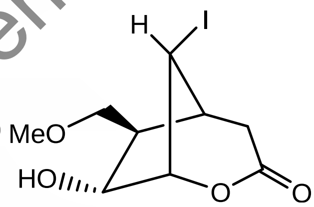
31. The major product in the following reaction sequence is



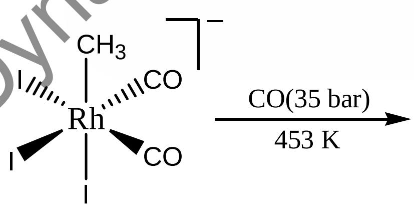
(a)


(b)


(c)


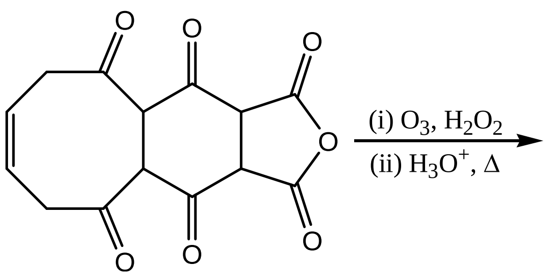
(d)


32. The elimination product of the following reaction is



(a) I_2 (b) CH_3I (c) CH_3COI (d) I_3^-

33. Number of carbonyl groups present in the final product of the following reaction sequence is



34. For the following reaction sequence,

$$3NH_4Cl + 3BCl_3 \xrightarrow[\text{(ii) LiBH}_4]{\text{(i) }\Delta,\ C_6H_5Cl} (X) \xrightarrow[\text{RT}]{3H_2O} (Y)$$

X and Y, respectively, are

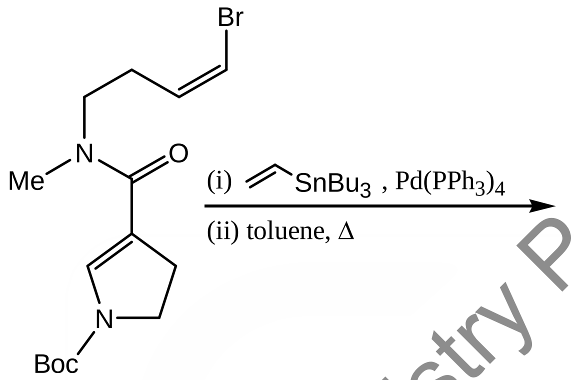
(a) $\{HB(NH)\}_3$ and $\{H(OH)B(NH_2)\}_3$

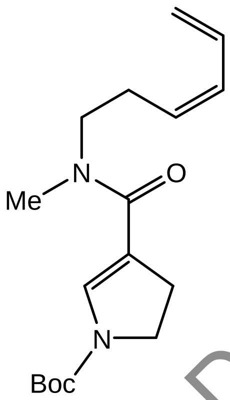
(b) $\{HB(NH)\}_3$ and $\{HB(NH_2OH)\}_3$

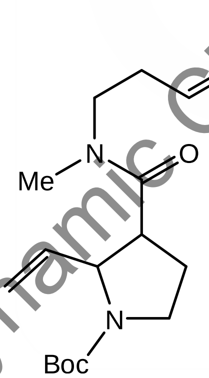
(c) $(NH_4)\{(H)_2(BH_2)_3\}$ and $\{H(OH)(NH_2OH)\}_3$

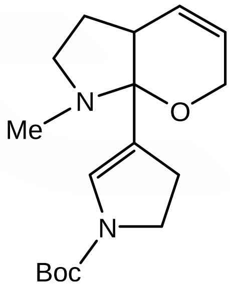
(d) $(NH_4)\{(H)_2(BH_2)_3\}$ and $\{HB(NH_2OH)\}_3$

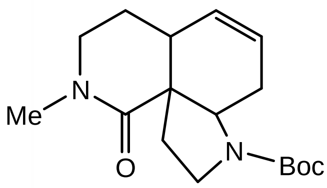
35. The major product of the following reaction sequence is



(a) 

(b) 

(c) 

(d) 

