Section-A

Q.1 – Q.25 : Carry ONE mark each.

1. The point group symmetry of $CH_2 = C = CH_2$ is:
(a) D_{2h} (b) C_{2h} (c) C_{2v} (d) D_{2d}

2. Two trial wave function $\phi = c_1 x(a-x)$ and $\phi_2 = c_1 x(a-x) + c_2 x^2 (a-x)^2$ give ground state energies E_1 and E_2, respectively, for the microscopic particle in a 1-D box by using the variation method. If the exact ground state energy is E_0, the correct relationship between E_0, E_1 and E_2 is:
(a) $E_0 = E_1 = E_2$ (b) $E_0 < E_1 < E_2$ (c) $E_0 < E_2 < E_1$ (d) $E_0 > E_2 = E_1$

3. The ground state energies of H atom and H_2 molecule are –13.6 eV and –31.7 eV, respectively. The dissociation energy of H_2 is _____ eV.

4. A 2 L vessel containing 2g of H_2 gas at 27ºC is connected to a 2L vessel containing 176 g of CO_2 gas at 27ºC. Assuming ideal behaviour of H_2 and CO_2, the partial pressure of H_2 at equilibrium is _____bar.

5. Consider the reaction, $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ at equilibrium,

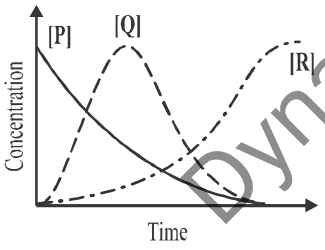
The equilibrium can be shifted towards the forward direction by
(a) Increasing the amount of carbon in the system
(b) Decreasing the volume of the system.
(c) Decreasing the pressure of the system.
(d) Increasing the temperature of the system

6. A sparingly soluble electrolyte M_2X ionizes as $M_2X \rightleftharpoons 2M^{+} + X^{2-}$.

The solubility product (K_{sp}), molal solubility (S) and molal activity coefficient $(\gamma_{\pm})$ are related by

(a) $K_{SP} = S^2\gamma_{\pm}^2$ (b) $K_{SP} = S^3\gamma_{\pm}^3$ (c) $K_{SP} = 4S^3\gamma_{\pm}^2$ (d) $K_{SP} = 4S^3\gamma_{\pm}^3$

7. For the first order consecutive reaction, $P \rightarrow Q \rightarrow R$, under steady state approximation to [Q], the variation of [P], [Q] and [R] with time are best reprsented by

(a)


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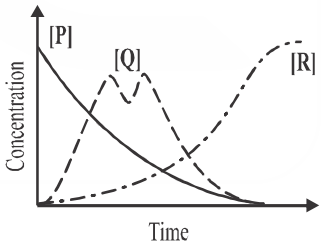

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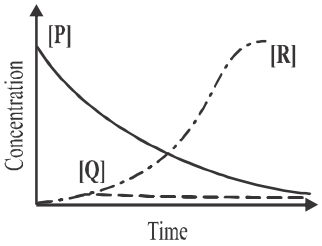

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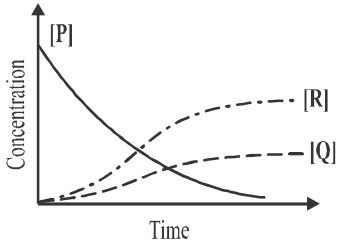


8. At 273 K and 10 bar, the langmuir adsorption of a gas on a solid surface gave the fraction of surface coverage as 0.01. The Langmuir adsorption isotherm constant is _____ bar^{-1}.

9. Conversion of boron trifluoride to tetrafluoroborate accompanies
(a) Increase in symmetry and bond elongation
(b) Increase in symmetry and bond contraction
(c) Decrease in symmetry and bond contraction
(d) Decrease in symmetry and bond elongation.

10. The correct statement with respect to the bonding of the ligands, Me_3N and Me_3P with the metal ions Be^{2+} and Pd^{2+} is,
(a) The ligands bind equally strong with both the metal ions as they are dicationic.
(b) The ligands bind equally strong with both the metal ions as both the ligands are pyramidal.
(c) The binding is stronger for Me_3N with Be^{2+} and Me_3P with Pd^{2+}.
(d) The binding is stronger for Me_3N with Pd^{2+} and Me_3P with Be^{2+}.

