

PAPER : CSIR-UGC-NET/JRF JUNE 2024

CHEMICAL SCIENCES

PART-B

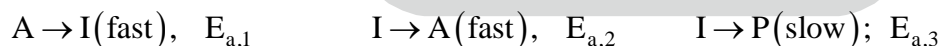
21. The substitution reaction of $[\text{Co}(\text{CN})_5\text{Cl}]^{3-}$ with OH^- to give $[\text{Co}(\text{CN})_5(\text{OH})]^{3-}$ is
- slow and depends on the concentration of both the reactants
 - fast and depends only on the concentration of the Co complex
 - slow and depends only on the concentration of the Co complex
 - fast and depends on the concentration of both the reactants

22. From the data given in the following table,

Ion	OH^-	Cl^-	Br^-	SO_4^{2-}
Ionic mobility ($\times 10^{-8} \text{ m}^2 \text{ S}^{-1} \text{ V}^{-1}$)	20.6	7.9	8.1	8.3

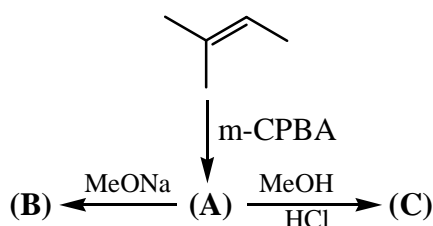
the correct order for an effective radius of the anions in water at 25°C is

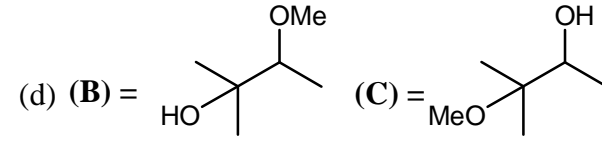
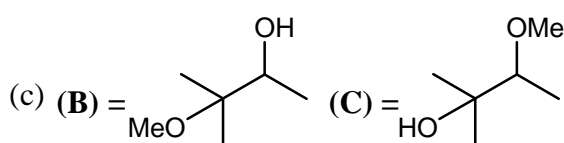
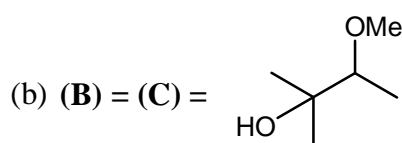
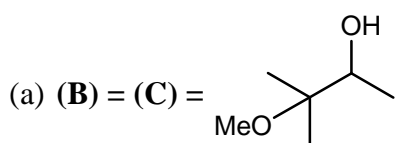
- $\text{OH}^- < \text{SO}_4^{2-} < \text{Br}^- < \text{Cl}^-$
 - $\text{OH}^- > \text{SO}_4^{2-} > \text{Br}^- > \text{Cl}^-$
 - $\text{OH}^- < \text{Cl}^- < \text{Br}^- < \text{SO}_4^{2-}$
 - $\text{OH}^- > \text{Cl}^- > \text{Br}^- > \text{SO}_4^{2-}$
23. The metals in the active site of acetylene hydratase, urease, carboxypeptidase and sulfite oxidase, respectively, are
- Cu, Mo, Ni and Zn
 - W, Ni, Zn and Mo
 - Mo, Ni, Zn and Co
 - W, Co, Mo and Cu
24. The reaction $\text{A} \rightarrow \text{P}$ consists of the following three elementary steps with their respective activation energies.



Activation energy of the overall reaction is

- $E_{a,1} + E_{a,2} + E_{a,3}$
 - $E_{a,1} + E_{a,2} - E_{a,3}$
 - $E_{a,2}$
 - $E_{a,1} - E_{a,2} + E_{a,3}$
25. An isolobal fragment of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$ is
- $\text{Fe}(\text{CO})_4$
 - CH_3^+
 - $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$
 - CH_3
26. The major products B and C formed in the following set of reactions are



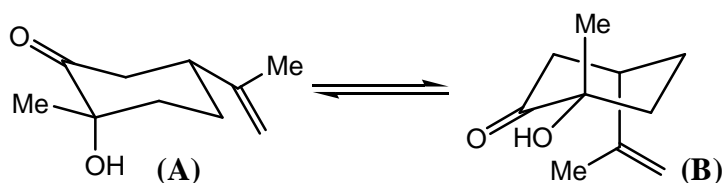


27. The correct statement about the pre-exponential factor in Arrhenius equation is that
- it is dimensionless.
 - it necessarily has s^{-1} in its dimension, regardless of the order of the reaction.
 - it does not necessarily have s^{-1} in its dimension.
 - it has concentration in its dimension, regardless of the order of the reaction.
28. According to Wade's rules, $T_eB_9H_{11}$ is an example of
- closo-borane
 - nido-borane
 - arachno-borane
 - hypho-borane
29. The high kinetic stability of $Cr(\text{norbornyl})_4$ is due to
- the absence of α -hydrogen atom
 - the β -hydride elimination leading to a bridgehead olefin
 - the absence of vacant coordination site on the Cr center
 - agostic interaction of β -C-H with Cr
30. The correct order of the slopes (magnitude) for the p vs T plot of various phase boundaries is
- solid-liquid > solid-vapour > liquid-vapour
 - liquid-vapour > solid-vapour > solid-liquid
 - solid-vapour > solid-liquid > liquid-vapour
 - solid-liquid > liquid-vapour > solid-vapour
31. The oxidation state and formal charge of nitrogen in the product (IR absorption band at 1553 cm^{-1}) of the reaction between butyl bromide and $AgNO_2$, respectively, are
- +3 and 0
 - +3 and +1
 - +5 and 0
 - +5 and +1
32. An ideal gas undergoes isothermal expansion from V_1 to V_2 in two different ways, (i) reversibly and (ii) irreversibly. The correct statement is [notations have their usual meaning]
- $|W_{\text{rev}}| > |W_{\text{irr}}|, |Q_{\text{rev}}| < |Q_{\text{irr}}|$
 - $|W_{\text{rev}}| > |W_{\text{irr}}|, |Q_{\text{rev}}| > |Q_{\text{irr}}|$
 - $|W_{\text{rev}}| < |W_{\text{irr}}|, |Q_{\text{rev}}| < |Q_{\text{irr}}|$
 - $|W_{\text{rev}}| < |W_{\text{irr}}|, |Q_{\text{rev}}| > |Q_{\text{irr}}|$
33. In a proton decoupled ^{13}C NMR of a compound, number of carbons in each signal cannot be calculated from the integration because signal intensities get affected by
- NOE induced by attached protons
 - different relaxation times of different carbons
 - poor isotopic abundance of ^{13}C
- Only ii
 - Both i and iii
 - Both ii and iii
 - Both i and ii

34. An isoelectronic, neutral, linear nitrosyl complex of $[(\eta^5\text{-C}_5\text{H}_5)\text{Cu}(\text{CO})]$ is

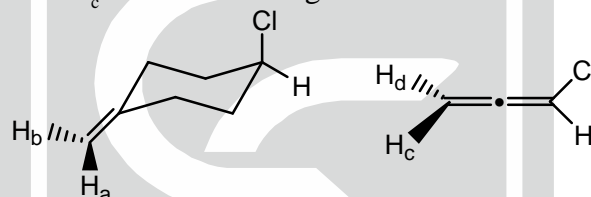
- (a) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{NO})]$ (b) $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2]_2$
 (c) $[\text{Mn}(\text{CO})_3\text{NO}]$ (d) $[\text{Fe}(\text{CO})(\text{NO})_2]$

35. The correct statements about the following conformational equilibrium of ketone are



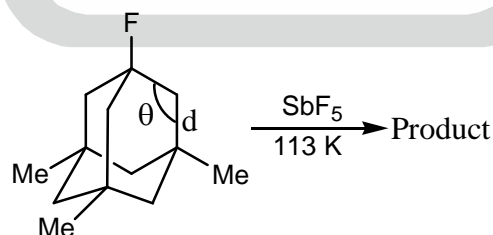
- (I) A predominates in DMSO due to opposing dipole interaction
 (II) B predominates in DMSO due to intramolecular hydrogen bonding
 (III) A predominates in isooctane due to opposing dipole interaction
 (IV) B predominates in isooctane due to intramolecular hydrogen bonding
 (a) I and III (b) I and IV (c) II and III (d) II and IV

36. The correct topicity of H_a and H_c in the following molecules is



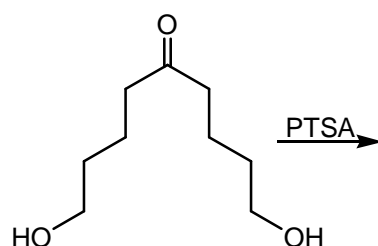
- (a) $\text{H}_a = \text{H}_c = \text{pro-R}$ (b) $\text{H}_a = \text{H}_c = \text{pro-S}$
 (c) $\text{H}_a = \text{pro-R}; \text{H}_c = \text{pro-S}$ (d) $\text{H}_a = \text{pro-S}; \text{H}_c = \text{pro-R}$

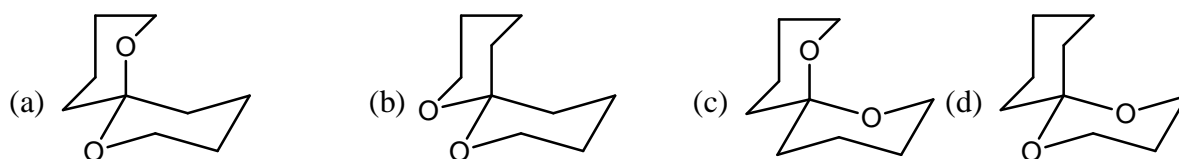
37. The corresponding bond angle (θ) and the bond length (d) of the product, respectively, are



