

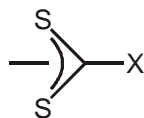
June-2017

BOOKLET-A

## Part-B

21. Which one of the following pairs has two magic numbers for closed nuclear shells ?  
(a) 8, 10                      (b) 10, 20                      (c) 50, 82                      (d) 82, 130
22. Identify the correct statement(s) for phosphorimetric measurement from the following :  
A. It is done after a time delay when fluorescence, if present becomes negligible  
B. Immobilization of analyte increases phosphorescence  
C. Phosphorescence decreases in the presence of heavy atoms  
(a) A only                      (b) A and B                      (c) A and C                      (d) B and C
23. Choose the isoelectronic pair among the following :  
A.  $[\text{V}(\text{CO})_6]$   
B.  $[\text{Cu}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})]$   
C.  $[\text{Co}(\text{CO})_4]^-$   
D.  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$   
(a) A and B                      (b) B and C                      (c) C and D                      (d) A and D
24. An organometallic fragment that is isolobal to  $\text{CH}_3^+$  is  
(a)  $[\text{Fe}(\text{CO})_5]$                       (b)  $[\text{Mn}(\text{CO})_5]$                       (c)  $[\text{Cr}(\text{CO})_5]$                       (d)  $[\text{Ni}(\text{CO})_3]^+$
25. The calculated and observed magnetic moments (in B.M.) of aqua complex of a lanthanide ion are 0 and  $\sim 3.5$ , respectively. The lanthanide ion is  
(a)  $\text{Pm}^{3+}$                       (b)  $\text{Pr}^{3+}$                       (c)  $\text{Eu}^{3+}$                       (d)  $\text{Sm}^{3+}$
26. The compound that gives a basic solution in HF is :  
(a)  $\text{AsF}_5$                       (b)  $\text{PF}_5$                       (c)  $\text{BF}_3$                       (d)  $\text{BrF}_3$
27. Based on VSEPR theory, the predicted shapes of  $[\text{XeF}_5]^-$  and  $\text{BrF}_5$  respectively, are  
(a) pentagonal planar and square pyramidal  
(b) square pyramidal and trigonal bipyramidal  
(c) trigonal bipyramidal and square pyramidal  
(d) square pyramidal and pentagonal planar
28. Both potassium and sulfuric acid form intercalation compounds with graphite. The graphite layers are  
(a) reduced in both the cases  
(b) oxidized in both the cases  
(c) oxidized in the case of potassium and reduced in the case of sulphuric acid  
(d) reduced in the case of potassium and oxidized in the case of sulphuric acid
29. The resonance Raman stretching frequencies (in  $\text{cm}^{-1}$ ) of the bound  $\text{O}_2$  species in oxy-hemerythrin and oxy-hemoglobin, respectively, are  
(a)  $\sim 850$  and  $1100$                       (b)  $\sim 750$  and  $850$                       (c)  $\sim 850$  and  $850$                       (d)  $\sim 1100$  and  $850$
30.  $\text{CdS}$ ,  $\text{HgS}$  and  $\text{BiI}_3$ , are coloured due to  
(a)  $\text{L} \rightarrow \text{M}$  charge transfer transitions  
(b)  $d \rightarrow d$  electronic transitions  
(c)  $\text{M} \rightarrow \text{L}$  charge transfer transitions  
(d) combination of  $\text{L} \rightarrow \text{M}$  charge transfer and  $d \rightarrow d$  electronic transitions

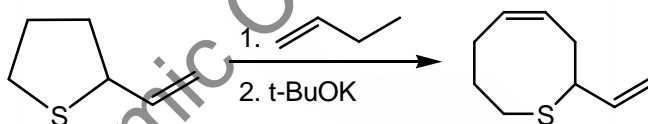
31. The relative rates of water exchange for the hydrated complexes of (1)  $\text{Ni}^{2+}$ , (2)  $\text{V}^{2+}$  and (3)  $\text{Cr}^{3+}$  ions follows the trend  
 (a) (1) > (2) > (3) (b) (1) < (2) < (3) (c) (1) > (2) < (3) (d) (1) < (2) > (3)
32. Consider the following sulfur donor atom bearing bidentate ligand where X and name of ligands are given in following columns :



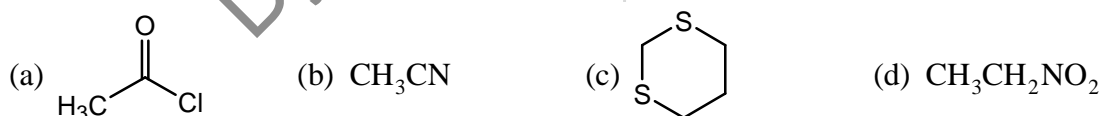
X	Ligand name
A. $\text{NR}_2$	I. Dithiocarbonate
B. OR	II. Dithiocarbamate
C. $\text{O}^-$	III. Xanthate
D. SR	IV. Thioxanthate

Correct match of entries given in two columns is

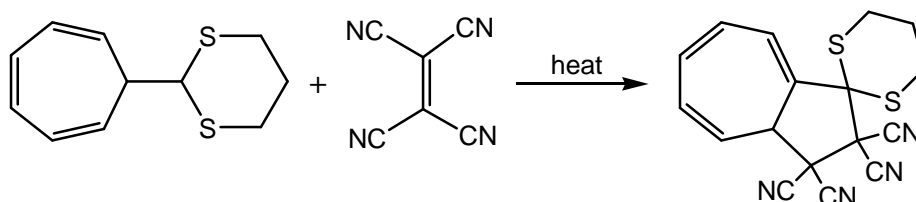
- (a) A-II, B-III, C-I, D-IV (b) A-III, B-II, C-IV, D-I  
 (c) A-I, B-II, C-III, D-IV (d) A-IV, B-I, C-II, D-III
33. *In vitro* reaction of an excess of  $\text{O}_2$  with free heme B in aqueous medium the end product is  
 (a) hematin (b)  $[\text{O}_2^- \text{Fe(III)-protoporphyrin-IX}]$   
 (c) heme B( $\text{O}_2$ ) (d) oxoferrylprotoporphyrin-IX cation radical
34.  $^{13}\text{C}$  NMR spectrum of  $\text{DMSO-d}_6$  gives a signal at  $\delta$  39.7 ppm as a  
 (a) singlet (b) triplet (c) quintet (d) septet
35. Following reaction is an example of



- (a) Ramberg-Bäcklund reaction (b) [2, 3]-sigmatropic shift  
 (c) [3, 3]-sigmatropic shift (d) Pummerer rearrangement
36. Among the following, the synthetic equivalent of acetyl anion is

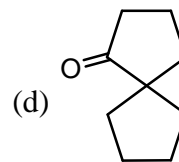
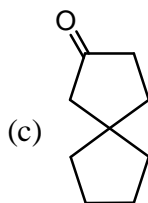
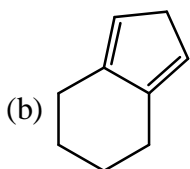
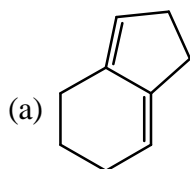
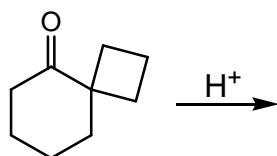