11. A crystal has the lattice parameters $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^o$. The crystal system is
(a) Tetragonal (b) Monoclinic (c) Cubic (d) Orthorhombic

12. The by-product formed in the characteristic reaction of $(CO)_5 Cr = C(OMe)(Me)$ with $MeNH_2$ is
(a) CO (b) MeOH (c) MeCHO (d) $MeCONH_2$.

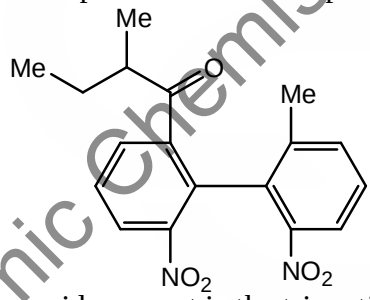
13. The catalyst and co-catalyst used in Wacker process, respectively, are
(a) $PdCl_2$ and Cu (b) $CuCl_2$ and $[PdCl_4]^{2-}$
(c) Pd and CuCl (d) $[PdCl_4]^{2-}$ and $CuCl_2$.

14. Oxymyoglobin $Mb(O_2)$ and oxhyhemoglobin $Hb(O_2)_4$, respectively, are
(a) Paramagnetic and paramagnetic (b) Diamagnetic and diamagnetic
(c) Paramagnetic and diamagnetic (d) Diamagnetic and paramagnetic.

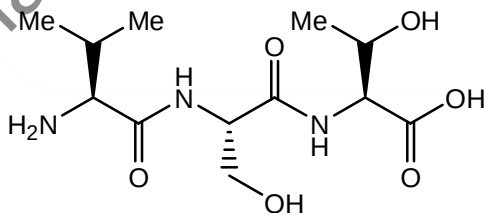
15. Hapticity of cycloheptatriene in $Mo(C_7H_8)(CO_3)$ is _____

16. The number of oxygen molecule(s) that a molecule of hemerythrin can transport is _____

17. The maximum number of stereoisomers possible for the compound given below is _____



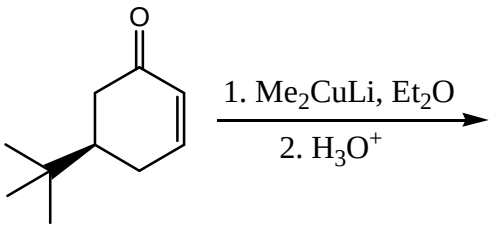
18. The correct sequence of the amino acids present in the tripeptide given below is

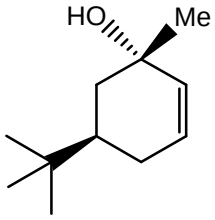


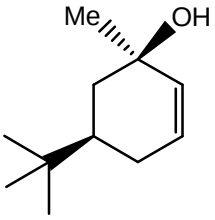
(a) Val-Ser-Thr (b) Val-Thr-Ser (c) Leu-Ser-Thr (d) Leu-Thr-Ser

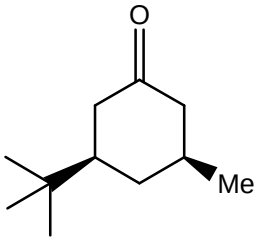
19. Among the compounds given in the options (a)–(d), the one that can be used as a formyl anion equivalent (in the presence of a strong base) is:
(a) ethylene (b) nitroethane (c) 1, 3-dithiane (d) 1, 4-dithiane

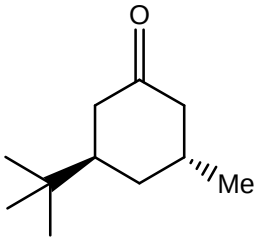
20. The major product formed in the reaction given below is:



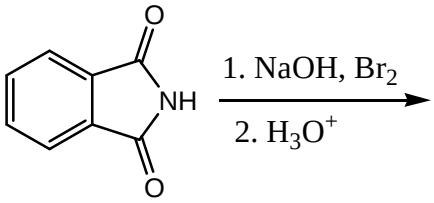
(a) 

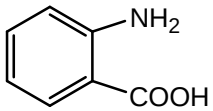
(b) 