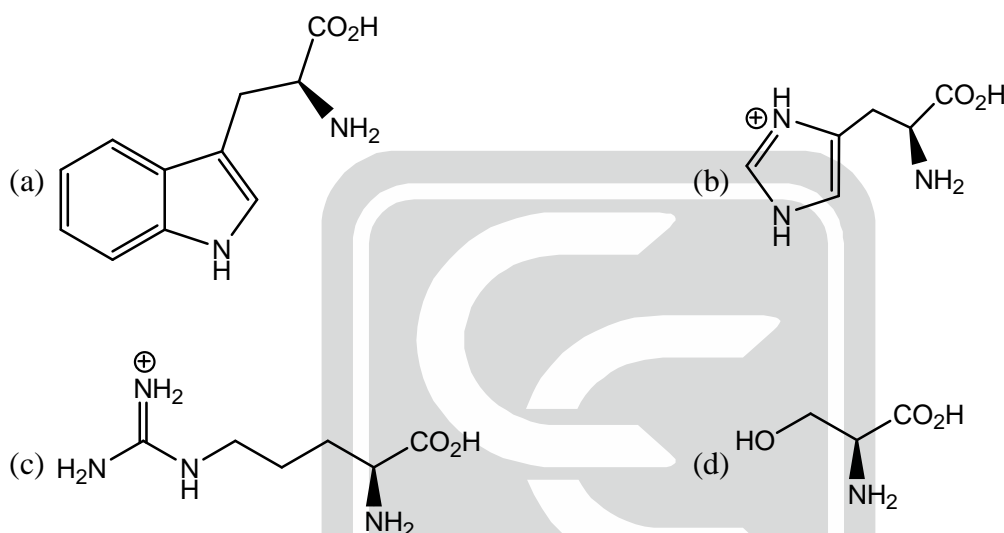
- (a) 100.6° and 1.608 \AA (b) 112.3° and 1.608 \AA
 (c) 100.6° and 1.430 \AA (d) 112.3° and 1.430 \AA

38. The major product formed in the following reaction is



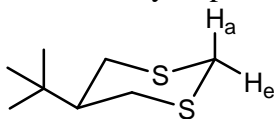


39. The correct statement about Diels-Alder reaction of furan and maleic anhydride is
 (a) the major product is endo and its formation is thermodynamically controlled
 (b) the major product is endo and its formation is kinetically controlled
 (c) the major product is exo and its formation is thermodynamically controlled
 (d) the major product is exo and its formation is kinetically controlled
40. Assuming that the amide backbone of a protein does not play significant role in binding, the amino acid that can effectively recognize HPO_4^{2-} in a protein is



41. Symmetry number of a molecule is defined as the order of rotational subgroup of the molecular point group to which the molecule belongs. The symmetry number of BCl_3 is
 (a) 3 (b) 2 (c) 6 (d) 5
42. Based on Derjaguin, Landau, Verwey and Overbeek (DLVO) theory, the stability of colloids depends on
 (a) only electrical double layer repulsion.
 (b) only van der Waals attraction.
 (c) electrical double layer repulsion and van der Waals attraction.
 (d) electrical double layer and van der Waals attractions.

43. In the following dithiane, the correct statement about acidity of H_a and H_c protons and the reason for the stability of the carbanion formed by deprotonation is

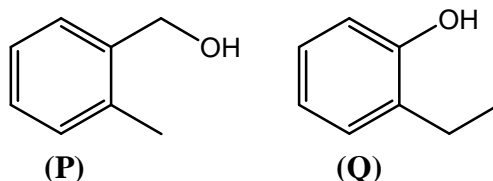


- (a) H_a is more acidic; axial carbanion is delocalised into the σ^* orbital of C-S bond
 (b) H_c is more acidic; equatorial carbanion is delocalised into the σ^* orbital of C-S bond
 (c) H_a is more acidic; axial carbanion is delocalised into the empty 3d orbital of sulfur
 (d) H_c is more acidic; equatorial carbanion is delocalised into the empty 3d orbital of sulfur
44. In the rotational Raman spectrum of a diatomic molecule, the energy gap between the first Stokes and first anti-Stokes lines is
 [B: rotational constant]
 (a) 6B (b) 4B (c) 12B (d) 8B
45. The first reflection in powder X-ray diffraction pattern of a cubic crystal system arises from the plane (111). The Bravais lattice is
 (a) face-centered cubic. (b) body-centered cubic.
 (c) simple cubic. (d) indeterminable due to insufficient data.
46. Consider the following statements regarding ZnS.
 (I) ZnS shows both cubic and hexagonal structures
 (II) Sphalerite exhibits ZnS structure
 (III) ZnS is a semiconductor
 (IV) ZnS can be precipitated from an aqueous acidic solution of zinc salts by passing H_2S
 The option containing the correct statements is
 (a) I, II and III only (b) II and IV only (c) I and III only (d) II, III and IV only
47. The transition(s) giving rise to the yellow sodium D line(s) is/are
 (a) ${}^2P_{3/2} \leftarrow {}^2S_{1/2}$ and ${}^2P_{1/2} \leftarrow {}^2S_{1/2}$ (b) ${}^2D_{3/2} \leftarrow {}^2P_{1/2}$
 (c) ${}^2D_{3/2} \leftarrow {}^2S_{1/2}$ and ${}^2P_{1/2} \leftarrow {}^2S_{1/2}$ (d) ${}^2D_{3/2} \leftarrow {}^2P_{3/2}$ and ${}^2P_{3/2} \leftarrow {}^2S_{1/2}$
48. The reaction given below

$$[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \rightarrow [Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$$
 takes place by the
 (a) inner-sphere mechanism mediated by the CN^- bridge
 (b) outer-sphere mechanism mediated by the CN^- bridge
 (c) inner-sphere mechanism with no net chemical change
 (d) outer-sphere mechanism with no net chemical change
49. The correct order of covalency in the X-F bonds among the following species is
 (a) $SiF_4 < PF_5 < SF_6 < IF_7$ (b) $SiF_4 < PF_5 < IF_7 < SF_6$
 (c) $IF_7 < SF_6 < PF_5 < SiF_4$ (d) $IF_7 < SiF_4 < PF_5 < SF_6$



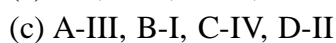
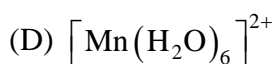
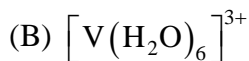
50. The commutator $[x^2, p_x^2]$ is equal to $[x$: position operator, p_x : momentum operator]
- (a) $2xi\hbar$ (b) $2i\hbar$ (c) $4i\hbar$ (d) $2i\hbar(xp_x + p_x x)$
51. In the upper atmosphere, SF_6 undergoes photolysis to form species **A**. Species **A** combines with O_2 giving a radical **B**. The correct statement is
- (a) Unpaired electrons in **A** and **B** are located on sulfur and oxygen atoms, respectively
 (b) Unpaired electrons in **A** and **B** are on sulfur atom only
 (c) Species **A** is diamagnetic
 (d) The hybridization of central atoms in **A** and **B** are different
52. The base peaks (m/z) in the EI mass spectra of compounds P and Q appear, respectively, at



- (a) 91 and 107 (b) 104 and 107 (c) 107 and 104 (d) 107 and 93

53. Match Columns I and II

Column-I



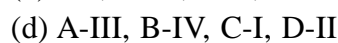
Column-II ($\epsilon, M^{-1}cm^{-1}$)

(I) ~ 500

(II) ~ 0.02

(III) $\sim 10^4$

(IV) ~ 10



54. The mean and variance are equal for

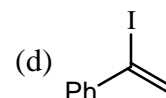
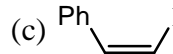
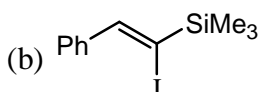
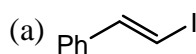
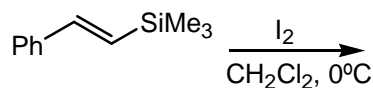
(a) Gaussian distribution

(c) Exponential distribution

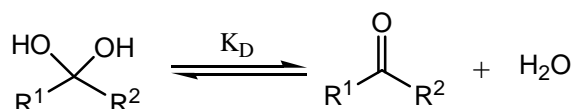
(b) Poisson distribution

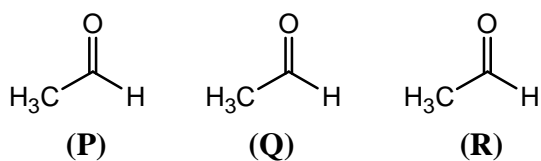
(d) Uniform distribution

55. The major product formed in the following reaction is



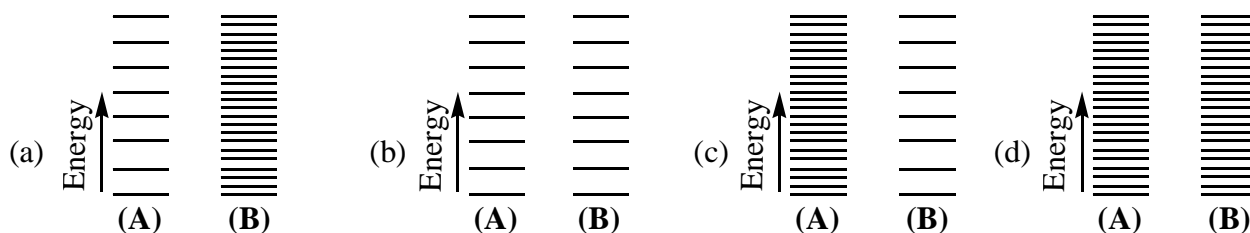
56. The correct order of the dissociation constants for hydrates of the following compounds is