37. Following reaction is an example of

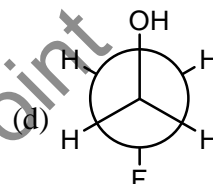
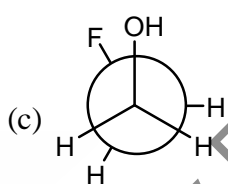
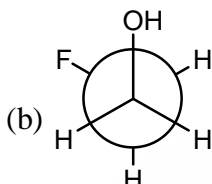
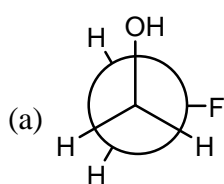


- (a) [3 + 2] cycloaddition (b) [4 + 2] cycloaddition  
 (c) [6 + 2] cycloaddition (d) [8 + 2] cycloaddition

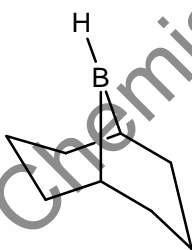
38. The major product of the following reaction is



39. The most stable conformation of 2-fluoroethanol is



40. The IUPAC name of the following compound is



(a) 9-borabicyclo[3.3.1]nonane

(b) 1-borabicyclo[3.3.1]nonane

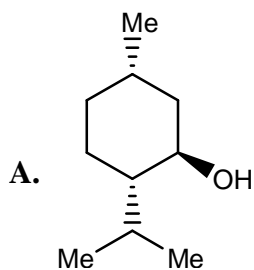
(c) 9-borabicyclo[3.3.0]octane

(d) 1-borabicyclo[3.3.0]octane

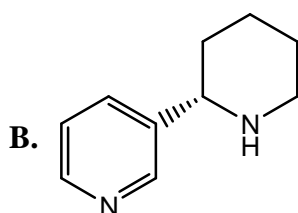
41. The correct match of natural products in **Column-I** with their biosynthetic precursors in **Column-II** is

**Column-I**

**Column-II**



I. L-Lysine



II. L-Ornithine

III. Farnesyl

#### IV. Geranyl pyrophosphate

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

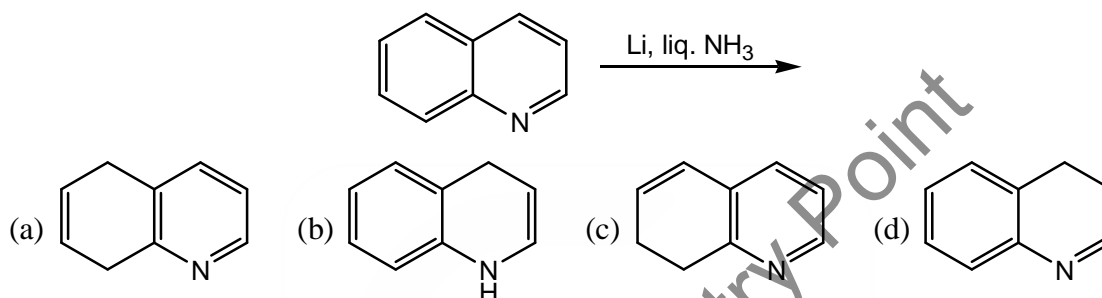
42. The correct order of pKa values for the following species is

- (a)  $\text{PhNH}_3^+ < i\text{-Pr}_2\text{NH}_2^+ < \text{Ph}_2\text{NH}_2^+$       (b)  $\text{Ph}_2\text{NH}_2^+ < \text{PhNH}_3^+ < i\text{-Pr}_2\text{NH}_2^+$   
 (c)  $i\text{-Pr}_2\text{NH}_2^+ < \text{Ph}_2\text{NH}_2^+ < \text{PhNH}_3^+$       (d)  $\text{PhNH}_3^+ < \text{Ph}_2\text{NH}_2^+ < i\text{-Pr}_2\text{NH}_2^+$

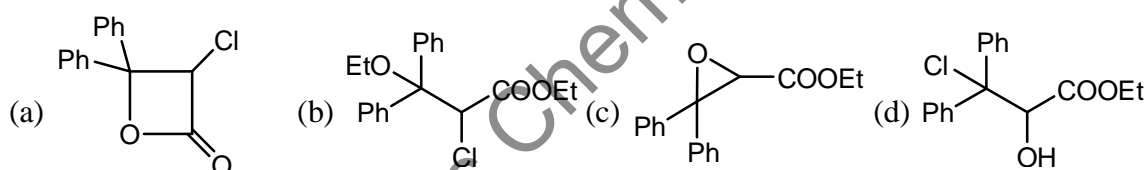
43. Among the following, the natural product that is a steroid and contains an  $\alpha, \beta$ -unsaturated ketone is

- (a) estrone      (b) prostaglandin      (c) cortisone      (d) morphine

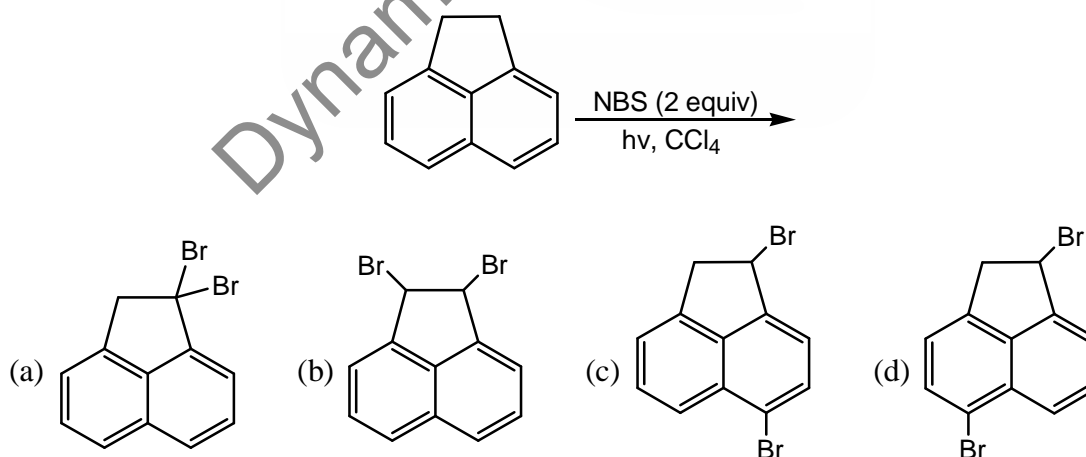
44. The major product formed in the following reaction is



45. The major product formed in the sodium ethoxide mediated reaction between benzophenone and ethyl chloroacetate is



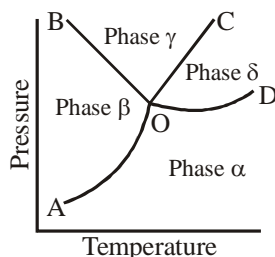
46. The major product formed in the following reaction is



47. Consider a particle in its ground state confined to a one-dimensional box in the interval (0, 8). The probability of finding it between  $4.0 - \frac{\delta}{2}$  and  $4.0 + \frac{\delta}{2}$  is close to ( $\delta$  is sufficiently small so that the wavefunction can be taken as a constant in this interval).