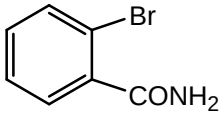
(c) 

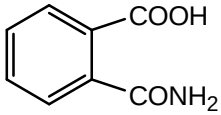
(d) 

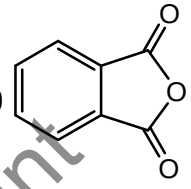
21. The major product formed in the reaction given below is



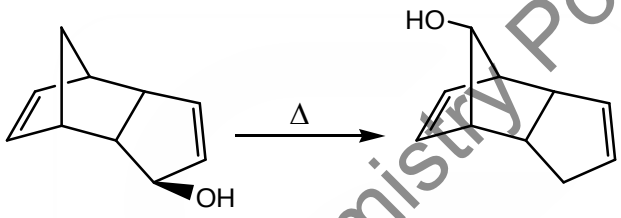
(a) 

(b) 

(c) 

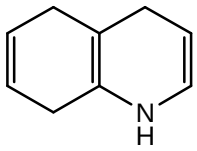
(d) 

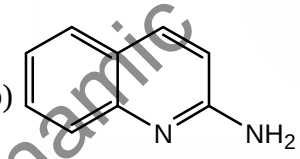
22. The pericyclic reaction given below is an example of

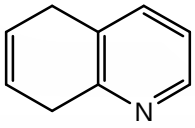


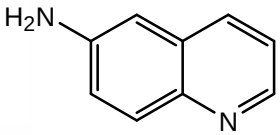
(a) [1, 3]-sigmatropic shift (b) [1, 5]-sigmatropic shift
(c) [3, 5]-sigmatropic shift (d) [3, 3]-sigmatropic shift.

23. The major product formed in the reaction of quinoline with potassium amide (KNH_2) in liquid ammonia is:

(a) 

(b) 

(c) 

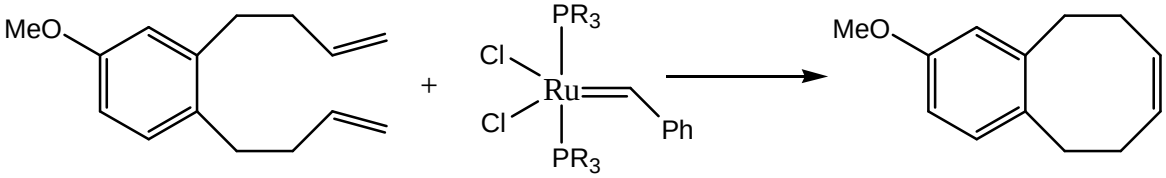
(d) 

24. The number of signals that appear in the proton decoupled ^{13}C NMR spectrum of benzonitrile (C_7H_5N) is _____

25. Among the compounds given in the option (a) to (d), the one that exhibits a sharp band at around 3300 cm^{-1} in the IR spectrum is:
(a) 1, 2-butadiene (b) 1, 3-butadiene (c) 1-butyne (d) 2-butyne

Q.26 – Q.55 : Carry TWO marks each.

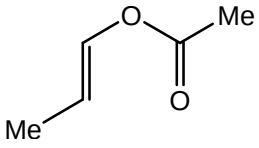
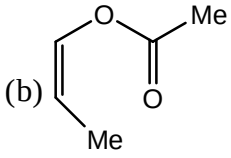
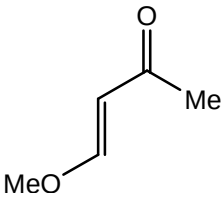
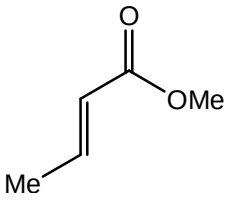
26. In the metathesis reaction given below, 4.32 g of the compound X was treated with 822 mg of the catalyst Y to yield 2.63 g of the product Z. The mol% of the catalyst Y used in this reaction is _____
[Atomic weights of Ru = 101; P = 31; Cl = 35.5]