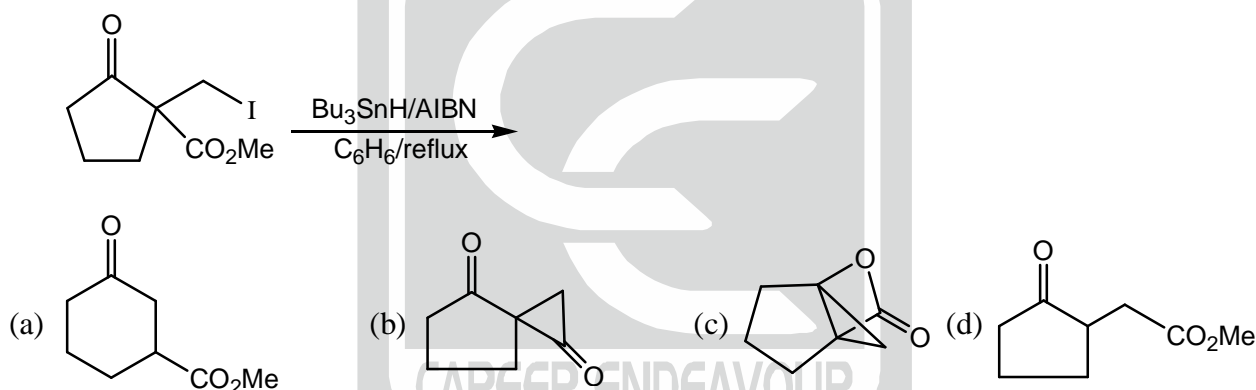


- (a) $R > Q > P$ (b) $R > P > Q$ (c) $Q > R > P$ (d) $P > Q > R$

57. Consider the chemical reaction, $A(g) \rightleftharpoons B(g)$ at a particular temperature with equilibrium constant greater than one. The Schematic energy levels of molecules A and B are given below. The correct option of energy levels, among the following, is



58. The major product formed in the following reaction is



59. The [Re-Re] bond order follows

- (a) $K_2[Re_2Cl_8] > [Re_2Cl_4(PMe_2Ph)_4] > [Re_2Cl_4(PMe_2Ph)_4]Cl$
 (b) $[Re_2Cl_4(PMe_2Ph)_4]Cl > [Re_2Cl_4(PMe_2Ph)_4] > K_2[Re_2Cl_8]$
 (c) $K_2[Re_2Cl_8] > [Re_2Cl_4(PMe_2Ph)_4]Cl > [Re_2Cl_4(PMe_2Ph)_4]$
 (d) $[Re_2Cl_4(PMe_2Ph)_4]Cl > [Re_2Cl_4(PMe_2Ph)_4] > K_2[Re_2Cl_8]$

60. The reaction of $[(\eta^5-C_5H_5)Fe(CH_3)(CO)_2]$ with PPh_3 results in

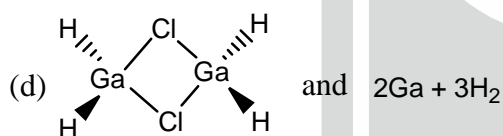
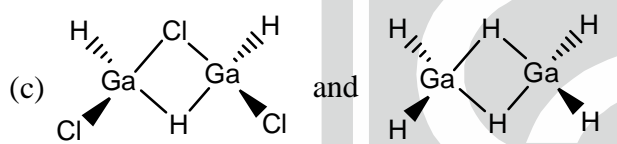
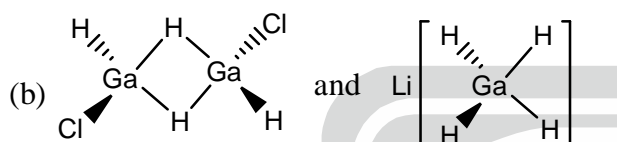
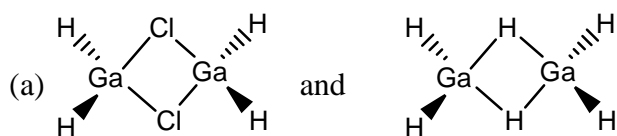
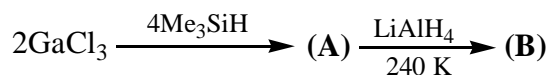
- (a) $[(\eta^5-C_5H_5)Fe(CH_3)(CO)(PPh_3)] + CO$ (b) $[(\eta^5-C_5H_5)Fe(CH_3)(CO)_2(PPh_3)]$
 (c) $[(\eta^5-C_5H_5)Fe(COCH_3)(CO)(PPh_3)]$ (d) $[(\eta^5-C_5H_5)Fe(COCH_3)(PPh_3)] + CO$

PART-C

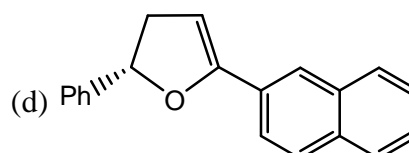
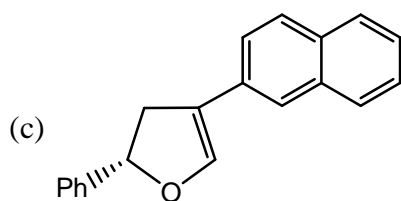
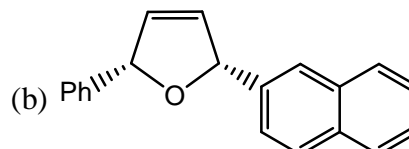
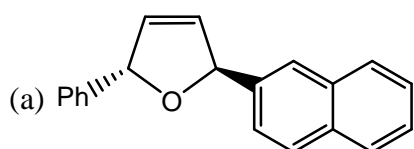
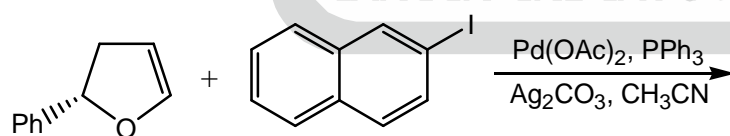
61. At a given temperature, an atom accesses ${}^2S_{1/2}$, ${}^2P_{1/2}$ and ${}^2P_{3/2}$ atomic states with energies $0k_B T$, $0.5k_B T$ and $0.5k_B T$, respectively. The fraction of atoms in the P states is

(a) $\frac{3e^{-0.5}}{1+3e^{-0.5}}$ (b) $\frac{e^{-0.5}}{1+2e^{-0.5}}$ (c) $\frac{e^{-0.5}}{1+4e^{-0.5}}$ (d) $\frac{2e^{-0.5}}{1+2e^{-0.5}}$

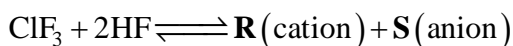
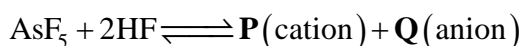
62. In the following reaction, **A** and **B**, respectively, are



63. The major product formed in the following transformation is



64. Consider the following reactions and the related statements:

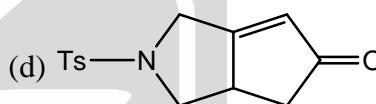
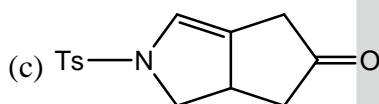
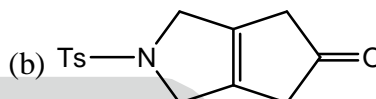
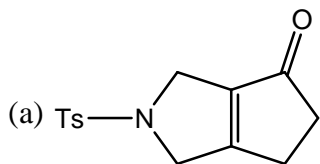
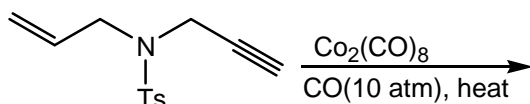


(A) P is bent (B) Q is octahedral (C) R is bent (D) S is linear

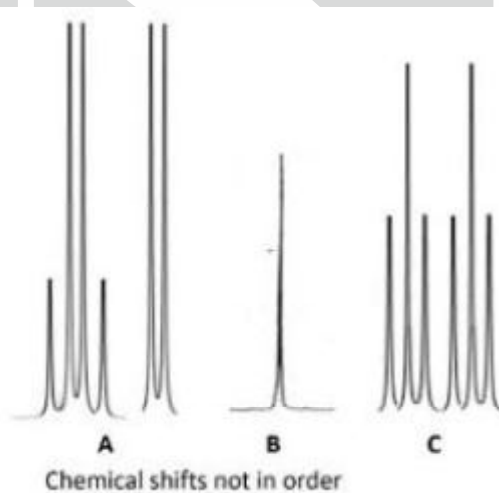
The option containing the correct statement is

(a) A, B, C and D (b) B and C only (c) A, C and D only (d) B and D only

65. The major product formed in the following reaction is



66. Reaction of white phosphorous with sulfur gives a mixture of products A, B and C. The ^{31}P NMR spectral features of the resultant mixture are shown below.