36. For a diatomic vibrating rotor, in vibrational level $v = 3$ and rotational level J, the sum of the rotational and vibrational energies is 11493.6 cm^{-1}. Its equilibrium oscillation frequency is 2998.3 cm^{-1}, anharmonicity constant is 0.0124 and rotational constant under rigid rotor approximation is 9.716 cm^{-1}. The value of J is ___________(Upto nearest integer)

37. At temperature T, the canonical partition function of a harmonic oscillator with fundamental frequency (v) is given by

$$q_{vib}(T) = \frac{e^{-hv/2k_BT}}{1-e^{-hv/k_BT}}$$

For $\dfrac{hv}{k_BT} = 3$, the probability of finding the harmonic oscillation in its ground vibrational state is _____________(Upto two decimal places)

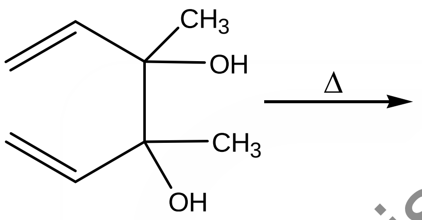
38. A one-dimensional anharmonic oscillator is treated by perturbation theory. The harmonic oscillator is used as the unperturbed system and the perturbation is $\frac{1}{6}\gamma x^3$ (γ is a constant). Using only the first order correction, the total ground state energy of the anharmonic oscillator is

(**Note:** For a one-dimensional harmonic oscillator $\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2}$; $\alpha = \left(\frac{k\mu}{h^2}\right)^{1.2}$

(a) $\frac{1}{2}\hbar\left(\frac{k}{\mu}\right)^{1/2}$ (b) $\left(\frac{1}{2}+\frac{\gamma}{6}\right)\hbar\left(\frac{k}{\mu}\right)^{1/2}$ (c) $\left(\frac{1}{2}+\frac{\gamma}{3}\right)\hbar\left(\frac{k}{\mu}\right)^{1/2}$ (d) $\left(\frac{1}{2}+\frac{\gamma}{12}\right)\hbar\left(\frac{k}{\mu}\right)^{1/2}$

39. The rate constant of a first order reaction, $X \rightarrow Y$, is 1.6×10^{-1} s–1 at 300K. Given that the activation energy of the reaction is 28 kJ mol^{-1} and assuming Arrhenium behaviour for the temperature dependence, the total time required to obtain 90% of Y at 350 K is ________________s. (Upto to one decimal place, use R = 8.31 JK^{-1} mol^{-1}).

40. The strongest band observed in the IR spectrum of the final product of the following reaction appears, approximately at ____________________$\times$100 cm^{-1} (Upto one decimal place)



41. The reaction of PCl_3 with PhLi in 1 : 3 molar ratio yields X as one of the products, which on further treatment with CH_3I gives Y. The reaction of Y with n-BuLi gives product Z. The product X, Y and Z respectively, are

(a) $[PPh_4]Cl, [Ph_2P=CH_2]$ and $Ph_2P(n\text{-}Bu)$

(b) $PPh_3, [Ph_3PI](CH_3)$ and $Ph_2P(n\text{-}Bu)_3$

(c) $PPh_3, [Ph_3P(CH_3)]I$ and $Ph_3P=CH_3$

(d) $[PPh_4]Cl, [Ph_3P=CH_2]$ and $[Ph_3P(n\text{-}Bu)]Li$

42. The π electrons in benzene can be modelled as particles in a ring that follow Pauli's exclusion principle. Given that the radius of benzene is 1.4Å, the longest wavelength of light that is absorbed during an electronic transition in benzene is ____nm. (Upto one decimal place. Use $m_e = 9.1\times10^{-31}$ kg, $h = 6.6\times10^{-34}$ Js, $c = 3.0\times10^8$ ms^{-1})

43. Second-order are constant for the reaction between $[Co(NH_3)_5X]^{n+}$ (n = 3 for X = NH_3 and H_2O; n = 2 for X = Cl^-) and $[Cr(H_2O)_6]^{2+}$ at room temperature varies with the X as