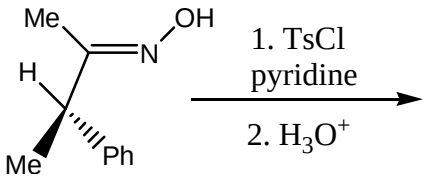
X **Y** **Z**

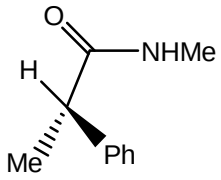
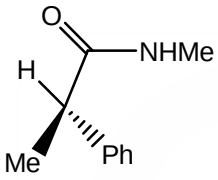
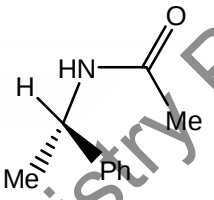
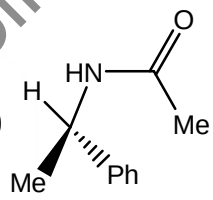
(R=cyclohexyl)

27. An organic compound **Q** exhibited the following spectral data:
IR: 1760 cm^{-1}
^{1}H NMR : δ (ppm) : 7.2 (1H, d, J = 16.0 Hz), 5.1 (1H, m), 2.1 (3H, s), 1.8(3H, d, J = 7.0 Hz)
^{13}C NMR : δ (ppm); 170 (carbonyl carbon),
Compound **Q** is

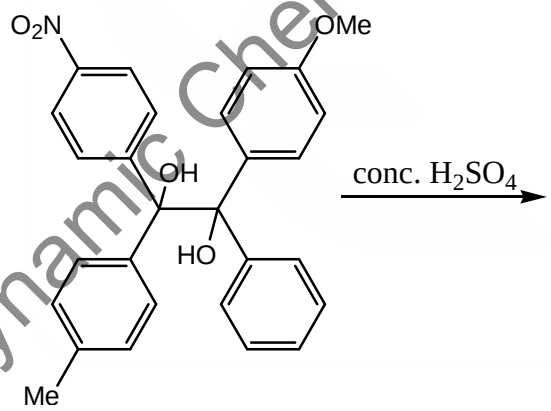
(a) 
(b) 
(c) 
(d) 

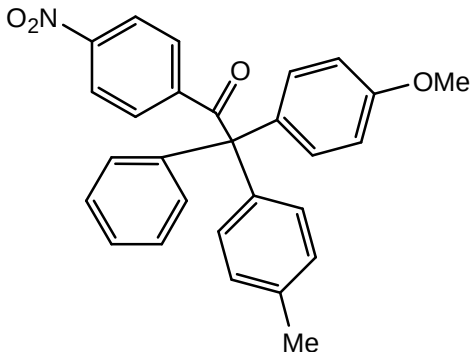
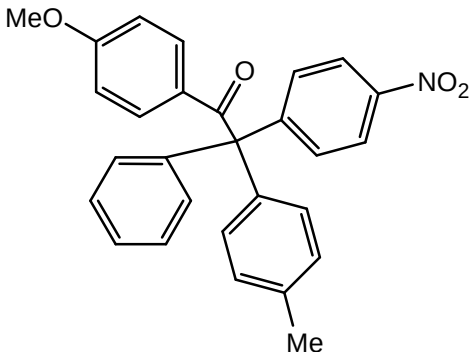
28. The major product formed in the Beckmann rearrangement of the compound given below is:

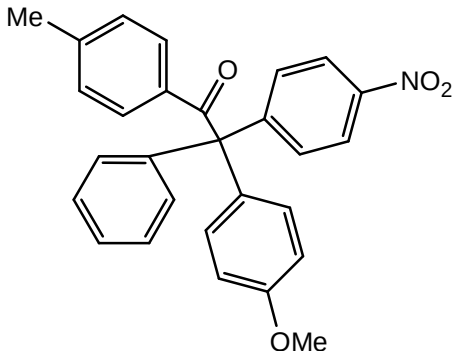


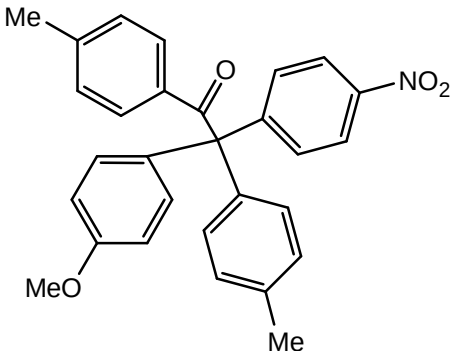
(a) 
(b) 
(c) 
(d) 