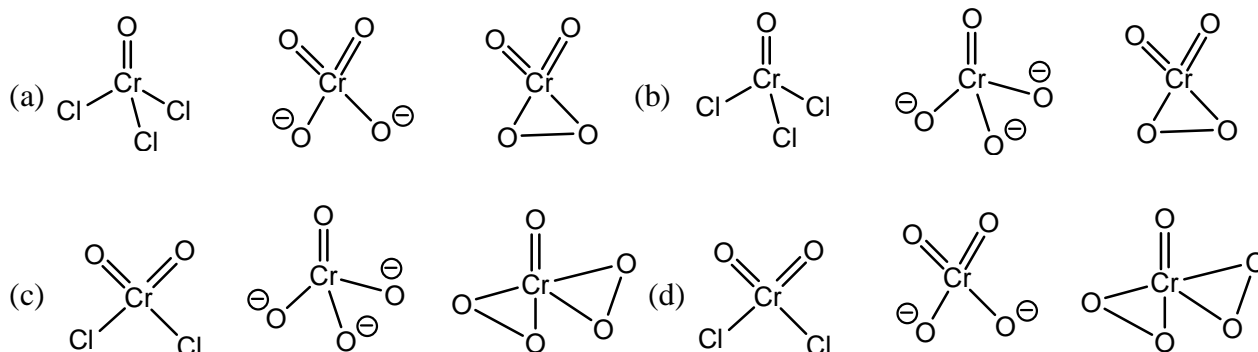
The products A, B and C, respectively, are

- (a) P_4S_3 , P_4S_{10} and P_4S_7 (b) P_4S_7 , P_4S_{10} and P_4
 (c) P_4S_3 , P_4 and P_4S_{10} (d) P_4S_{10} , P_4 and P_4S_7

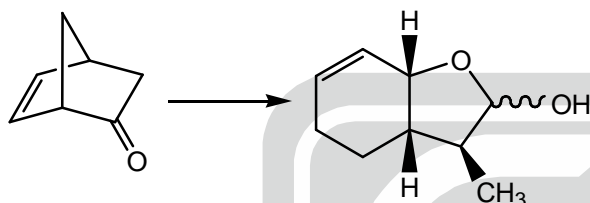


67. Exposing CrO_3 to hydrogen chloride gas gives a red-vapor of compound P. When P is passed through a dilute solution of NaOH it turns yellow due to the formation complex ion Q. Adding acidified H_2O_2 to a solution of Q results in a dark blue compound R.

The option containing the correct structures of P, Q and R, respectively, is



68. The correct sequence of reagents to effect the following transformation is

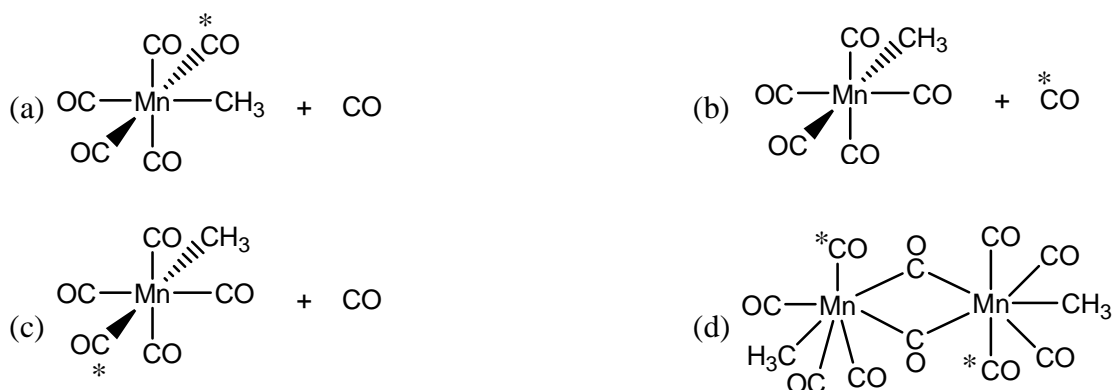


- (a) (i) $\text{CH}_3\text{CO}_3\text{H}$, H^+ then $2\text{N H}_2\text{SO}_4$; (ii) LDA , MeI ; (iii) DIBAL-H , -78°C
 (b) (i) DIBAL-H , -78°C ; (ii) $\text{CH}_3\text{CO}_3\text{H}$, H^+ then $2\text{N H}_2\text{SO}_4$; (iii) LDA , MeI
 (c) (i) $\text{CH}_3\text{CO}_3\text{H}$, H^+ then $2\text{N H}_2\text{SO}_4$; (ii) DIBAL-H , -78°C ; (iii) LDA , MeI
 (d) (i) LDA , MeI ; (ii) DIBAL-H , -78°C ; (iii) $\text{CH}_3\text{CO}_3\text{H}$, H^+ then $2\text{N H}_2\text{SO}_4$

69. In the following reaction,



the product(s) is/are



70. Match the species given in List-I with the appropriate descriptions in List-II

List-I

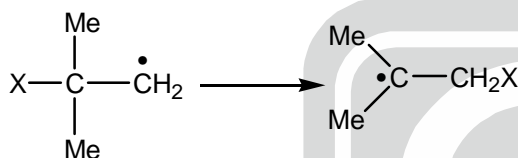
- (A) Al_2Me_6
 (B) LiH
 (C) HF
 (D) CH_3Li

List-II

- (I) 1D-polymeric
 (II) 3c-2e bonds
 (III) 4c-2e bonds
 (IV) Ionic hydride

The correct option is

- (a) A-II, B-IV, C-III, D-I
 (b) A-III, B-I, C-IV, D-II
 (c) A-II, B-IV, C-I, D-III
 (d) A-III, B-II, C-I, D-IV
71. The separation between first two reflection planes of a face-centred cubic crystal is [a is the unit cell length]
 (a) $0.077 a$ (b) $0.77 a$ (c) $0.57 a$ (d) $0.057 a$
72. The correct order of the rate for the following rearrangement that involves a three membered intermediate is

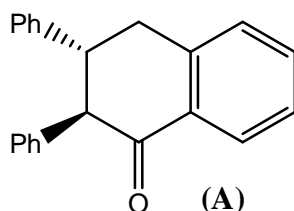


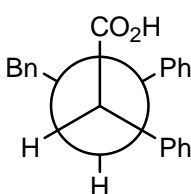
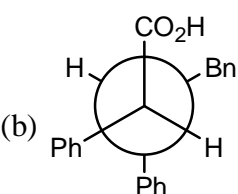
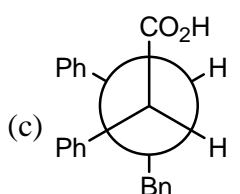
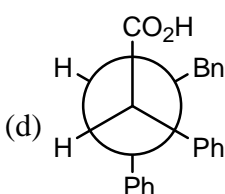
- (P) $\text{X} = -\text{CH}=\text{CH}_2$ (Q) $\text{X} = \text{Me}_3\text{CC}(\text{O})^-$ (R) $\text{X} = -\text{C}\equiv\text{N}$
 (a) $\text{P} > \text{Q} > \text{R}$ (b) $\text{R} > \text{P} > \text{Q}$ (c) $\text{Q} > \text{P} > \text{R}$ (d) $\text{P} > \text{R} > \text{Q}$
73. The rate constant (k_{CT}) of a bimolecular reaction according to collision theory is given by

$$k_{\text{CT}} = N_A \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} \sigma e^{-E_0/RT}$$

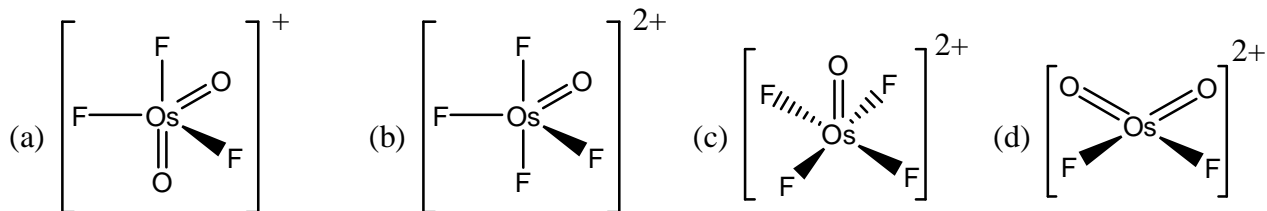
E_0 is related to activation energy (E_a) of the Arrhenius equation as

- (a) $E_0 = \frac{RT}{2} + E_a$ (b) $E_a = RT + \frac{1}{2}E_0$ (c) $E_0 = RT + \frac{1}{2}E_a$ (d) $E_a = \frac{RT}{2} + E_0$
74. The conformer of threo-2, 3-4-triphenylbutyric acid that gives the product A in the presence of anhydrous HF is



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

75. Consider a 0.3 M solution of *cis*-OsO₂F₄ in neat SbF₅. The ¹⁹F NMR spectrum of the Os containing species in this solution shows a doublet and a triplet at 122.4 ppm and 129.5 ppm, respectively. The Os species generated as



76. Two moles of calcium phosphate on reduction with carbon in the presence of silica resulted in the formation of a phosphorus compound X in 90% yield. The weight of X is (Atomic weight, Ca 40, P 31, Si 28, O 16, C 12, H 1)

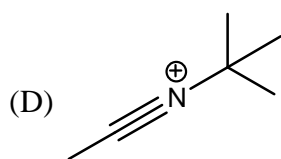
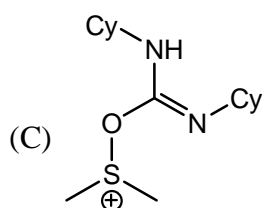
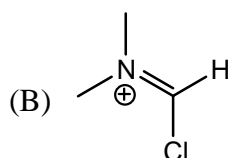
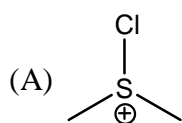
(a) 124 g (b) 111.6 g (c) 255.6 (d) 198 g

77. During the growth of semiconductor nanoparticles, the fluorescence changes with time as

(a) blue → violet → green → red (b) red → green → violet → blue
(c) violet → blue → green → red (d) blue → red → violet → green