- (a)  $\frac{\delta}{4}$       (b)  $\frac{\delta}{3}$       (c)  $\frac{\delta}{2}$       (d)  $\delta$

48. Which of the functions below is a common eigenfunction of  $\frac{d}{dx}$  and  $\frac{d^2}{dx^2}$  operators ?  
 (a)  $\cos x$  (b)  $kx$  (c)  $e^{ix}$  (d)  $e - x^2$
49. A one-component system with the associated phase diagram (see the figure) is not possible because



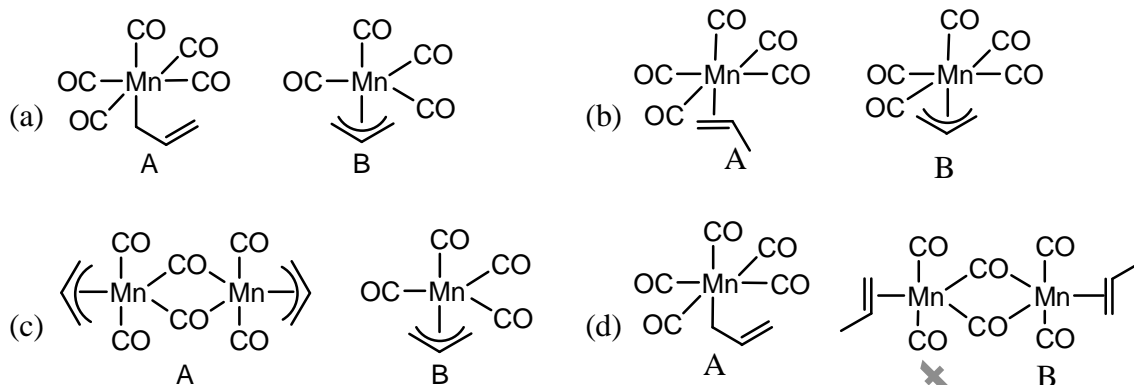
- (a) OB has a negative slope (b) OC has a positive slope  
 (c) Both OB and OC are linear (d) OB, OC and OD cannot all coexist, given OA
50. A phase transition process is always  
 (a) isothermal – isentropic (b) isochoric – isothermal  
 (c) isobaric – isochoric (d) isothermal – isobaric
51. The correct statement for any cyclic thermodynamic process is  
 (a)  $\oint dq = 0$  (b)  $\oint dw = 0$  (c)  $\oint dU = 0$  (d)  $\oint Vdq = 0$
52. Metallic silver crystallizes in face-centred-cubic lattice structure with a unit cell of length 40 nm. The first order diffraction angle of X-ray beam from (2, 1, 0) plane of silver is  $30^\circ$ . The wavelength of X-ray used is close to  
 (a) 11 nm (b) 18 nm (c) 25 nm (d) 32 nm
53. If the pre-exponential factor in Arrhenius equation is  $1.6 \times 10^{12} s^{-1}$ , the value of the rate constant at extremely high temperature will be close to  
 (a)  $1.6 \times 10^{12} s^{-1}$  (b)  $4.2 \times 10^{12} s^{-1}$  (c)  $2.4 \times 10^9 s^{-1}$  (d)  $1.2 \times 10^6 s^{-1}$
54. In kinetic study of a chemical reaction, slopes are drawn at different times in the plot of concentration of reactants versus time. The magnitude of slopes with increase of time  
 (a) remains unchanged (b) increases  
 (c) decreases (d) increases and decreases periodically
55. The electrochemical cell potential (E), after the reactants and products reach equilibrium, is ( $E^0$  is the standard cell potential and  $n$  is the number of electrons involved)  
 (a)  $E = E^0 + nF/RT$  (b)  $E = E^0 - RT/nF$  (c)  $E = E^0$  (d)  $E = 0$
56. For the electronic configuration  $1s^2 2s^2 2p^4$ , two of the possible term symbols are  $^1S$  and  $^3P$ . The remaining term is  
 (a)  $^1D$  (b)  $^1F$  (c)  $^3D$  (d)  $^3F$

57. The  $v = 0$  to 1 vibration-rotation spectrum of a diatomic molecule exhibits transitions for  $R(0)$ ,  $R(1)$ ,  $P(1)$  and  $P(2)$  lines at 2241, 2254, 2216 and 2203  $\text{cm}^{-1}$ , respectively. From this data, we can conclude that the molecule
- (a) has rigid rotation and harmonic vibration (b) has anharmonic vibration  
(c) has rotational-vibrational interaction (d) is affected by nuclear spin-statistics
58. Consider aqueous solutions of two compounds A and B of identical concentrations. The surface tension of the solution of A is smaller than that of pure water while for B it is greater than that of pure water under identical conditions. From this one infers that
- (a) surface concentration of A is smaller than its bulk concentration  
(b) surface concentration of B is larger than its bulk concentration  
(c) surface concentration of A is larger than that of B  
(d) surface concentration of A is smaller than that of B
59. For a monodisperse polymer, the number-average molar mass ( $\bar{M}_n$ ) and weight-average molar mass ( $\bar{M}_w$ ) are related according to
- (a)  $\bar{M}_w < \bar{M}_n$  (b)  $\bar{M}_w = \bar{M}_n$  (c)  $\bar{M}_w > \bar{M}_n$  (d)  $\bar{M}_w < \log \bar{M}_n$
60. An intense purple colour (Plasmon band) is exhibited by a colloid consisting of spherical
- (a) silver particles of 10 nm diameter (b) silicon particles of 5 nm diameter  
(c) gold particles of 5 nm diameter (d) iron particles of 3 nm diameter

### Part-C

61. Choose the correct statement for magnitude of threshold energy of an endoergic nuclear reaction between stationary nucleus and a moving projectile.
- (a) It is greater than ' $|Q|$ ' of nuclear reaction.  
(b) It has to be more than kinetic energy of a projectile.  
(c) It is less than ' $|Q|$ ' of nuclear reaction.  
(d) It has to be equal to kinetic energy of a projectile.
62. Identify correct statements from the following:
- A. Area of differential thermal analysis peak is proportional to amount of sample.  
B. Area of differential thermogravimetric analysis curve is proportional to mass loss.  
C. Phase transition cannot be studied with differential scanning calorimetry.  
D. Simultaneous determination of two metal ions is possible with thermogravimetric analysis.
- Answer is
- (a) A, B and C (b) A, B and D (c) B, C and D (d) A, C and D
63. Consider following statements for fission of  $^{235}\text{U}$  with thermal neutrons.
- A. The % of nuclei undergoing unsymmetrical fission is maximum.  
B. In each fission, one thermal neutron is produced.  
C. Magnitude of energy released per fission is of the order 200 MeV
- Correct statement(s) is/are
- (a) A and B (b) A and C (c) B and C (d) C only
64. Addition of two electrons to the bismuth cluster  $\text{Bi}_5^{3+}$  results in a change of structure type from
- (a) closo to nido (b) nido to arachno (c) closo to arachno (d) arachno to hypho

65. Reaction of  $\text{Na}[\text{Mn}(\text{CO})_5]$  with  $\text{H}_2\text{C}=\text{CHCH}_2\text{Cl}$  gives **A** along with  $\text{NaCl}$ . Photolysis of compound **A** results in compound **B** together with elimination of  $\text{CO}$ . the correct structural formulations of compounds **A** and **B** are respectively,