29. The major product formed in the reaction given below is

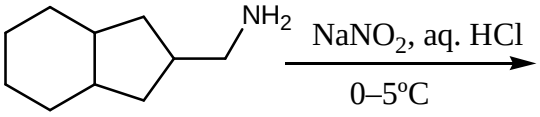


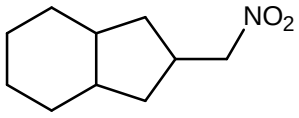
(a) 
(b) 

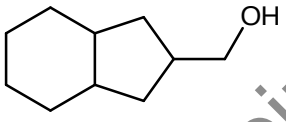
(c) 

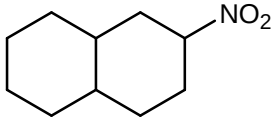
(d) 

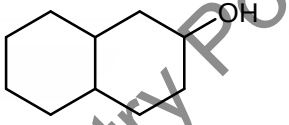
30. The major product formed in the reaction given below is



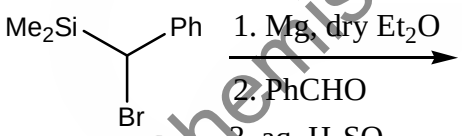
(a) 

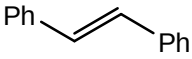
(b) 

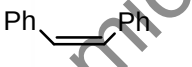
(c) 

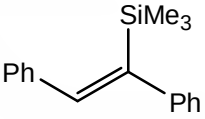
(d) 

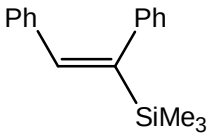
31. The major product(s) fromed in the reaction sequence given below is/are

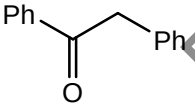


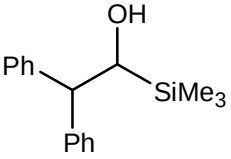
(a) 

and 

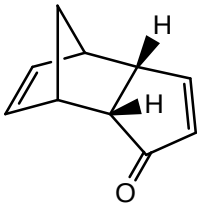
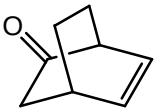
(b) 

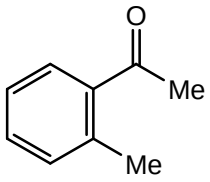
and 

(c) 

(d) 

32. Match the compounds in the **Column-I** with photochemical reactions that they can undergo given in the **Column-II:**

Column-I	Column-II
(i) 	(p) oxa-di-π-methane rearrangement
(ii) 	(q) Paterno-Buchi reaction

(iii) 

(r) intramolecular [2+2]-cycloaddition.

(a) (i)-(q); (ii)-(s); (iii)-(p) (b) (i)-(r); (ii)-(p); (iii)-(s)
(c) (i)-(p); (ii)-(r); (iii)-(q) (d) (i)-(r); (ii)-(q); (iii)-(s)

33. e^{-2x^2} is an eigen function of the operator $\left(\frac{d^2}{dx^2}-16x^2\right)$. The corresponding eigen value is

(a) +4 (b) –4 (c) +2 (d) –2

34. The infrared spectrum of HCl gas shows an absorption band centered at 2885 cm^{-1}. The zero point energy of HCl molecule under hamonic oscillator approximation is:
(a) 2.8665×10^{-22} J (b) 2.8665×10^{-20} J
(c) 5.7330×10^{-22} J (d) 5.7330×10^{-20} J

35. For the reaction $X_2O_4(\ell) \rightarrow 2XO_2(g)$ at 298K, given the values,

given the values, $\Delta U = 9kJ$ and $\Delta S = 84\ J\ K^{-1}$, ΔG is
(a) –11.08 kJ (b) +11.08 kJ (c) –13.55 kJ (d) +13.55 kJ

36. The change in enthalpy when 3 mol of liquid benzene transforms to the vapour state at its boiling temperature (80°C) and at 1 bar pressure is _____kJ.