78. The correct match for the intermediates given in Column P with the reactions given in Column Q is

Column P



Column Q

(I) Pfitzner-Moffatt oxidation

(II) Vilsmeier-Haack reaction

(III) Ritter reaction

(IV) Swern oxidation

(a) A-IV, B-III, C-I, D-II
(c) A-I, B-III, C-IV, D-II

(b) A-III, B-II, C-I, D-IV
(d) A-IV, B-II, C-I, D-III

79. For elements P, Q, R and S, the corresponding valenceis and average orbital energies are listed below.

Element	Valency	Average Valence Orbital Energy (eV)
P	i	-19
Q	j	-22.5
R	k	-9
S	l	-7

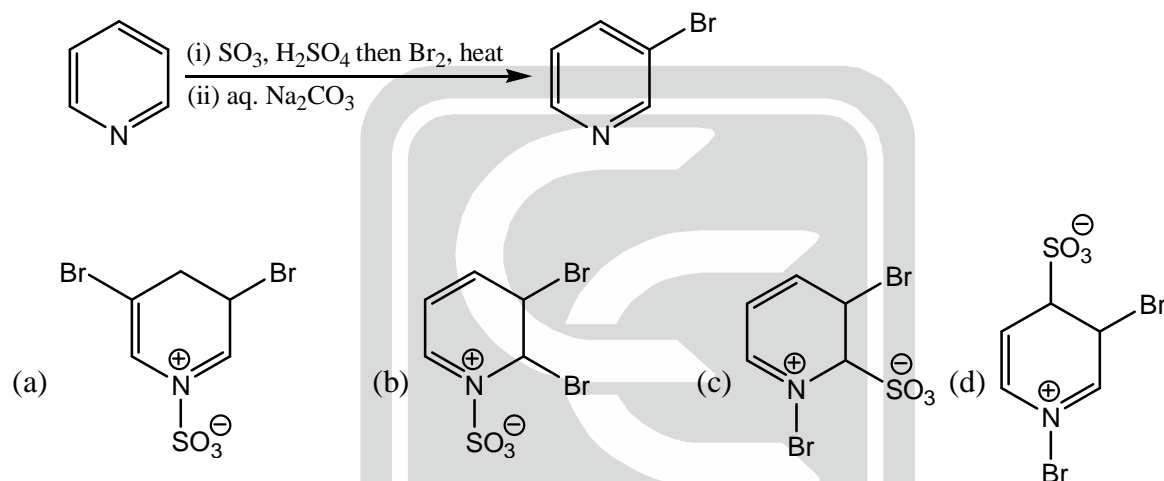
Based on the Van-Arkel diagram, the correct option from the following

- (A) S_jQ_l is covalent (B) P_kR_i is ionic
 (C) R_lS_k is metallic (D) P_jQ_i is covalent

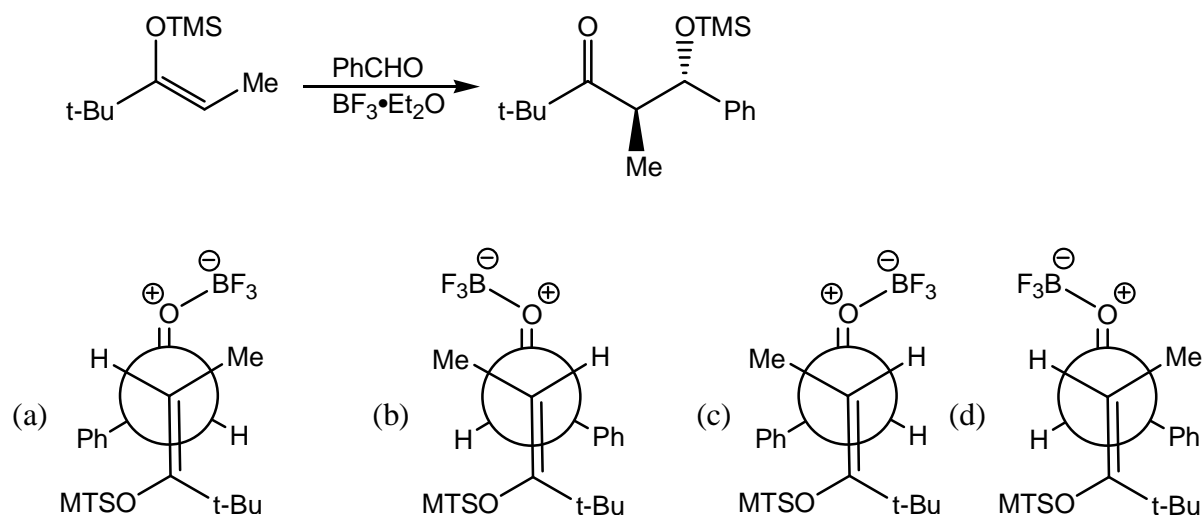
is

- (a) A, B and C only (b) A, C and D only (c) B, C and D only (d) B and D only

80. The intermediate involved in the following reaction is

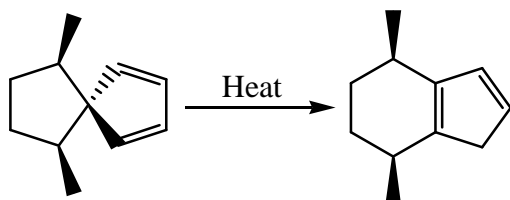


81. The transition state arrangement that explains the stereochemistry of the product in the following reaction is

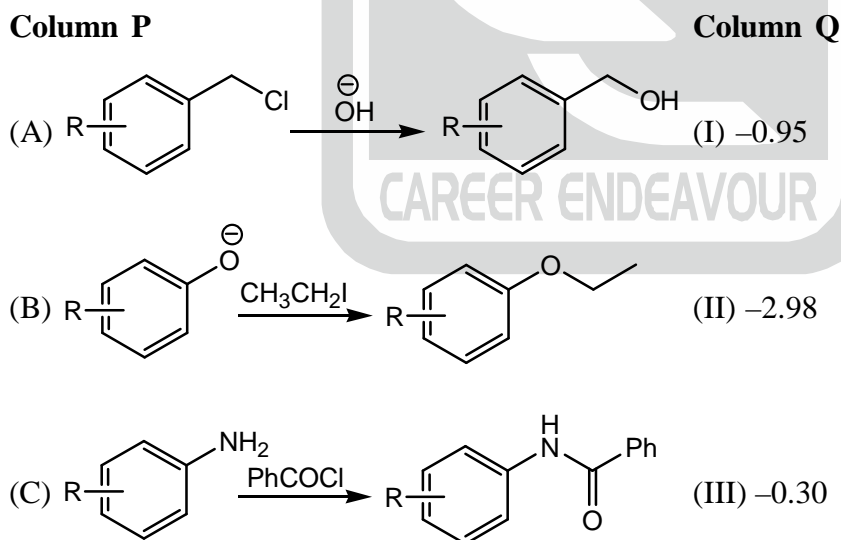


82. The β -activity of 0.9 g of carbon from the wood of a present-day tree is 0.25 Bq. If the activity of 0.9 g carbon isolated from the wood of an ancient artifact is 0.19 Bq under the same conditions (^{14}C : $t_{1/2} = 5730$ years), the age of the ancient artifact is
 (a) 4010 years (b) 3000 years (c) 2268 years (d) 5573 years

83. The correct statement about the following transformation is

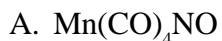


- (a) [1,5]-carbon shift with inversion and [1,5]-hydrogen shift with retention
 (b) both [1,5]-carbon shift and [1,5]-hydrogen shift with inversion
 (c) [1,5]-carbon shift with retention and [1,5]-hydrogen shift with inversion
 (d) both [1,5]-carbon shift and [1,5]-hydrogen shift with retention
84. A vanadium compound **X** is obtained by heating NH_4VO_3 . **X** reacts with dil. HCl to form another vanadium compound **Y** along with chlorine gas. **Y** is
 (a) VCl_3 (b) VCl_5 (c) VOCl_2 (d) VOCl_3
85. The correct match for the reaction given in Column **P** with the Hammett reaction constant (ρ) given in Column **Q** is



- (a) A-I, B-II, C-III (b) A-III, B-I, C-II (c) A-III, B-II, C-I (d) A-II, B-III, C-I

86. From the following 18-electron complex(es), identify those which predominantly undergoes/undergo substitution reaction by $\text{P}(\text{OMe})_3$ via an associative mechanism.



The correct option is

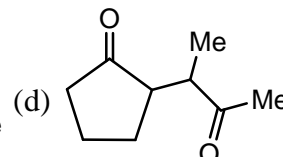
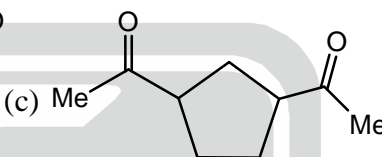
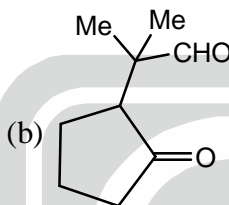
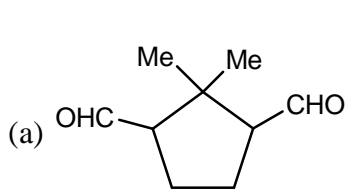
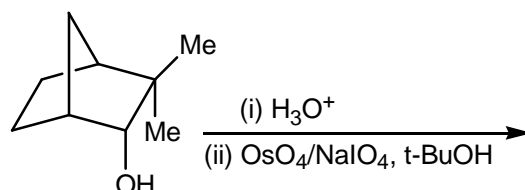
(a) A, B and C only

(b) A only

(c) A and D only

(d) B and D only

87. The major product formed in the following sequence of reactions is



88. The symmetry of the first excited state of one of the normal modes in NH_3 is E. Based on the character table for the C_{3v} point group given below, the symmetry of the second excited state for this mode in terms of the irreducible representations is