66. A copper(II) complex having distorted octahedral geometry shows an absorption band at 625 nm. Given spin-orbit coupling of the complex as  $-625 \text{ cm}^{-1}$ , the  $\mu_{\text{eff}}$  (in B.M.) is  
 (a) 1.73 (b) 1.81 (c) 1.63 (d) 1.93
67. Match items in column A with items in column B:

Column A	Column B
I: $\text{SbF}_5 + \text{BrF}_3 \rightarrow [\text{BrF}_2]^+ + [\text{SbF}_6]^-$	A. Lewis acid behaviour of $\text{BrF}_3$
II: $[\text{BrF}_2][\text{SbF}_6] + \text{Ag}[\text{BrF}_4] \rightarrow \text{Ag}[\text{SbF}_6] + 2\text{BrF}_3$	B. Lewis base behaviour of $\text{BrF}_3$
III: $\text{KF} + \text{BrF}_3 \rightarrow \text{K}^+ + [\text{BrF}_4]^-$	C. Self ionisation
IV: $2\text{BrF}_3 \rightarrow [\text{BrF}_2]^+ + [\text{BrF}_4]^-$	D. Neutralisation

The correct answer is

- (a) I-(A); II-(B); III-(C); IV-(D) (b) I-(B); II-(D); III-(C); IV-(A)  
 (c) I-(C); II-(D); III-(B); IV-(A) (d) I-(B); II-(D); III-(A); IV-(C)
68. Mössbauer spectrum of complex  $[\text{Fe}(1,10\text{-phenanthroline})_2(\text{NCS})_2]$  shows two lines at 300 K, four lines at 186 K, and again two lines at 77 K. This can be attributed to  
 A. change in the coordination mode of NCS  
 B. change in the spin-state of iron  
 C. cis-trans isomerisation  
 D. change in metal-ligand bond distances  
 The correct statements are  
 (a) A and B (b) B and C (c) A and C (d) B and D
69.  $(\text{R}_3\text{Ge})_2$  on photolysis gives a radical which shows ESR spectrum. The ESR signals carrying the signature of  $^{73}\text{Ge}$  ( $I = 9/2$ ) are in terms of  
 (a) Nine lines (b) Ten lines (c) Two lines (d) One line

70. Mass fragment of  $[\text{IrCl}]^+$  in mass spectrometry shows three mass peaks at  $m/z = 226, 228,$  and  $230$ . Given that natural abundances of  $^{191}\text{Ir}$ ,  $^{193}\text{Ir}$ ,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  are 37%, 63%, 76%, and 24% respectively, the intensities of the mass peaks are in the order  
 (a) 49.5 : 100 : 26.6 (b) 100: 49.5: 26.6 (c) 26.6: 100: 49.5 (d) 26.6: 49.5: 100
71. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $2,2,6,6\text{-N}_4\text{P}_4\text{Cl}_4(\text{NMe}_2)_4$  is expected to show  
 (a) two triplets (b) two doublets  
 (c) one doublet and one triplet (d) one quartet and one doublet
72. The number of bonding molecular orbitals and the number of available skeletal electrons in  $[\text{B}_6\text{H}_6]^{2-}$ , respectively, are  
 (a) 7 and 14 (b) 6 and 12 (c) 18 and 12 (d) 11 and 14
73. The compound  $\text{N}_2\text{F}_2$  has two isomers. Choose the correct option from the following:  
 (a) both isomers possess  $\sigma_v$  plane  
 (b) both isomers possess  $\sigma_h$  plane  
 (c) one isomer has  $\sigma_h$  plane while the other has a  $\sigma_v$  plane  
 (d) none of them have a  $\sigma_h$  plane
74. Consider the following statements for metallothioneins:  
 A. they contain about 30% cysteine residues  
 B. they prefer to bind soft metal ions such as  $\text{Cd(II)}$ ,  $\text{Hg(II)}$  and  $\text{Zn(II)}$   
 C. they are involved in electron transfer reactions  
 D. they are low molecular weight proteins  
 Correct statements are  
 (a) A, B and C (b) A, B and D (c) A, C and D (d) B and C  
 deoxy-hemocyanin:  
 B. they contain two metal ions in their active site  
 C. active site metal centres are bridged by amino acid residues  
 D. they prefer to bind only one  $\text{O}_2$  per active site  
 The correct statements are  
 (a) A, B and D (b) A, C and D (c) B, C and D (d) A and C
76. Consider the following statements for octahedral complexes, (a)  $[\text{CrF}_6]^{3-}$ , (b)  $[\text{Cr}(\text{ox})_3]^{3-}$  and (c)  $[\text{Cr}(\text{en})_3]^{3+}$ :  
 A. their  $d \rightarrow d$  transitions are at 14900, 17500, and 21800  $\text{cm}^{-1}$ , respectively  
 B. their spin-only magnetic moments are same  
 C. two of them have optical isomers  
 D. all of them show Jahn-Teller distortion  
 The correct statements are  
 (a) A, B, and C (b) A, C, and D (c) B, C, and D (d) B and D

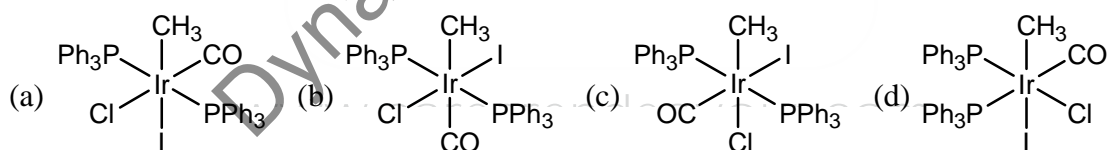


77. Addition of  $\text{NaBH}_4$  to  $\left[ (\eta^5\text{-Cp})\text{Fe}(\eta^6\text{-C}_6\text{H}_6) \right]^+$  will give
- (a)  $\left[ (\eta^5\text{-Cp})\text{Fe}(\text{H})_2 \right]^-$  (b)  $\left[ (\eta^5\text{-Cp})\text{Fe}(\text{H})(\eta^6\text{-C}_6\text{H}_6) \right]$   
(c)  $\left[ (\eta^5\text{-Cp})\text{Fe}(\eta^6\text{-C}_6\text{H}_6) \right]$  (d)  $\left[ (\eta^5\text{-Cp})\text{Fe}(\eta^6\text{-C}_6\text{H}_7) \right]$
78. The  $\mu_{\text{eff}}$  of  $\left[ \text{Fe}(\text{S}_2\text{CNET}_2)_3 \right]$  changes with temperature with the involvement of two electronic states. The states are
- (a) low spin  $^2\text{T}_{2g}$  and high-spin  $^6\text{A}_{1g}$ . (b) low spin  $^1\text{A}_{1g}$  and high-spin  $^3\text{T}_{2g}$   
(c) low spin  $^2\text{E}_g$  and high-spin  $^6\text{A}_{1g}$ . (d) low spin  $^2\text{T}_{2g}$  and high-spin  $^4\text{T}_{1g}$ .
79. Match the items in the three columns.