37. The moment of inertia of a homonuclear diatomic molecule is 7.5×10^{-45} kg m^2. Its rotational partition function at 500 K is _____

38. For a reaction of the type $X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Y$, the correct rate expression is ($[X]_0$ and $[X]$ corresponds to the concentration of X at time t = 0 and t = t, respectively)

(a) $-\frac{d[X]}{dt} = k_1[X]_0 - (k_1+k_2)[X]$ (b) $-\frac{d[X]}{dt} = (k_1+k_2)[X] - k_2[X]_0$

(c) $-\frac{d[X]}{dt} = (k_1+k_2)[X]_0 - k_1[X]$ (d) $-\frac{d[X]}{dt} = (k_1-k_2)[X] - k_1[X]_0$

39. The temperature dependence of partition are as follows:

$q_{translation} \propto T^{3/2}$ $q_{vibration} \propto T^0$

$q_{rotation} \propto T\,(\text{linear molecule})$ $q_{rotation} \propto T^{3/2}\,(\text{non}-\text{linear molecule})$

According to the Conventional Transition State Theory (CTST), the temperature dependence of the Arrhenius pre-exponential factor for a reaction of the type given below is

linear molecule + linear molecule $\rightleftharpoons$ non-liner linear transition state $\longrightarrow$ products.

(a) T^{-1} (b) T^0 (c) T^1 (d) T^2.

40. Decarbonylation reaction of [cis-$(CH_3CO)Mn(^{13}CO)(CO)_4$] yields X, Y and Z, where
X = [$(CH_3)Mn(CO)_5$]; Y = [cis-$(CH_3)Mn(^{13}CO)CO_4$]; [Z = trans–$(CH_3)Mn(^{13}CO)(CO)_4$]
The molar ratio of the products (X : Y : Z) in this reaction is
(a) 1 : 1 : 1 (b) 1 : 2 : 1 (c) 1 : 1 : 2 (d) 2 : 1 : 1

41. According to polyhedral electron count rule, the structure of $Rh_6(CO)_{16}$ is:
(a) closo (b) nido (c) arachno (d) hypho

42. The increasing order of melting points of the halides NaCl, CuCl and NaF is:
(a) CuCl < NaCl < NaF (b) NaF < NaCl < CuCl
(c) NaF < CuCl < NaCl (d) CuCl < NaF < NaCl

43. The correct electronic configuration and spin only magnetic moment of Gd^{3+} (atomic number 64) are
(a) $[Xe]4f^7$ and 7.9 BM (b) $[Xe]4f^7$ and 8.9 BM
(c) $[Xe]4f^65d^1$ and 7.9 BM (d) $[Rn]5f^7$ and 7.9 BM

44. Among the following octahedral complexes, the one that has the highest enthalpy of hydration is
(a) $[Ca(H_2O)_6]^{2+}$ (b) $[Mn(H_2O)_6]^{2+}$ (c) $[V(H_2O)_6]^{2+}$ (d) $[Cr(H_2O)_6]^{2+}$

45. A metal crystallizes in the face-centered cubic lattice parameter of 4.20Å. The shortest atom to atom contact distance in the lattice is
(a) 4.20 Å (b) 2.97Å (c) 2.42Å (d) 2.10Å

46. Polarographic method of analysis to obtain individual amounts of Cu^{2+} and Cd^{2+} in a given mixture of the two ions (Cu^{2+} and Cd^{2+}) is achieved by measuring their
(a) half-wave potentials (b) migration currents
(c) decomposition potentials (d) diffusion currents

47. The ground state term $[Ni(H_2O)_6]^{2+}$ is:
(a) $^3T_{1g}$ (b) $^3T_{2g}$ (c) $^3A_{2g}$ (d) $^4T_{1g}$

Commond Data Questions:
Commond data for Q.48 and Q.49:
N, N-Dimethylformamide (DMF) gives different patterns of signals for the methyl protons whenits ^1H NMR spectrum is recorded at different temperatures.

48. Match the patterns of the NMR signals given in the **Column-I** with temperatures given in the **Column-II**.

Column-I	**Column-II**
(i) Two singlets, for three protons each, at δ 2.87 and 2.97 ppm	(x) 25ºC
(ii) One sharp singlet for six protons at δ 2.92 ppm	(y) 120ºC
(iii) One broad signal for six protons	(z) 150ºC

(a) (i)-(x); (ii)-(y); (iii)-(z) (b) (i)-(x); (ii)-(z); (iii)-(y)
(c) (i)-(z); (ii)-(x); (iii)-(y) (d) (i)-(z); (ii)-(y); (iii)-(x)

49. Based on the above data, the calculated difference in the frequencies of the two methyl singlets, if the spectrum is recorded on a 300 MHz spectrometer, is _____Hz.

