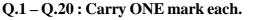
GATE-CY 2007

Section-A

(d) SO_3



- 1. The rate of sulphonation of benzene can be significantly enhanced by the use of
 - (a) a mixture of HNO₃ and H_2SO_4 (b) conc. H_2SO_4

(c) a solution of SO_3 in H_2SO_4

2. The reaction,

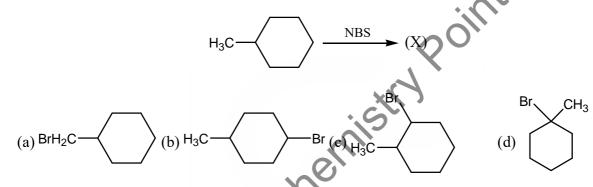
+
$$2Na + 2C_2H_5OH$$
 + $2C_2H_5ONa$

is an example of a

- (a) Birch reduction
- (c) Wolff-Kishner reduction

(b) Clemmenson reduction(d) hydride reduction

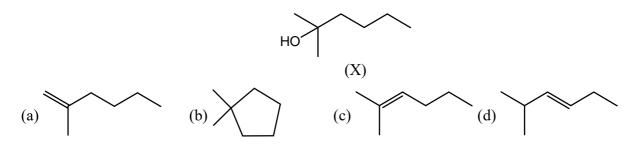
3. The major product (X) of the monobromination reaction is



4. Benzene can not be iodinated with I_2 directly. However, in presence of oxidants such as HNO₃, iodination is possible. The electrophile formed in this case is

(a)
$$\begin{bmatrix} I^+ \end{bmatrix}$$
 (b) I^* (c) $\begin{bmatrix} *\delta & \delta \\ I & OH_2 \end{bmatrix}^+$ (d) $\begin{bmatrix} *\delta & \delta \\ I & OH_2 \end{bmatrix}^+$

- 5. Classify the following species as electrophiles (E) and nucleophiles (N) in routine organic synthesis
- 6. The major product obtained upon treatment of compound X with H_2SO_4 at 80°C is:



7.	BaTi $[Si_3O_9]$ is a cl (a) ortho silicate	ass of (b) cyclic silicate	(c) chain silicate	(d) sheet silicate			
8.	The ground state term fro V^{3+} ion is						
0.	(a) ${}^{3}F$	(b) ${}^{2}F$	(c) ${}^{3}P$	(d) ${}^{2}D$			
9.	In photosynthesis, the predominant metal present in the reaction centre of photosystem II is (a) Zn (b) Cu (c) Mn (d) Fe						
10.	The octahedral comp (a) Triglycinatocobalt (c) Dichlorodiglycina	t (III)	shows both facial and me (b) Tris(etihylenediam (d) Trioxalactocobalt	nine) cobalt(III)			
11.		n carbonic anhydrase is co-ordinated by three histidine and one water molecule. The reaction of CO_2 this enzyme is an example of					
	(a) electrophilic addit (c) nucleophilic addit		(b) electron transfer (d) electrophilic subst	itution			
12.	The difference in the measured and calculated magnetic moment (based on spin-orbit coupling) is obtained for						
	(a) Pm^{3+}	(b) Eu ³⁺	(c) Dy^{3+}	(d) Lu ³⁺			
13.		For a redox reaction, $Cd^{2+} + 2e^{-} \longrightarrow Cd$, the $(E_p)_{anodic}$ observed in cyclic voltametry at hanging mercury					
	drop electrode is -650 mV vs. SCE. The expected value for $(E_p)_{\text{cathodic}}$ is						
	(a)-708 mV	(b) -679 mV	(c) -650 mV	(d)-621 mV			
14.	The dimension of Pla		d T denote mass, length				
	(a) ML^3T^{-2}		(c) $M^2 L^{-1} T^{-1}$	(d) $M^{-1}L^2T^{-2}$			
15.	For a homonuclear diatomic molecule, the bonding molecular orbital is						
	(a) σ_u of lowest energy	rgy	(b) σ_u of second low	vest energy			
(a) σ_u of lowest energy (b) σ_u of second low (c) π_g of lowest energy (d) π_u of lowest energy (d) π_u of lowest energy (e) π_g of lowest energy (f) π_u of lowest energy (h)							
16.	The selection rules for the appearance, of P branch in the rotational-vibrational absorption spectra of a diatomic molecule within rigid rotor-harmonic oscillator model are						
	_		(b) $\Delta v = +1$ and $\Delta J = +1$				
	(c) $\Delta v = +1$ and $\Delta J = -1$		(d) $\Delta v = -1$ and $\Delta J = -1$				
17.	The S_2 operation on a molecule with the axis of rotation as the z axis, moves a nucleus at (x, y, z) to						
	(a) $(-x, -y, x)$	(b) $(x, -y, -z)$	(c) $(-x, y, -z)$	(d) $(-x, -y, -z)$			
18.	The expression which	h represents the chemica	l potential of the i th speci	$ies(\mu_i)$ in a mixture $(i \neq j)$ is:			
	(a) $\left(\partial E / \partial n_i\right)_{s,v,nj}$	(b) $\left(\partial H / \partial n_{i}\right)_{s,v,nj}$	(c) $\left(\partial A / \partial n_{i}\right)_{s,v,nj}$	(d) $\left(\partial G / \partial n_i\right)_{s,v,nj}$			
19.	(a) It increases the ra(b) It is not consumer(c) It provides an alter	ng statements is NOT co te of a reaction d in the course of a react ernate pathway for the re stivation energy of the re	ion				