C_{3v}	E	2C_3	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

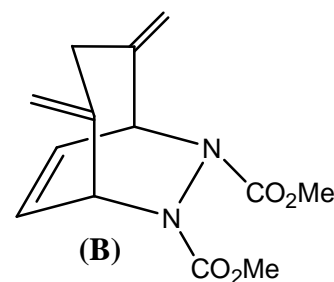
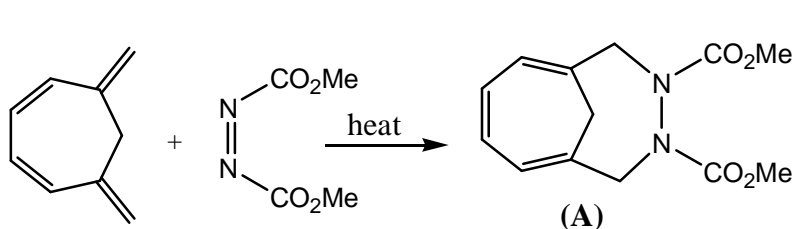
(a) $2\text{A}_2 + \text{E}$

(b) $2\text{A}_1 + \text{E}$

(c) $\text{A}_1 + \text{A}_2 + \text{E}$

(d) $2\text{A}_1 + 2\text{A}_2$

89. The major cycloaddition product (A or B) formed and the orbital interactions involved in the following transformation, respectively are



(a) A and $8\pi_s + 2\pi_s$

(b) A and $8\pi_s + 2\pi_a$

(c) B and $4\pi_s + 2\pi_s$

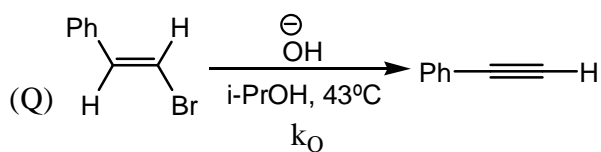
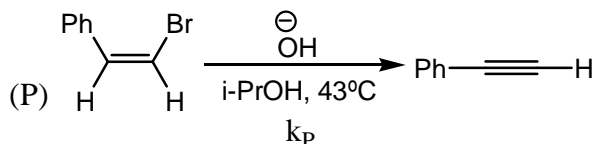
(d) B and $4\pi_s + 2\pi_a$



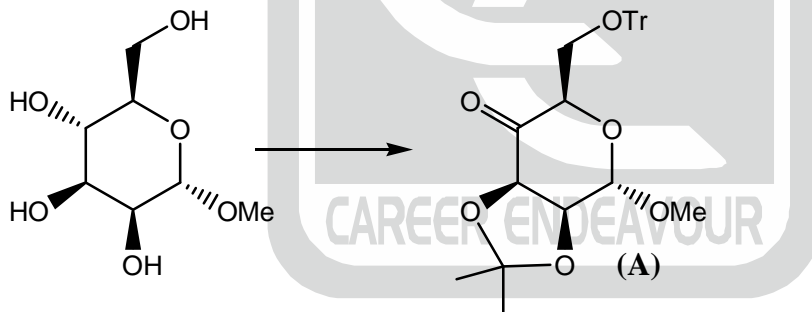
90. The resistances of 0.1 M KCl and 0.05 M NaCl in a conductivity cell are $90\ \Omega$ and $200\ \Omega$, respectively. If the specific conductivity of 0.1 M KCl is $11.2 \times 10^{-3}\ \text{S cm}^{-1}$, then the molar conductance (in $\text{S cm}^2\ \text{mol}^{-1}$) of 0.05 M NaCl is closest to

(a) 10^5 (b) 10^2 (c) 10^3 (d) 10^4

91. The correct statement for the reactions P and Q is

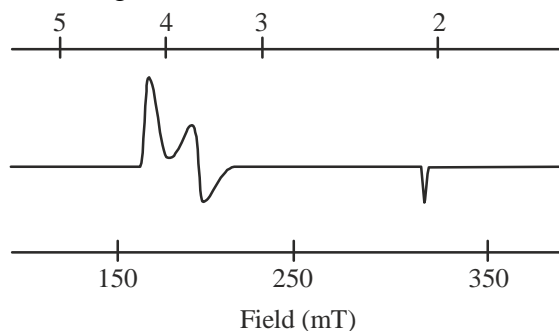


- (a) $k_P > k_Q$; **P** goes via an E2 and **Q** goes via an E1cB pathway
 (b) $k_P > k_Q$; both **P** and **Q** go via an E2 pathway
 (c) $k_Q > k_P$; **P** goes via an E1cB and **Q** goes via an E2 pathway
 (d) $k_Q > k_P$; both **P** and **Q** go via an E1cB pathway
92. The correct sequence of reagents which will give A as the major product is



- (a) **i.** 2,2-dimethoxypropane, PTSA; **ii.** Dess-Martin periodinane; **iii.** TrCl, Et_3N
 (b) **i.** TrCl, Et_3N ; **ii.** 2,2-dimethoxypropane, PTSA; **iii.** Dess-Martin periodinane
 (c) **i.** TrCl, Et_3N ; **ii.** Dess-Martin periodinane; **iii.** 2,2-dimethoxypropane, PTSA
 (d) **i.** Dess-Martin periodinane; **ii.** TrCl, Et_3N ; **iii.** 2,2-dimethoxypropane, PTSA
93. Reaction of an aqueous acidic solution of CoCl_2 with KNO_2 gives a yellow precipitate **X** and with NH_4SCN , a blue-colored compound **Y**. Compounds **X** and **Y**, respectively, are
- (a) $\text{K}_4[\text{Co}(\text{NO}_2)_6]$ and $\text{Co}(\text{SCN})_2$ (b) $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ and $\text{Co}(\text{SCN})_2$
 (c) $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ and $(\text{NH}_4)_2[\text{Co}(\text{SCN})_4]$ (d) $\text{K}_4[\text{Co}(\text{NO}_2)_6]$ and $(\text{NH}_4)_2[\text{Co}(\text{SCN})_4]$

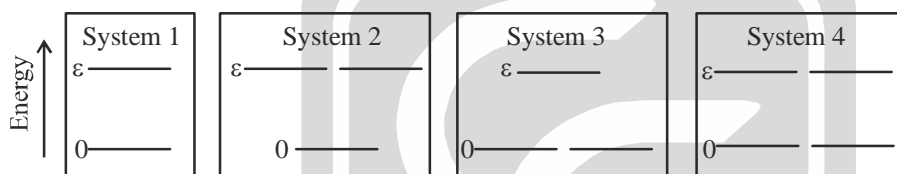
94. The EPR spectrum along with the g values of FeMo co-factor in nitrogenase is shown below:



The overall spin of the system is

- (a) $1/2$ (b) $3/2$ (c) $5/2$ (d) $7/2$
95. The ground state term symbols of the metal hydrates $[\text{Eu}(\text{H}_2\text{O})_n]^{3+}$ and $[\text{Tb}(\text{H}_2\text{O})_n]^{3+}$, respectively are
- (a) 7F_0 and 7F_6 (b) 7F_0 and ${}^2F_{7/2}$ (c) ${}^2F_{5/2}$ and 7F_6 (d) 3H_4 and 5I_8
96. From the energy diagrams of different single particle systems given below, the one with the lowest

Helmholtz free energy at a temperature $T = \frac{\epsilon}{k_B}$ is $\left[\frac{1}{e} = 0.37\right]$



- (a) System 1 (b) System 2 (c) System 3 (d) System 4
97. The raising and lowering operators are denoted as L_+ and L_- , respectively. The correct commutator relation between angular momentum (L) and its various components (L_x , L_y and L_z) is
- (a) $[L^2, L_+] = [L^2, L_-] = \hbar L_z$ (b) $[L^2, L_+] = [L^2, L_-] = \hbar L_x$
- (c) $[L^2, L_+] = [L^2, L_-] = \hbar L_y$ (d) $[L^2, L_+] = [L^2, L_-] = 0$
98. The formation constant ($\log K_1$) of metal ions X^{n+} , Y^{m+} and Z^{p+} with halides in water is given below.

Metal ion	F^-	Cl^-	Br^-
X^{n+}	6.0	1.5	0.5
Y^{m+}	1.0	6.5	13.0
Z^{p+}	0.5	8.5	15.5

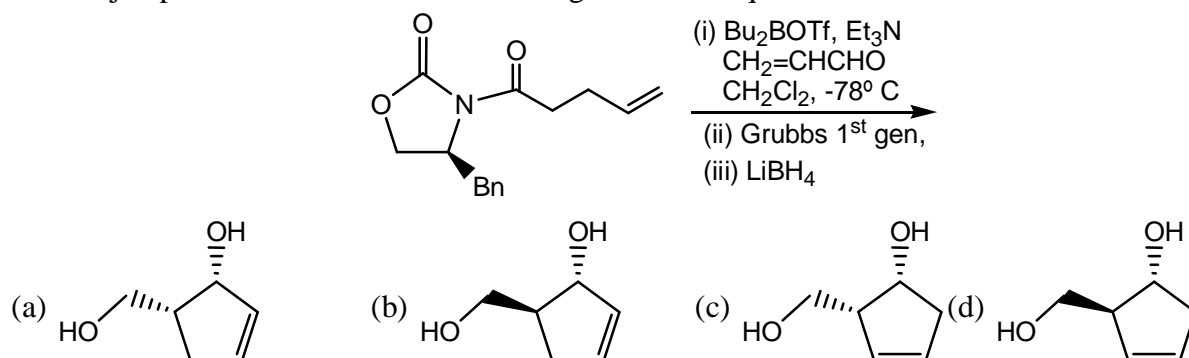
Consider the following statements

- (A) X^{n+} is a hard acid; Y^{m+} is a soft acid
 (B) X^{n+} is a soft acid; Z^{p+} is a hard acid
 (C) Y^{m+} is a soft acid; Z^{p+} is a soft acid