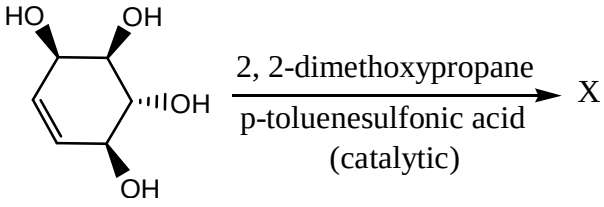
Common data for Q.50 and Q.51:
Heating a mixture of ammonium chloride and sodium tetrahydridoborate gives one liquid product (X), along with other products under ambient conditions.

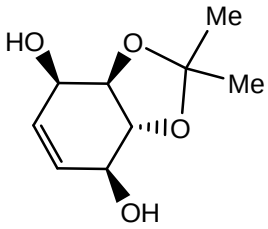
50. Compound X is:
(a) $NH_4[BH_4]$ (b) $[(NH_3)_2BH_2][BH_4]$
(c) $N_3B_3H_6$ (d) $N_3B_3H_{12}$

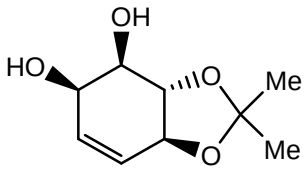
51. Compound X is an example of
(a) Ionic liquid (b) saturated heterocycle
(c) molecular cage (d) unsaturated heterocycle.

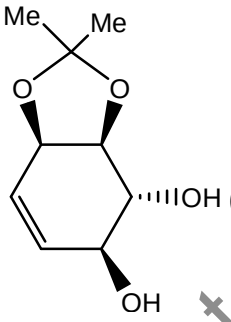
Linked Answer Q.52 and Q.53:

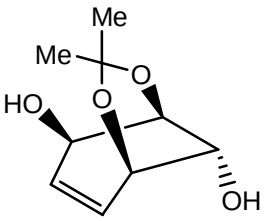
52. The major product X formed in the reaction given below is



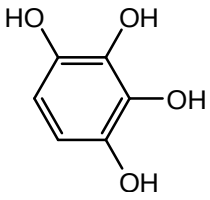
(a) 

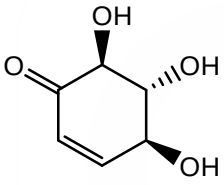
(b) 

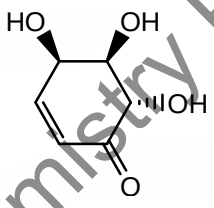
(c) 

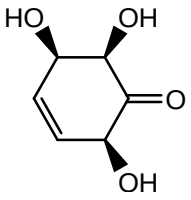
(d) 

53. Oxidation of the product X, obtained in the above reaction, with active manganse dioxide, followed by acidic hydrolysis gives

(a) 

(b) 

(c) 

(d) 

Statement for Linked Answer Q.54 and Q.55:

The standard half-cell reduction potential of Fe^{3+} (aq)|Fe is – 0.036 V and that of OH^- (aq) |$Fe(OH)_3$(s)|Fe is – 0.786 V

54. For the determination of solubility product (K_{SP}) of $Fe(OH)_3$, the appropriate cell representation and its emfare, respectively.

(a) $\langle Fe \mid Fe(OH)_3(s) \mid OH^-(aq) Fe^{3+}(aq) \mid Fe \rangle$, –0.750V

(b) $\langle Fe \mid Fe^{3+}(aq) OH^-(aq) \mid Fe(OH)_3(s) \mid Fe \rangle$, –0.750V

(c) $\langle Fe \mid Fe(OH)_3(s) \mid OH^-(aq) Fe^{3+}(aq) \mid Fe \rangle$, +0.750V

(d) $\langle Fe \mid Fe^{3+}(aq) OH^-(aq) \mid Fe(OH)_3(s) \mid Fe \rangle$, –0.822V

55. The value of $\log_e(K_{SP})$ for $Fe(OH)_3$ at 298 K is

(a) –38.2 (b) +87.6 (c) –96.0 (d) –87.6