20.	The value of the rate constant for the gas phase reaction $2NO_2 + F_2 \rightarrow 2NO_2F$ is 38 dm ³ mol ⁻¹ s ⁻¹ at 300K. The order of the reaction is						
	(a) 0 (b) 1	(c) 2	(d) 3				
	Q.21 – Q.75 : Carry TWO marks each.						
21.	Boric acid in aqueous solution in presence of glycerol behaves as a strong acid due to the formation(a) an anionioc metal-chelate(b) borate anion(c) glycerate ion(d) a charge transfer complex						
22.	Match the compounds in List I with the corres List - I	sponding structue / prop List - II	erty given in List II				
	A. $(Ph_3P)_3$ RhCl	(i) Spinel					
	B. LiC ₆	(ii) Intercalation					
	C. PtF_6	(iii) Oxidising agent	×				
	D. Ni ₃ S ₄	(iv) Catalyst for alken					
	(a) A-iii, B-i, C-ii, D-iv(c) A-iii, B-ii, C-i, D-iv	(b) A-iv, B-ii, C-iii, I(d) A-iv, B-iii, C-ii, I					
23.	$W(CO)_6$ reacts with MeLi to give an interme X is represented as		then the CH_2N_2 gives a compound X.				
	(a) WMe ₆	(b) $(CO)_{5}$ W–Me					
	(c) $(CO)_5$ W=C(Me)OMe	(b) $(CO)_5$ W-Me (c) $(CO)_5$ W=CMe					
24.	Considering the quadrupolar nature of	f M-M bond in [Re	$\left[\frac{1}{2} \operatorname{Cl}_{8} \right]^{2-}$, the M-M bond order in				
	$\left[\operatorname{Re}_{2}\operatorname{Cl}_{4}\left(\operatorname{PMe}_{2}\operatorname{Ph}\right)_{4}\right]^{+}$ and $\left[\operatorname{Re}_{2}\operatorname{Cl}_{4}\left(\operatorname{PMe}_{2}\operatorname{Ph}\right)_{4}\right]$ respectively are						
	(a) 3.0 and 3.0 (b) 3.0 and 3.5	(c) 3.5 and 3.5	(d) 3.5 and 3.0				
25.	A student recorded a polarogram of 2.0 mM Cd ²⁺ solution and forgot to add KCl solution. What type of error do you expect in his results? (a) Only migration current will be observed (b) Only diffusion current will be observed (c) both migration current as well as diffusion current will be observed (d) Both catalytic current as well as diffusion current will be observed						
26.	The separation of trivalent lanthanide ions, Lu resion using ammonia o-hydroxy isobutyrate (a) Lu ³⁺ , Yb ³⁺ , Dy ³⁺ , Eu ³⁺ (c) Dy ³⁺ , Yb ³⁺ , Eu ³⁺ , Lu ³⁺	•	n which the ions will be separated is Lu^{3+}				
27.	Arrange the following metal complexes in ord	ε.					
	$\begin{bmatrix} \mathbf{M}_{r}(\mathbf{H},\mathbf{O}) \end{bmatrix}^{2+} \begin{bmatrix} \mathbf{V}(\mathbf{H},\mathbf{O}) \end{bmatrix}^{2+}$	$\begin{bmatrix} \mathbf{N} : (\mathbf{H} \mathbf{O}) \end{bmatrix}^{2+}$	$[T; (II o)]^{2+}$				