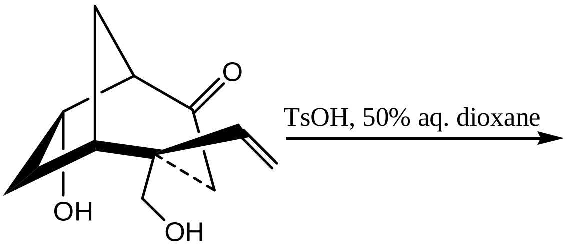
(a) $NH_3 > H_2O > Cl^-$ (b) $Cl^- > H_2O > NH_3$
(c) $NH_3 > Cl^- > H_2O$ (d) $H_2O > NH_3 > Cl^-$

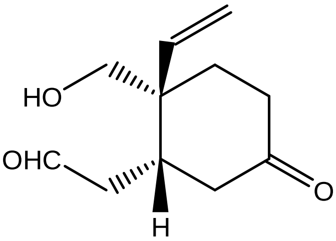
44. The Latimer diagram of oxygen is given below. The value of x is _______________V. (Upto two decimal places)

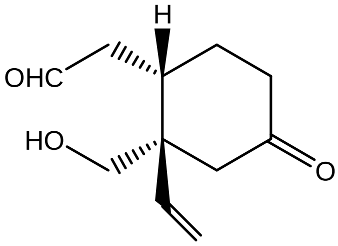
$$O_2 \xrightarrow{+0.70\text{ V}} H_2O_2 \xrightarrow{+1.76\text{ V}} H_2O$$

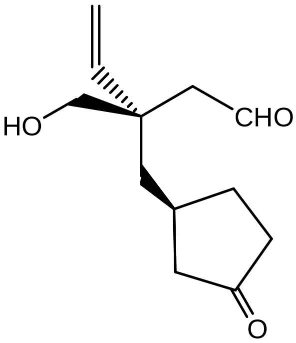
$$O_2 \xrightarrow{x\text{V}} H_2O$$

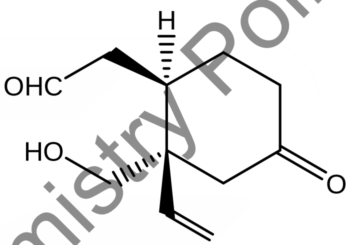
45. The major product formed in the following retro-aldol reaction is



(a) 

(b) 

(c) 

(d) 

46. The enthalpy of vaporization of a liquid at its boiling point $\left(T_b = 200\ K\right)$ is 15.3 kJ mol^{-1}. If the molar volumes of the liquid and the vapour at 200 K are 110 and 12000 cm^3 mol^{-1}, respectively, then the slope $\dfrac{dP}{dT}$ of the liquid-boundary is ________________kPa K^{-1} (Upto two decimal places. Note : 1 Pa = 1 J m^{-1})

47. The O_2 coordinated to metal ion centres in oxy-myoglobin and oxy-hemocyanin exists, respectively, as
(a) superoxide and peroxide
(b) superoxide and superoxide
(c) peroxide and peroxide
(d) superoxide and oxygen

48. For an inverse spinel, AB_2O_4, the A and B, respectively, can be
(a) Ni(II) and Ga(III)
(b) Zn(II) and Fe(III)
(c) Fe(II) and Cr(III)
(d) Mn(II) and Mn(III)

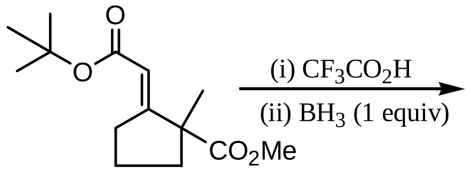
49. The molar conductivity of a 0.01 M weak acid (HX) at 298K, measured in a conductivity cell with cell constant of 0.4 cm^{-1}, is 64.4 Scm^2 mol^{-1}. The limiting molar conductivities at infinite dilution of H^+ and X^- at 298K are 350 and 410 S cm^2 mol^{-1}. Ignoring activity coefficients, the pK_a of HX at 298K is ______________(Upto two decimal places)