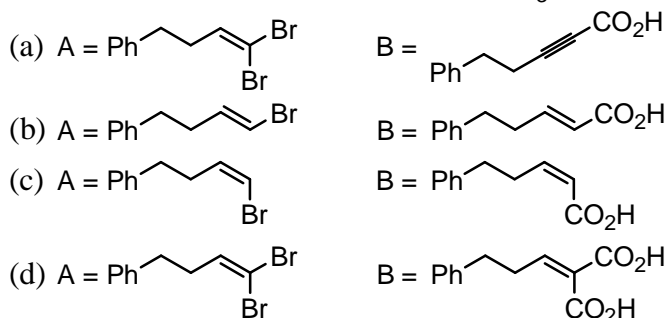
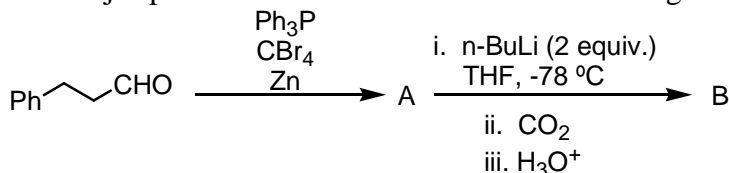
Complex (column 1)	Color (column 2)	Absorption max ( $\lambda_{\text{max}}$ , nm) (column 3)
A. $\left[ \text{Ni}(\text{H}_2\text{O})_6 \right] (\text{NO}_3)_2$	I. Blue	X. 675
B. $\left[ \text{Ni}(\text{NH}_3)_6 \right] (\text{NO}_3)_2$	II. Green	Y. 565
C. $\left[ \text{Ni}(\text{en})_3 \right] (\text{NO}_3)_2$	III. Violet	Z. 615

The correct answer is

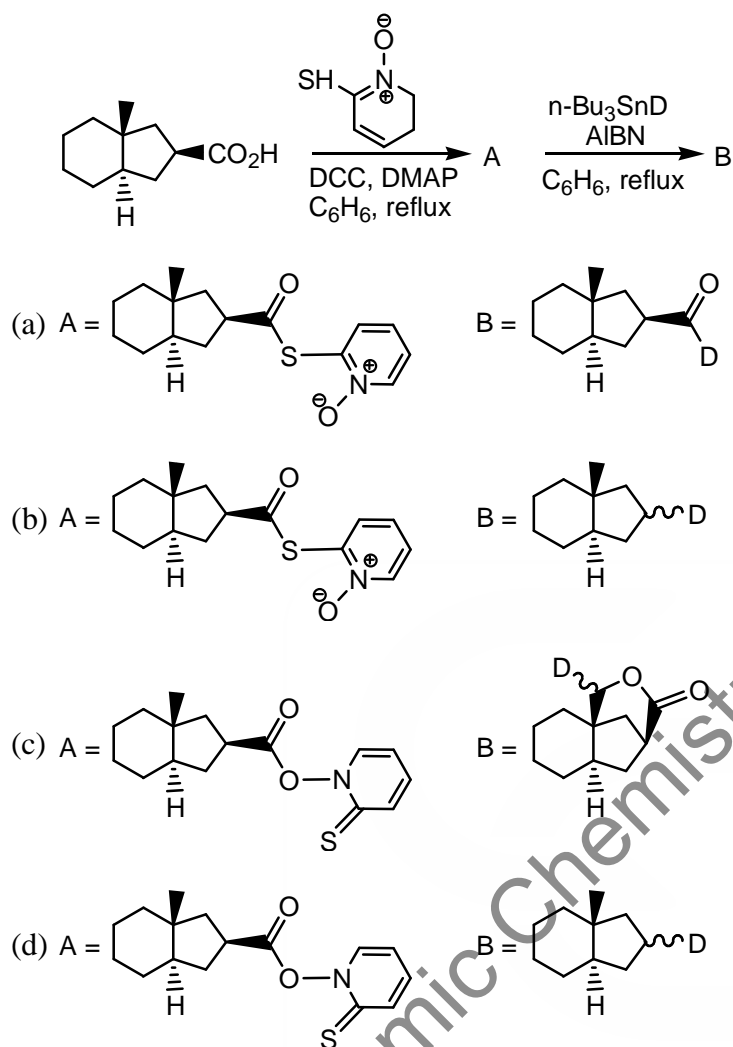
- (a) A-II-X; B-I-Z; C-III-Y (b) A-I-X; B-II-Y; C-III-Z  
(c) A-III-Y; B-I-Z; C-II-X (d) A-I-X; B-II-Z; C-III-Y
80. Identify the product in the reaction between



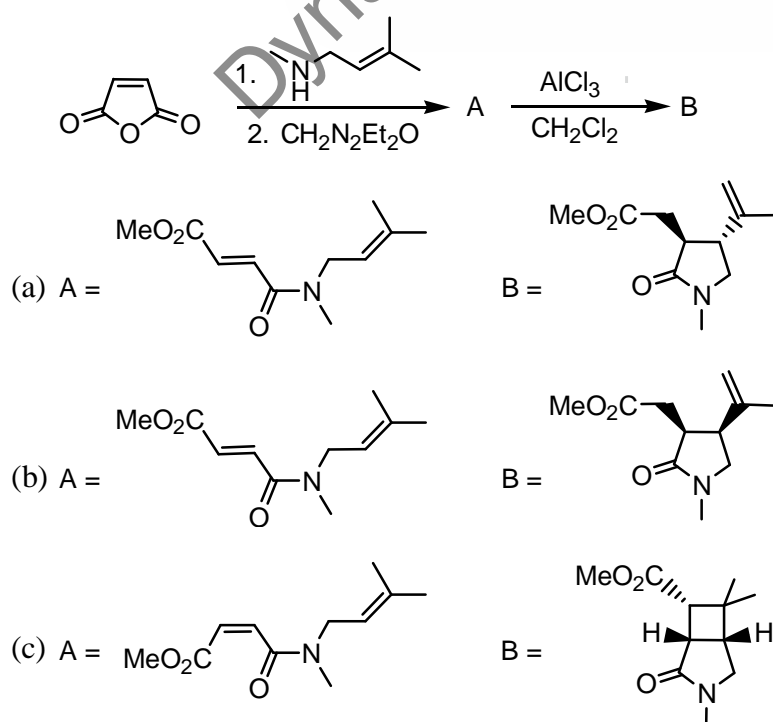
81. The major products A and B formed in the following reactions sequence are