$$\begin{bmatrix} Mn(H_2O)_6 \end{bmatrix}^{2+} \qquad \begin{bmatrix} V(H_2O)_6 \end{bmatrix}^{2+} \qquad \begin{bmatrix} Ni(H_2O)_6 \end{bmatrix}^{2+} \qquad \begin{bmatrix} Ti(H_2O)_6 \end{bmatrix}^{2+} \\ (a) P < S < Q < R \qquad (b) P < Q < R < S \qquad (c) Q < P < R < S \qquad (d) S < R < Q < P \\ \end{bmatrix}$$

28. In the complex,
$$\left[N_{12}^{i}(n^{2}-Cp)_{2}(CO)_{2}\right]$$
, the IR stretching frequency appears at 1857 cm⁻¹ (strong) and 1897 cm⁻¹ (weak). The valence electron count and the nature of the M-CO bond respectively are (a) 16 e⁻, bridging (b) 17 e⁻, bridging (c) 18 e⁻, terminal (d) 18 e⁻, bridging.
29. The correct classification of $[B, H_{1}]^{2}$, B, H_{2} and B, H_{1} , respectively is (a) closo, arachno, nido (b) arachno, closo, nido (c) closo, nido, arachno (d) nido, arachno, closo (d) $N = (EtO)_{2} P(S)SH$; $Y = (EtO)_{2} P(C) (b) X = (EtO)_{2} P(S)SH$; $Y = (EtO)_{2} P(S)SH$; $Y = (EtO)_{2} P(S) P(S) = (d) X = (EtO)_{2} P(S) P(S) = (d) X = (EtO)_{2} P(S) P(S) = (d) X = (EtO)_{2} P(S) = (d) X =$

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37. Zeise's salt is represented as

(a)
$$H_2PtCl_6$$
 (b) $[PtCl_4]^{2-}$ (c) $[ZnCl_4]^{2-}$ (d) $[PtCl_3(\eta^2 - C_2H_4)]^{2-}$

38. The catalyst used in the conversion of ethylene to acetaldehyde using Wacker process is

(a)
$$HCo(CO)_4$$
 (b) $[PdCl_4]^{2-}$ (c) V_2O_5 (d) $TiCl_4$ in the presence of $Al(C_2H_5)_3$

39. The temperature of 54 g of water is raised from 15°C to 75°C at constant pressure. The change in the enthalpy of the system (given that $C_{p.m}$ of water =75 JK⁻¹mol⁻¹) is: (a) 4.5 kJ (b) 13.5 kJ (c) 9.0 kJ (d) 18.0 kJ

40. The specific volume of liquid water is 1.001 mL g^{-1} and that of ice is 1.0907 mL g^{-1} at °C. If the heat of fusion of ice at this temperature is 333.88 J g^{-1} , the rate of change of melting point of ice with pressure in deg atm⁻¹ will be (a) -0.0075 (b) 0.0075 (c) 0.075 (d) -0.075

- 41. Given that $E_0(Fe^{3+}, Fe) = -0.04 V$ and $E_0(Fe^{2+}, Fe) = -0.44 V$, the value of $E_0(Fe^{3+}, Fe^{2+})$ is: (a) 0.76 V (b) -0.40 V (c) -0.76 V (d) 0.40 V
- 42. For the reaction $P + Q + R \longrightarrow S$, experimental data for the measured initial rates is given below.

Expt.	Initial conc. P	Initial conc. Q	Initial conc. R	Initial rate
1	(M)	(M)	(M)	(Ms^{-1})
1	0.2	0.5	0.4	8.0×10^{-5}
2	0.4	0.5	0.4	3.2×10^{-4}
3	0.4	2.0	0,4	1.28×10^{-3}
4	0.1	0.25	1.6	4.0×10^{-5}

The order of the reaction with respect to P, Q and R respectively is:

- 43. Sucrose is converted to a mixture of glucose and fructose in a pseudo first order process under alkaline conditions. The reaction has a half life of 28.4 min. The time required for the reduction of a 8.0mM sample of sucrose to 1.0 mM is
 - (a) 56.8 min (b) 170.4 min (c) 85.2 min (d) 227.2 min
- 44. The reaction, $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

proceeds via the following steps

$$\begin{array}{ccc} \text{NO} + \text{NO} & \underline{k_a} & \text{N}_2\text{O}_2 \\ \text{N}_2\text{O}_2 & \underline{k_{a'}} & \text{NO} + \text{NO} \\ \text{N}_2\text{O}_2 + \text{O}_2 & \underline{k_b} & \text{NO}_2 + \text{NO}_2 \end{array}$$

The rate of this reaction is equal to

(a) $2k_{b}[NO][O_{2}]$ (b) $(2k_{a}k_{b}[NO]^{2}[O_{2}])/(k_{a}+k_{b}[O_{2}])$ (c) $2k_{b}[NO]^{2}[O_{2}]$ (d) $k_{a}[NO]^{2}[O_{2}]$

- 45. 40 millimoles of NaOH are added to 100 mL of a 1.2 M HA and Y M NaA buffer resulting in a solution of pH 5.30. Assuming that the volume of the buffer remains unchanged, the pH of the buffer ($K_{HA} = 1.00 \times 10^{-5}$) is
 - (a) 5.30 (b) 5.00 (c) 0.30 (d) 10.30
- 46. The entropy of mixing of 10 moles of helium and 10 moles of oxygen at constant temperature and pressure, assuming both to be ideal gas, is:

(a)
$$115.3 \text{ JK}^{-1}$$
 (b) 5.8 JK^{-1} (c) 382.9 JK^{-1} (d) 230.6 JK^{-1}

47. The ionisation potential of hydrogen atom is 13.6 eV. The first ionistaion potential of a sodium atom, assuming that the energy of its outer electron can be represented by a H-atom like model with an effective nuclear charge of 1.84, is
(a) 46.0 eV
(b) 11.5 eV
(c) 5.1 eV
(d) 2.9 eV

48. The quantum state of a particle moving in a circular path in a plane is given by

$$\Psi_{\rm m}(\phi) = (1/\sqrt{2\pi})e^{im\phi}, m = 0, \pm 1, \pm 2, \dots$$

When a perturbation $H_1 = P \cos \phi$ is applied (P is a constant), what will be the first order correction to the energy of the mth state

(a) 0 (b)
$$P/(2\pi)$$
 (c) $P/(4\pi)$

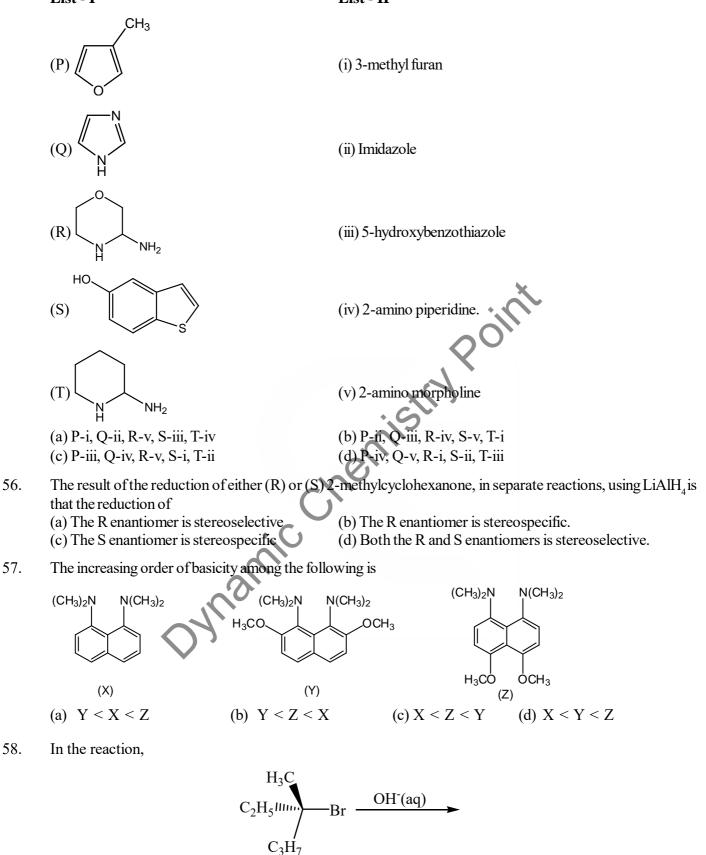
(i) The vibrational energy levels of a real diatomic molecule are equally spaced.