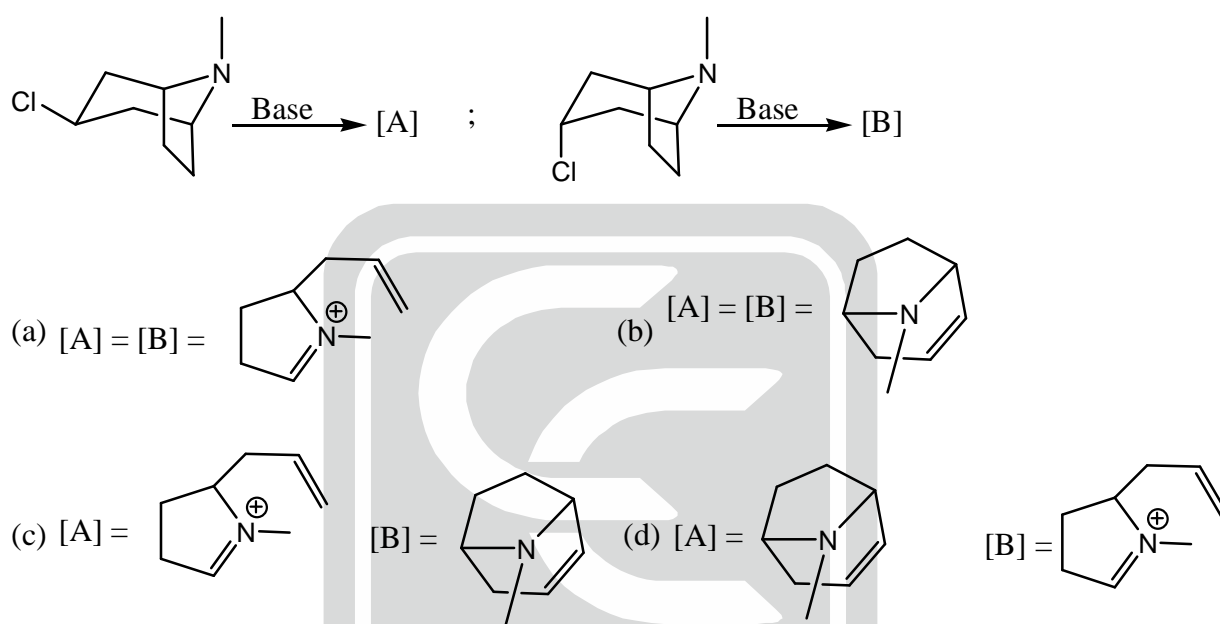
The correct option is

- (a) A and C only (b) A, B and C only (c) B and C only (d) A only

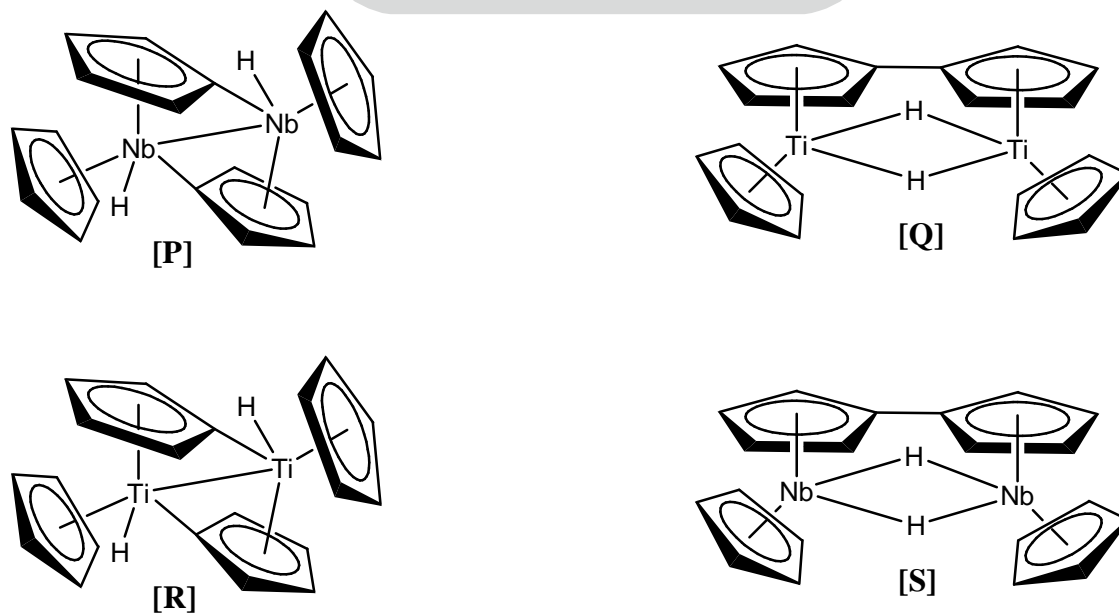
99. The major product formed in the following reaction sequence is



100. The major products A and B formed in the following transformations are



101. Consider the following structures.



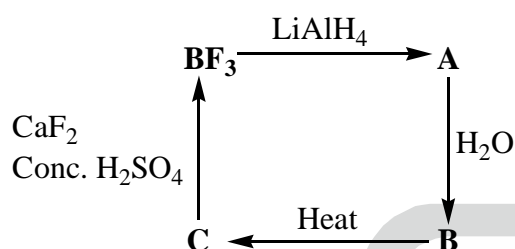
- (A) The structure for niobocene is P (B) The structure for titanocene is Q
 (C) The structure for niobocene is S (D) The structure for titanocene is R
 The option containing the correct statements is

(a) A and B (b) C and D (c) B and C (d) A and D

102. For the reaction $A(s) \rightarrow A(l)$, ΔG_m at 300 K is 6 kJ mol^{-1} . If the heat absorbed in the process is 9 kJ mol^{-1} , the temperature (in K) at which A starts melting is [Assume ΔH to be constant with temperature]

(a) 1000 (b) 900 (c) 1500 (d) 750

103. In the following reaction, A, B and C, respectively, are



- (a) LiBH_4 , $\text{BH}_2(\text{OH})$ and B_2O_3 (b) LiBH_4 , $\text{B}(\text{OH})_3$ and amorphous B
 (c) BH_3 , $\text{B}(\text{OH})_3$ and crystalline B_{12} (d) BH_3 , $\text{B}(\text{OH})_3$ and B_2O_3

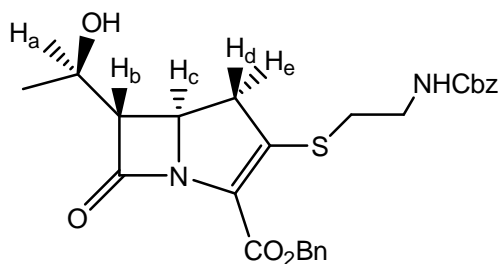
104. The fluorescence of A is quenched by 10 % in the presence of 10 mM of B. If the fluorescence lifetime of A in the absence of B is 5 ns, the rate constant (in $\text{M}^{-1}\text{s}^{-1}$) for interaction between B and photo-excited A is

(a) 1.2×10^9 (b) 2.2×10^9 (c) 3.2×10^9 (d) 4.2×10^9

105. The order of the reaction $A \rightarrow P$ is 2 when the concentration of A is small. However, at higher concentrations of A, the order changes to 1. The mechanism of the reaction is [Assume that steady state approximation can be applied on A^*]

- (a) $A \rightarrow P$ (b) $A \rightleftharpoons A^*$ (c) $A + A \rightleftharpoons A^* + A$ (d) $A + A \rightarrow A^* + A$
 $A^* \rightarrow P$ $A^* \rightarrow P$ $A^* \rightarrow P$

106. The ^1H NMR data corresponding to the labelled protons of the following compound is given below. The signal corresponding to H_b is





^1H NMR: δ 4.19(dt, $J = 9.0, 2.5$ Hz), 4.13(dq, $J = 7.0, 6.5$ Hz), 3.35(dd, $J = 18.0, 9.0$ Hz)
3.15(dd, $J = 7.0, 2.5$ Hz), 3.08(dd, $J = 18.0, 9.0$ Hz) ppm

- (a) 4.19 (dt, $J = 9.0, 2.5$ Hz) (b) 4.13 (dq, $J = 7.0, 6.5$ Hz)
(c) 3.35 (dd, $J = 18.0, 9.0$ Hz) (d) 3.15 (dd, $J = 7.0, 2.5$ Hz)

107. The unperturbed energies (in eV) of a three-level system are $\epsilon_0 = 2$, $\epsilon_1 = 4$ and $\epsilon_2 = 6$. The matrix elements of a perturbation V (in eV) between the levels (in subscript) are $V_{10} = 4$, $V_{20} = 6$ and $V_{12} = 10$. The second-order correction to the ground state energy (in eV) in the presence of perturbation V is

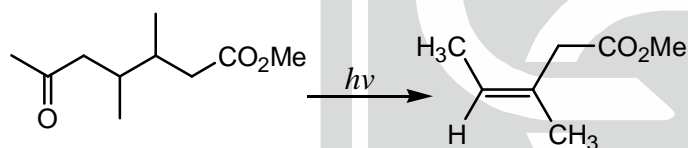
- (a) $-25/4$ (b) -67 (c) -17 (d) -16

108. For a point group having the irreducible representations A_1 , A_2 and E , the values of a , b and c in the following partial character table are