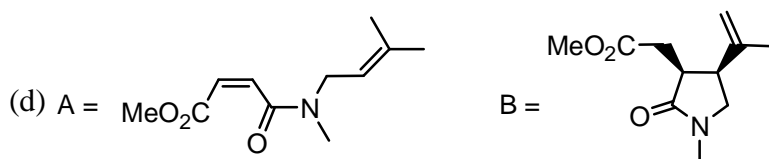


82. The intermediate **A** and product **B** formed in the following reaction sequence are

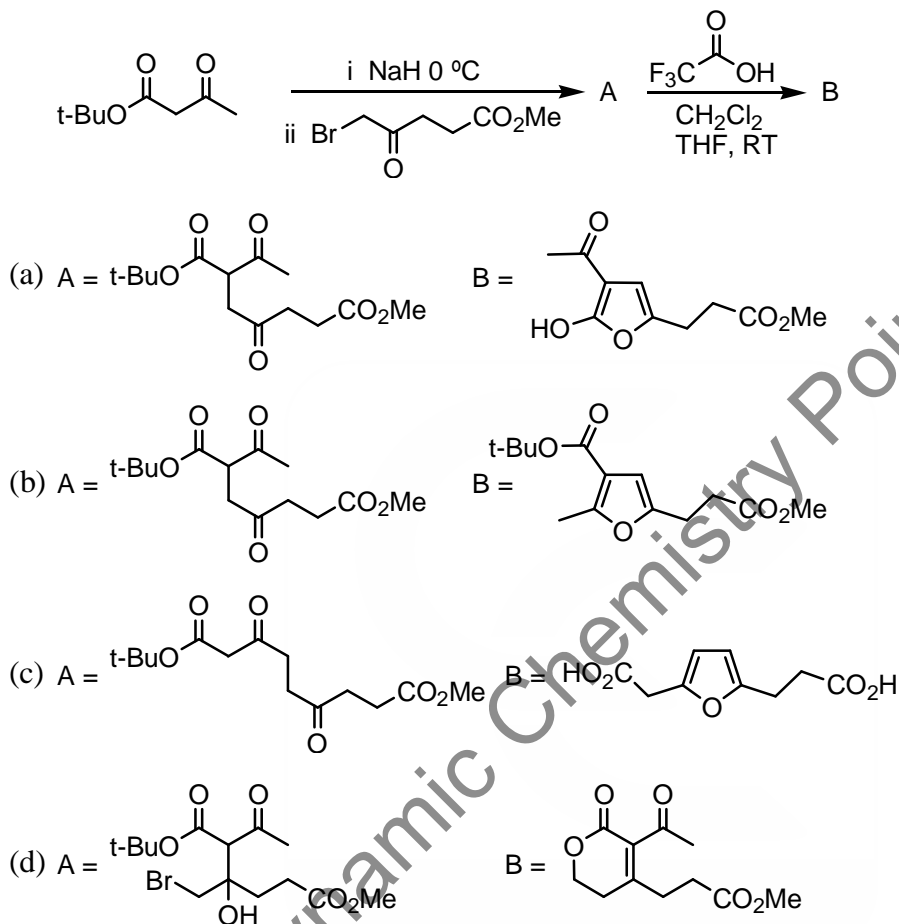


83. The major products **A** and **B** formed in the following reaction sequence are

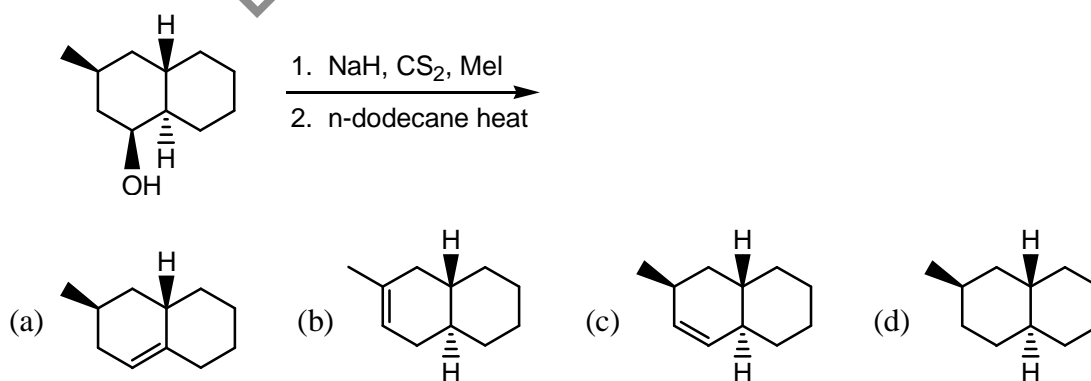




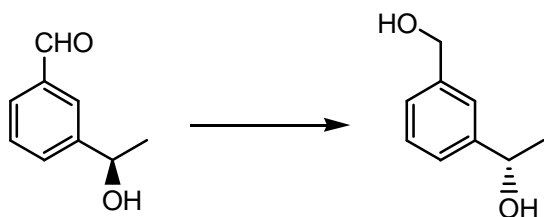
84. The major products **A** and **B** formed in the following reaction sequence are



85. The major product formed in the following reaction is

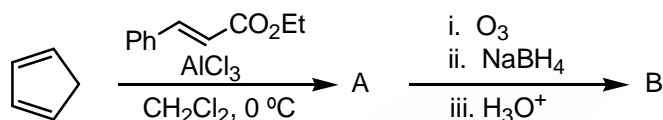


86. The correct combination of reagents to effect the following reaction is



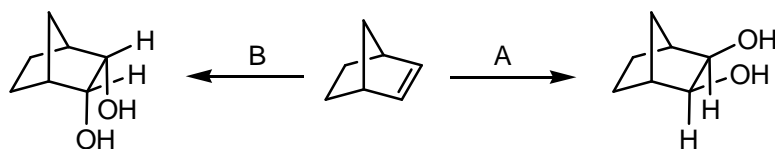
- (a) A.  $\text{POCl}_3$ , pyridine; B.  $\text{AgOAc}$ ; C.  $\text{LiAlH}_4$   
 (b) A.  $\text{NaBH}_4$ ; B.  $\text{Ph}_3\text{P}$ , DEAD,  $\text{PhCO}_2\text{H}$   
 (c) A.  $\text{Ph}_3\text{P}$ , DEAD,  $\text{PhCO}_2\text{H}$ ; B.  $\text{LiAlH}_4$   
 (d) A. PCC; B. L-selectride

87. The major products A and B formed in the following reaction sequence are



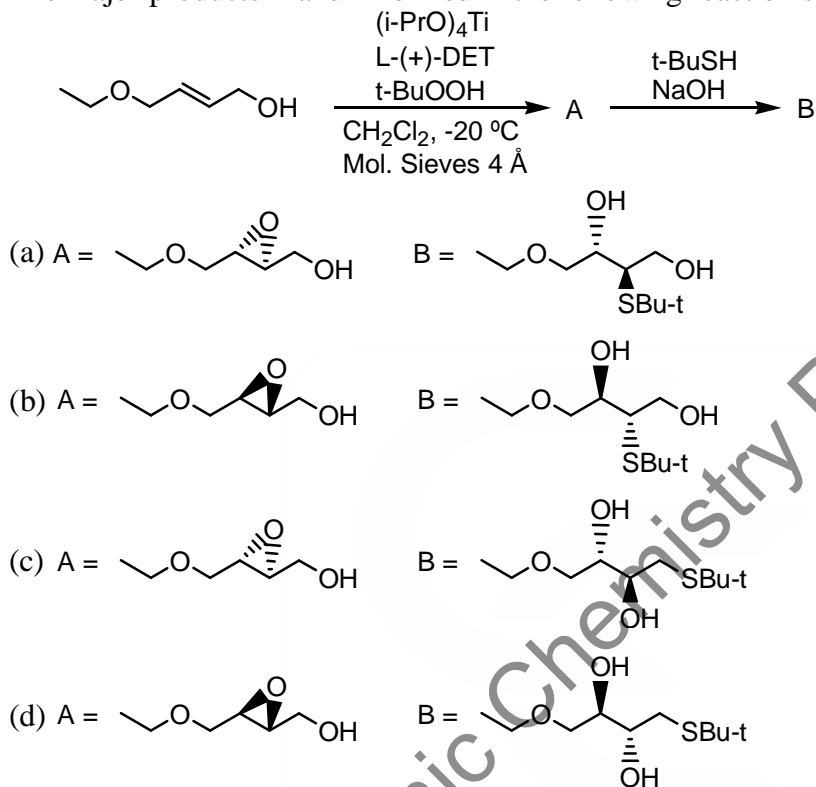
- (a) A = B =
- (b) A = B =
- (c) A = B =
- (d) A = B =