- (ii) At 500K, the reaction $A \rightarrow B$ is spontaneous when $\Delta H = 18.83 \text{ kJ mol}^{-1}$ and $\Delta S = 41.84 \text{ J K}^{-1} \text{mol}^{-1}$. (iii) The process of fluorescence involves transition from a singlet electronic state to another singlet electronic state by absorption of light.
- (iv) When a constant P is added to each of the possible energies of a system, its entropy remains unchanged.
 (a) Only i
 (b) Only ii
 (c) Both i and iii
 (d) Both ii and iv
- 50. Assuming H_2 and HD molecules having equal lengths, the ratio of the rotational partition functions of these molecules, at temperature above 100K is (a) 3/8 (b) 3/4 (c) 1/2 (d) 2/3
- 51. N non-interacting molecules are distributed among three non-degenerate energy levels $\varepsilon_0 = 0, \varepsilon_1 = 1.38 \times 10^{-21} \text{ J}$ and $\varepsilon_2 = 2.76 \times 10^{-21} \text{ J}$, at 100K. If the average total energy of the system at this temperature is $1.38 \times 10^{-18} \text{ J}$, the number of molecules in the system is: (a) 1000 (b) 1503 (c) 2354 (d) 2987
- 53. The rate constants of two reactions at temperature T are $k_1(T)$ and $k_2(T)$ and the corresponding activation energies are E_1 and E_2 with $E_2 > E_1$. When temperature is raised from T_1 and T_2 , which one of the following relations is correct?

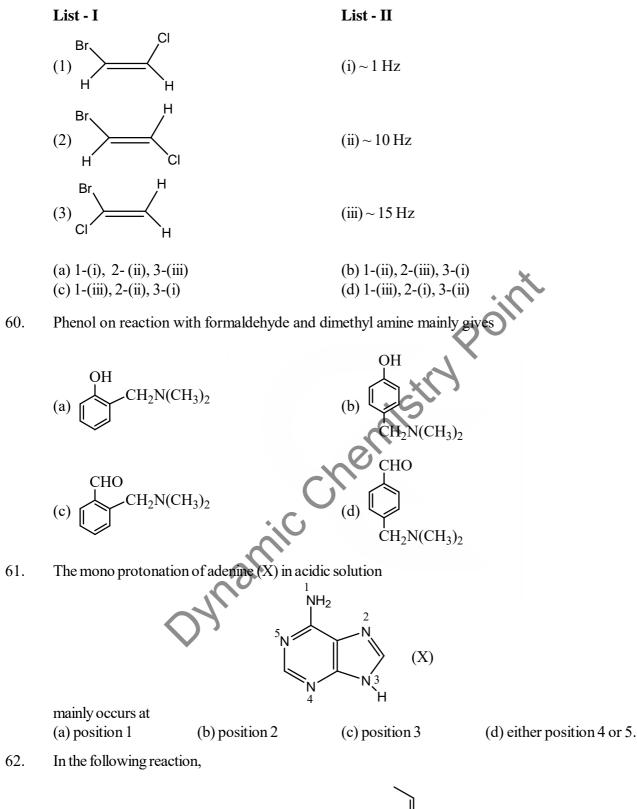
(a)
$$\frac{k_1(T_2)}{k_1(T_1)} = \frac{k_2(T_2)}{k_2(T_1)}$$
 (b) $\frac{k_1(T_2)}{k_1(T_1)} > \frac{k_2(T_2)}{k_2(T_1)}$ (c) $\frac{k_1(T_2)}{k_1(T_1)} \ge \frac{k_2(T_2)}{k_2(T_1)}$ (d) $\frac{k_1(T_2)}{k_1(T_1)} < \frac{k_2(T_2)}{k_2(T_1)}$

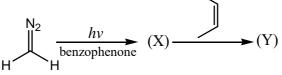
- 54. The number of degrees of freedom for a system consisting of NaCl(s), $Na^+(aq)$ and $Cl^-(aq)$ at equilibrium is
 - (a) 2 (b) 3 (c) 4 (d) 5

55. Match the structures in List - I with their correct names in List - II. List - I List - II



if the concentration of both the reactants is doubled, then the rate of the reaction will (a) remain unchanged (b) quadruple (c) reduce to one fourth (d) double 59. Match the structures in List - I with the coupling constant $\begin{bmatrix} {}^{1}H J(Hz) \end{bmatrix}$ given in List - II