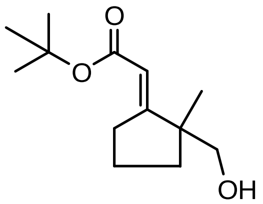
50. The spacing between the two adjacent lines of the microwave spectrum of $H^{35}Cl$, is 6.35×1011 Hz, given that bond length $D^{35}Cl$ is 5% greater than that of $H^{35}Cl$ the corresponding spacing for $D^{35}Cl$ is __________________$\times10^{11}$ Hz. (Upto two decimal places)

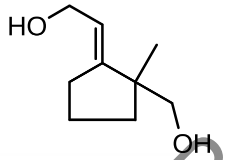
51. Generally, the coordination number and the nature of the electronic absorption band $(f \rightarrow f \text{ transition})$ of lanthanide (III) ion in their complexes are, respectively
(a) greater than 6 and sharp
(b) 6 and broad
(c) less than 6 and sharp
(d) greater than 6 and broad

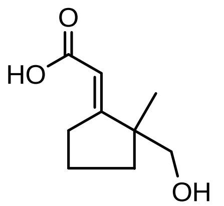
52. A tetrapeptide, made up of natural amino acids, has alanine as the N-terminal residue which is coupled to a chiral amino acid. Upon complete hydrolysis, the tetrapeptide gives glycine, alanine, phenylalanine and leucine. The number of possible sequences of the tetrapeptide is _______________

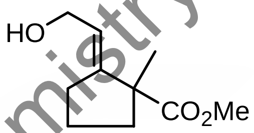
53. The major product formed in the following reaction sequence is



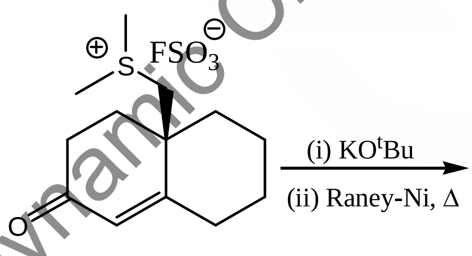
(a) 

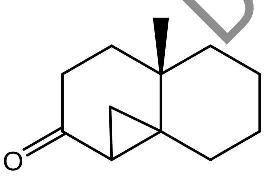
(b) 

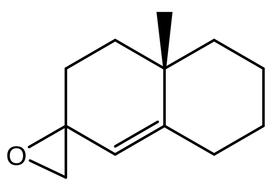
(c) 

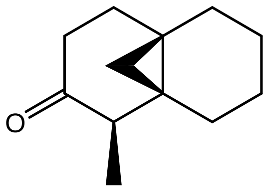
(d) 

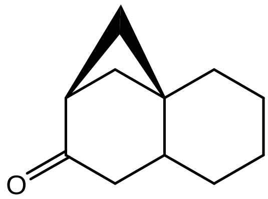
54. The major product formed in the following reaction sequence is



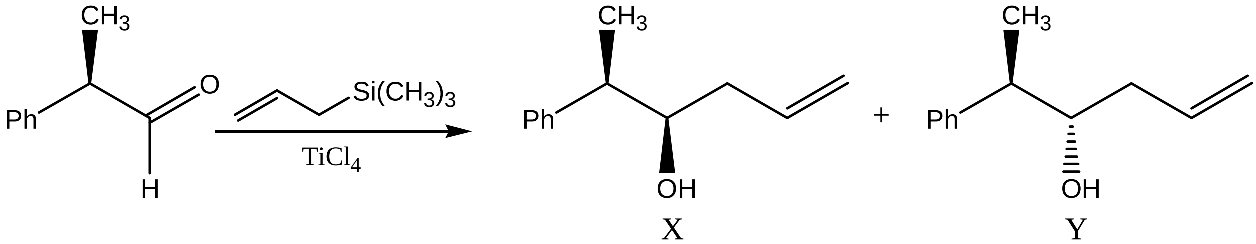
(a) 

(b) 

(c) 

(d) 

55. In the following reaction,



(a) X is the major product and Y is the minor product
(b) X is the only product
(c) Y is the only product
(d) X is the minor product and Y is the major product