88. The correct combination of reagents A and B to effect following transformations are

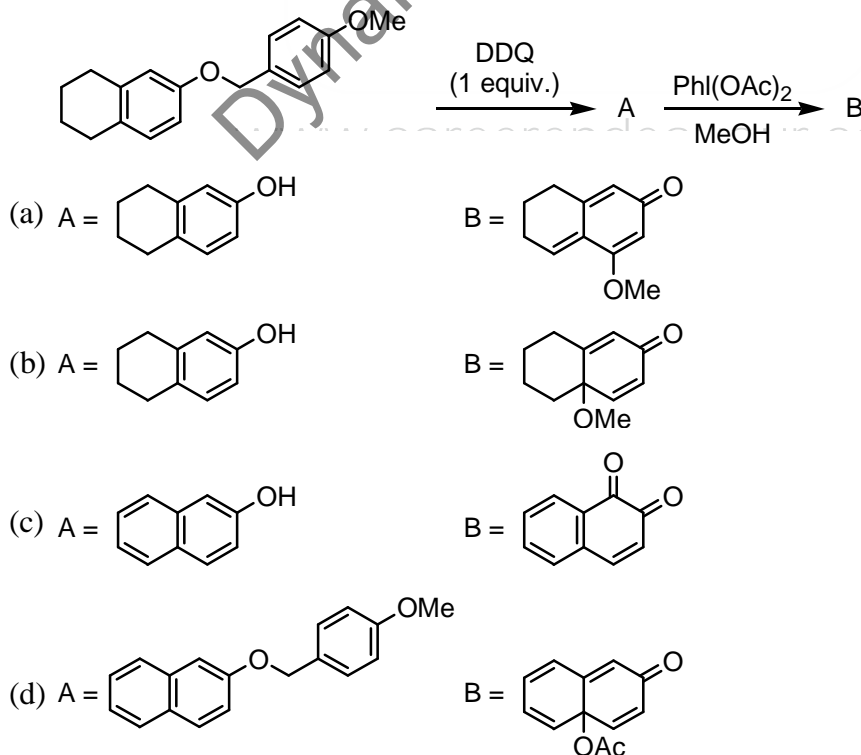


- (a) A = cat. OsO<sub>4</sub>, NMO; B = i. I<sub>2</sub>, PhCO<sub>2</sub>Ag, ii. aq. NaOH  
 (b) A = alkaline KMnO<sub>4</sub>; B = i. I<sub>2</sub>, PhCO<sub>2</sub>Ag, H<sub>2</sub>O, ii. aq. NaOH  
 (c) A = I<sub>2</sub>, PhCO<sub>2</sub>Ag, ii. aq. NaOH; B = cat. OsO<sub>4</sub>, TMEDA, NMO  
 (d) A = i. m-CPBA, ii. aq. NaOH; B = alkaline KMnO<sub>4</sub>

89. The major products A and B formed in the following reaction sequence are

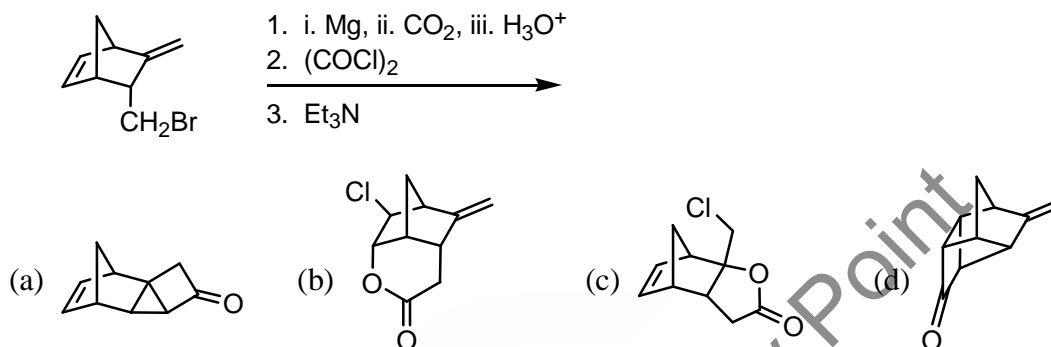


90. The major products A and B formed in the following reaction sequence are

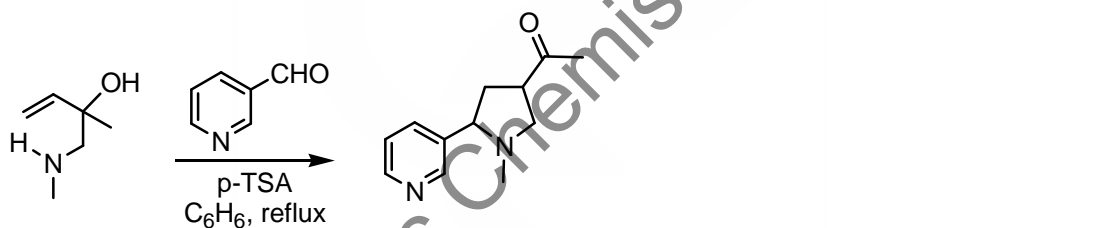


91. The specific rotation  $[\alpha]_D$  for (S)-(+)-2-butanol is  $10^\circ$  mL/g dm. The observed optical rotation ( $\alpha_{\text{obs}}$ ) of a sample composed of a mixture of (R)- and (S)-2-butanol is  $-0.45^\circ$ . If the cell path length is 0.6 dm and the concentration of 2-butanol in the sample is 0.15 g/mL, the percentages of (R) and (S) enantiomers in the sample are
- (a) (R) = 25%, (S) = 75%                      (b) (R) = 40%, (S) = 60%  
 (c) (R) = 60%, (S) = 40%                      (d) (R) = 75%, (S) = 25%

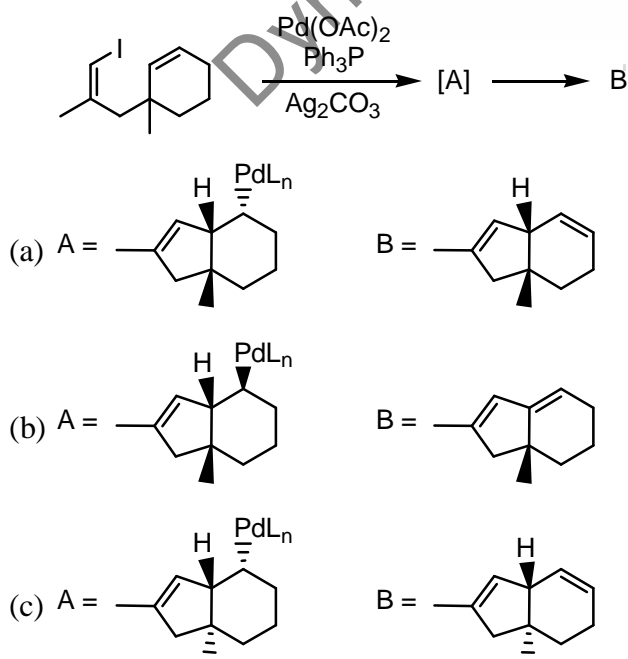
92. The major product formed in the following reaction is