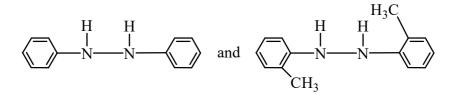


(X) and (Y) respectively are

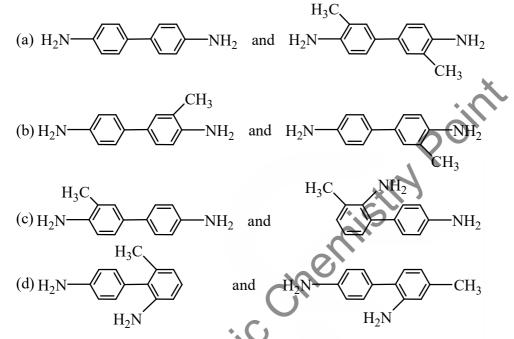
(a) ¹:CH₂ and cis 1, 2-dimethylcyclopropane

- (b) ³:CH₂ and cis 1, 2-dimethylcyclopropane
- (c) 1:CH, and a mixture of cis/trans 1, 2-dimethylcyclopropane
- (d) ³:CH₂ and a mixture of cis/trans 1, 2-dimethylcyclopropane

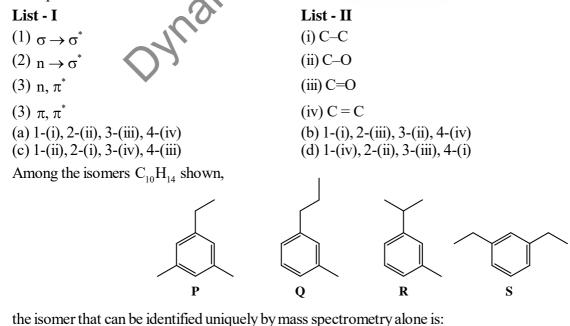
63. The major products obtained upon treating a mixture of



with a strongly acidic solution of H_2SO_4 is



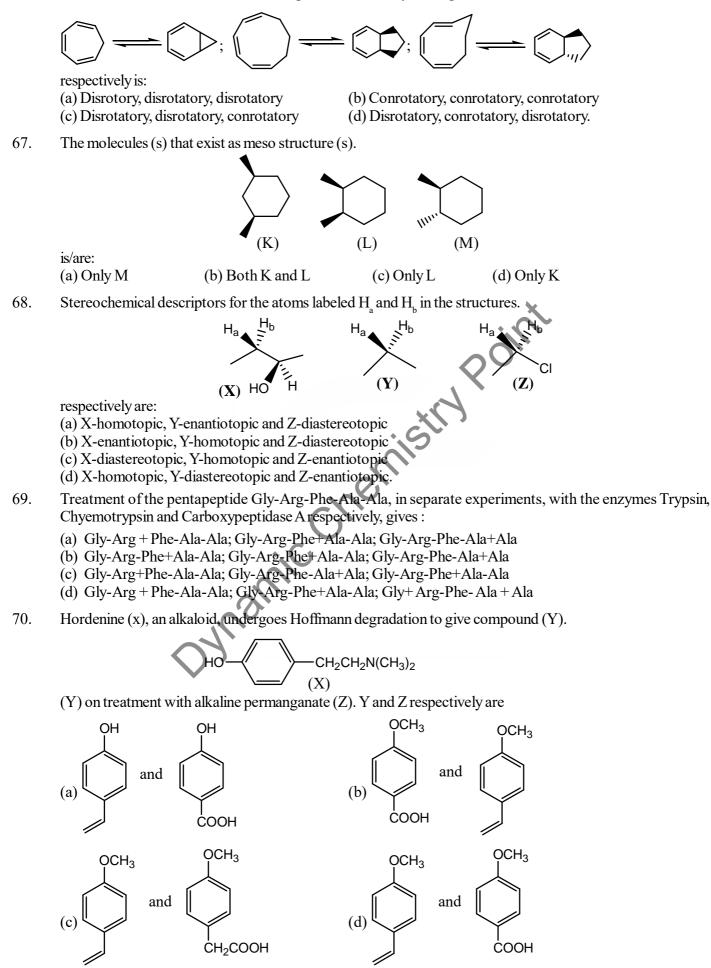
Match the observed pricipal absorptions in the visible spectrum shown in List - I with the bond shows this 64. absorption in List - II.



(d) S (a)P(b) Q (c) R

65.