	E	$2C_3$	$3C_2$
E	a	b	c

- (a) $a = 2, b = 1, c = 0$ (b) $a = 2, b = -1, c = 0$
(c) $a = -1, b = 2, c = 1$ (d) $a = 2, b = 1, c = -1$

109. The correct statement about the following transformation is



- (a) threo isomer gives the product via Norrish type-I reaction
(b) threo isomer gives the product via Norrish type-II reaction
(c) erythro isomer gives the product via Norrish type-I reaction
(d) erythro isomer gives the product via Norrish type-II reaction

110. Consider an arbitrary unnormalized wavefunction ψ , expanded in terms of eigenstates of Hamiltonian H , where

$$H|\phi_n\rangle = \epsilon_n|\phi_n\rangle, n = 0, 1, 2, \dots$$

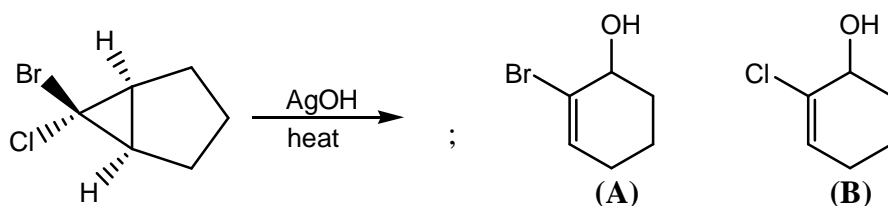
$$\epsilon_0 \leq \epsilon_1 \leq \epsilon_2 \text{ etc.}$$

$$\psi = \sum_n a_n |\phi_n\rangle$$

The correct option, which definitely holds for any set of $\{a_n\}$, is

- (a) $\frac{\sum_n |a_n|^2 \epsilon_n}{\sum_n |a_n|^2} < \epsilon_0$ (b) $\frac{\sum_n |a_n|^2 \epsilon_n}{\sum_n |a_n|^2} \geq \epsilon_0$ (c) $\frac{\sum_n a_n \epsilon_n}{\sum |a_n|} \geq \epsilon_0$ (d) $\frac{\sum_n a_n \epsilon_n}{\sum_n |a_n|^2} < \epsilon_0$

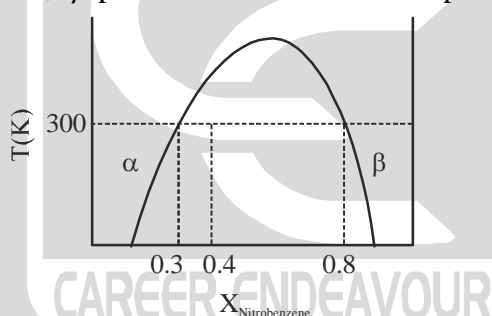
111. The correct statement about the following transformation is



- (a) **A** is formed as the major product via conrotatory ring opening
 (b) **A** is formed as the major product via disrotatory ring opening
 (c) **B** is formed as the major product via conrotatory ring opening
 (d) **B** is formed as the major product via disrotatory ring opening
112. The number-average degree of polymerization (\bar{X}_n) of self-catalyzed polyesterification, a 3rd order reaction, is expressed as

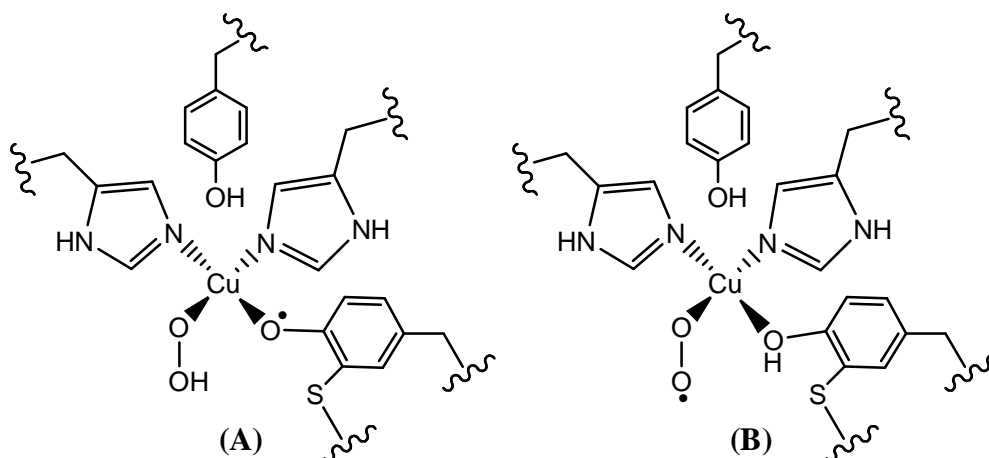
$[M]_0$: initial monomer concentration]

- (a) $\bar{X}_n^2 = 2[M]_0^2 kt + 1$ (b) $\bar{X}_n^2 = 2[M]_0 kt + 1$ (c) $\bar{X}_n^2 = [M]_0 kt + 1$ (d) $\bar{X}_n^2 = 2[M]_0^2 kt$
113. A mixture of 0.6 mol of hexane and 0.4 mol of nitrobenzene was prepared at 300 K. Based on the phase diagram given below, the number of moles of hexane in α phase is
 [α phase : hexane rich phase, β phase : nitrobenzene rich phase]



- (a) 0.56 (b) 0.42 (c) 0.38 (d) 0.32
114. The mean activity coefficient (γ_{\pm}) of 0.1 m aqueous solution of CdCl_2 at 298 K and 1 bar is 0.228. Under this condition, the potential of the cell, $\text{Cd(s)} | \text{CdCl}_2(\text{aq.}, 0.1 \text{ m}) | \text{AgCl(s)} | \text{Ag(s)}$, is
 [$E^\circ(\text{AgCl/Ag, Cl}^-) = 0.22 \text{ V}$; $E^\circ(\text{Cd}^{2+}/\text{Cd}) = -0.40 \text{ V}$]
 (a) 0.75 V (b) 0.62 V (c) 0.89 V (d) 0.49 V
115. Consider the following statements regarding molecular orbitals of a water molecule.
 A. The photoelectron spectrum of water shows that two MOs containing the lone-pairs are not of the same energy.
 B. The O–H bond orbitals have a_1 symmetry.
 C. The HOMO is predominantly an oxygen p orbital.
 D. Increasing H–O–H bond angle leads to the destabilization of the HOMO.
 The option containing the correct statements is
 (a) A and C only (b) A and D only (c) B and C only (d) B and D only

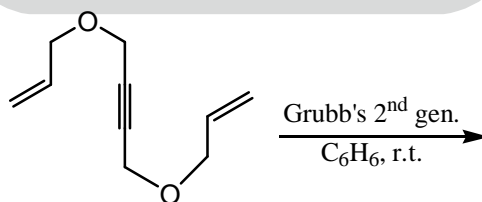
116. Intermediate compounds A and B, proposed in the catalytic cycle for the enzyme galactose oxidase, can be distinguished by one or more of the following methods.

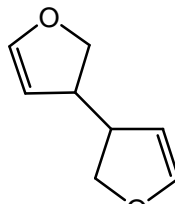
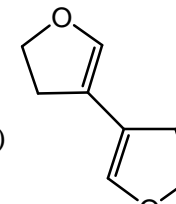
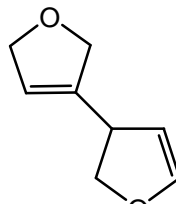
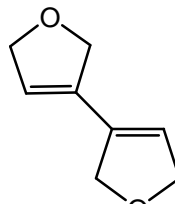


- A. Room temperature EPR spectroscopy
 B. Vibrational Spectroscopy
 C. Electrospray Ionisation Mass Spectrometry
 D. Electronic Spectroscopy

The correct option is

- (a) B and D only (b) A and B only
 (c) B, C, and D only (d) A, B and C only
117. The Huckel approximation, the π -energy for the cyclopropenyl cation is [α and β are coulomb integral and resonance integral, respectively]
 (a) $2\alpha + 4\beta$ (b) $\alpha + \beta$ (c) $3\alpha + 3\beta$ (d) $3\alpha + 6\beta$
118. The major product formed in the following reaction is



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

119. Unimolecular decomposition of NH_3 on tungsten surface is inhibited by one of the products, H_2 . The rate of surface catalyzed decomposition is given by
[P_i and K_i are, respectively, the partial pressure and surface binding constant of the i^{th} species; k_c is the rate constant of rate determining step]

(a)
$$\frac{k_c K_{\text{NH}_3} P_{\text{NH}_3} K_{\text{H}_2} P_{\text{H}_2}}{(1 + K_{\text{NH}_3} P_{\text{NH}_3} + K_{\text{H}_2} P_{\text{H}_2})^2}$$

(b)
$$\frac{k_c K_{\text{NH}_3} P_{\text{NH}_3}}{1 + K_{\text{NH}_3} P_{\text{NH}_3}}$$

(c)
$$\frac{k_c K_{\text{NH}_3} P_{\text{NH}_3}}{1 + K_{\text{NH}_3} P_{\text{NH}_3} + K_{\text{H}_2} P_{\text{H}_2}}$$

(d)
$$\frac{k_c K_{\text{NH}_3} P_{\text{NH}_3} K_{\text{H}_2} P_{\text{H}_2}}{1 + K_{\text{NH}_3} P_{\text{NH}_3} + K_{\text{H}_2} P_{\text{H}_2}}$$

120. The chemical shifts of CH_3 and CH_2 protons in a molecule are 1.15 and 3.35 ppm, respectively. When the magnetic field is 2 T, the absolute difference between the local magnetic fields (in T) for these two protons is
(a) 4.4×10^6 (b) 2.2×10^{-6} (c) 4.4×10^{-6} (d) 2.2×10^6