66. The direction of rotation of the following thermal electrocyclic ring closures.



Common data for Q.71, Q.72, Q.73:

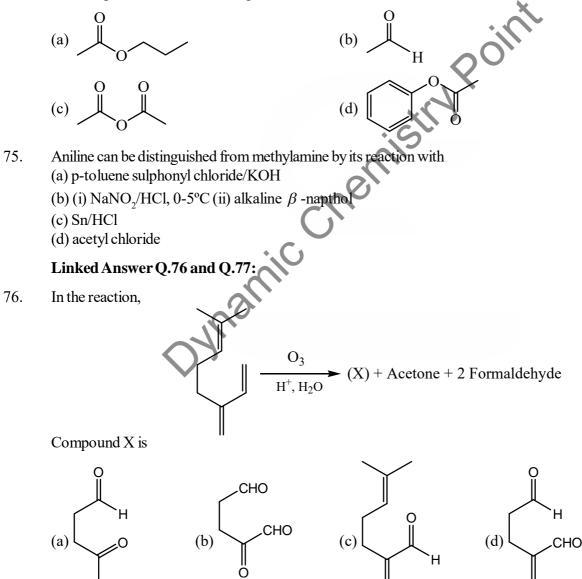
Trans 1, 2-difluoroethylene molecule has a 2-fold rotational axis, a symmetry plane perpendicular to the rotatinal axis and an inversion centre.

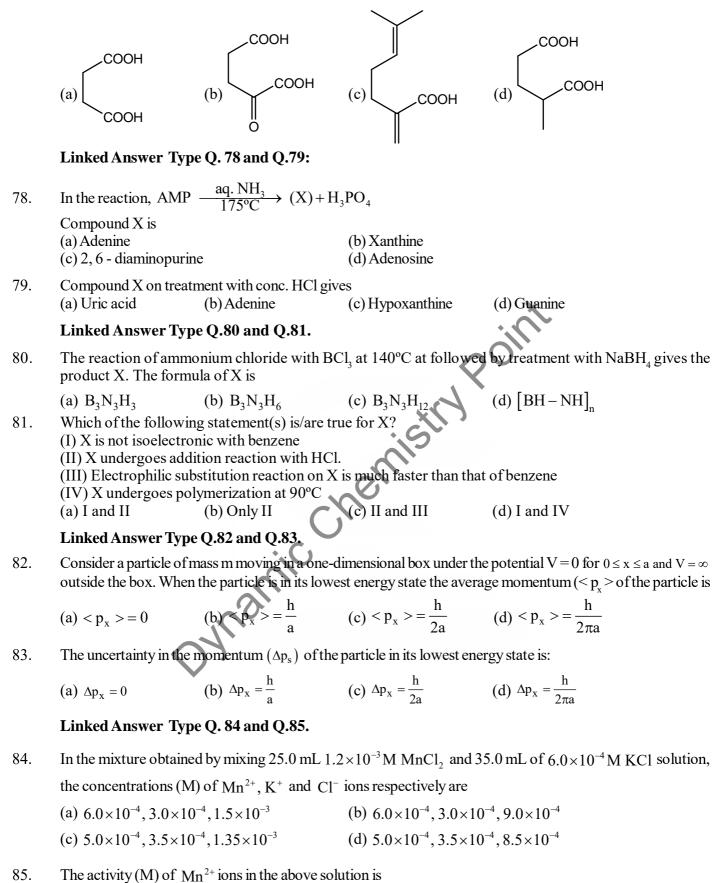
- 71. The number of distinct symmetry operations that can be performed on the molecule is:
 - (a) 2 (b) 4 (c) 6 (d) 8
- 72. The number of irreducible representations of the point group of the molecule is: (a) 1 (b) 2 (c) 3 (d) 4
- 73. If two H atoms of the above molecule are also replaced by F atoms, the point group of the resultant molecule will be
 - (a) C_i (b) C_{2h} (c) C_{2v} (d) D_{2h}

Common Data for Q.74 and Q.75 :

Reactivity of ary1 amines towards electrophilic aromatic substitution is much higher than that of aliphatic amines. Hence differential reactivity of the amino group is desirable in many reactions.

74. The compound which on reacting with aniline will NOT form an acetanilide is





(a) 1.0×10^{-4} (b) 2.0×10^{-4} (c) 3.0×10^{-4} (d) 4.0×10^{-4}