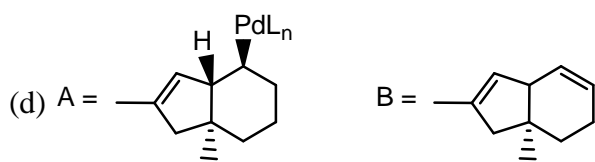


93. Following reaction involves

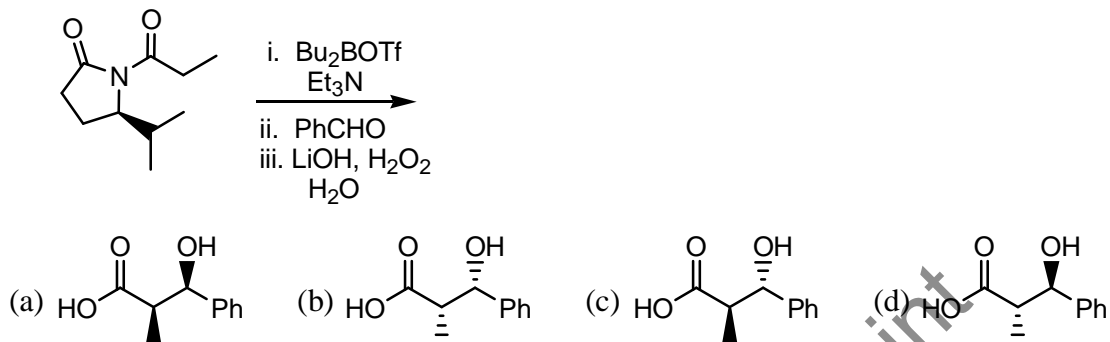


- (a) Claisen followed by Mannich reaction      (b) aza-Cope followed by Mannich reaction  
 (c) Claisen followed by aza-aldol reaction      (d) aza-Cope followed by aza-aldol reaction
94. The intermediate A and the major product B formed in the following reaction is

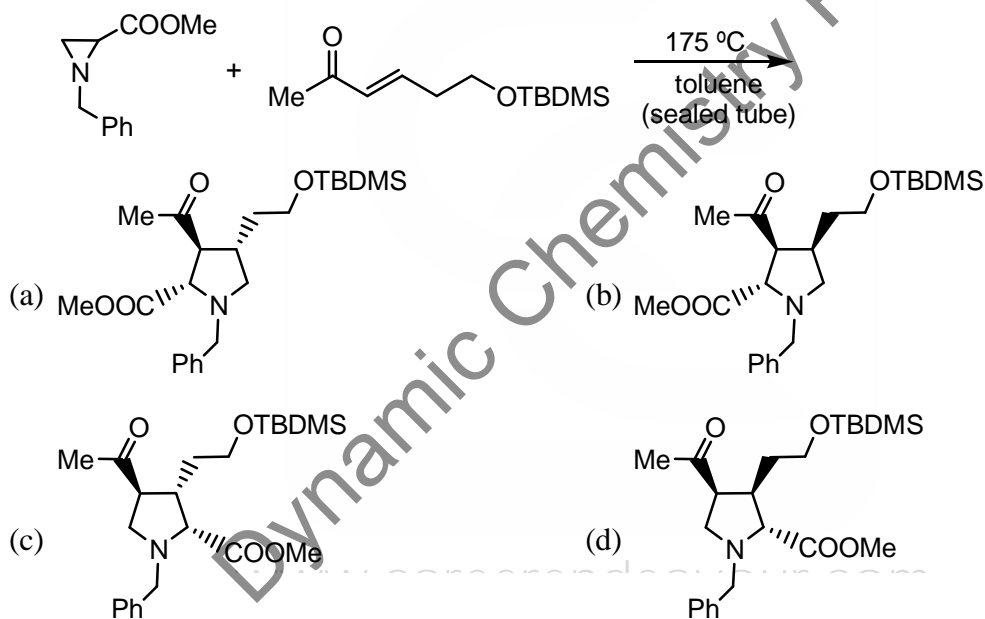




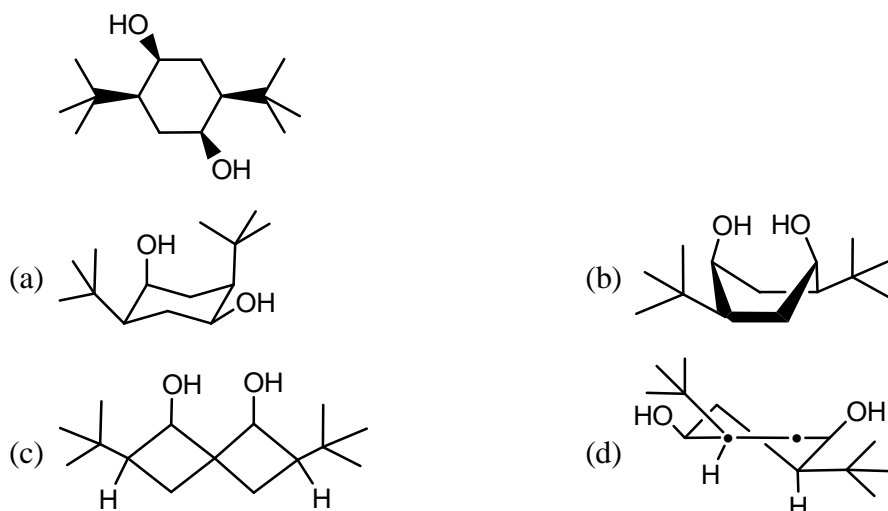
95. The major product formed in the following reaction is



96. The major product formed in the following reaction is



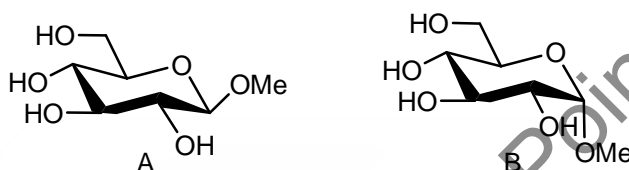
97. The most stable conformation for the following compound is



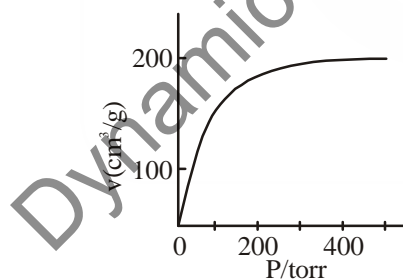
98. The correct structure of the compound based on the following characteristic spectral data is  
 IR:  $1736\text{ cm}^{-1}$   
 $^1\text{H NMR}$ :  $\delta$  3.59 (s, 3H), 3.32 (t, 2H), 2.25 (t, 2H), 1.85-1.75 (m, 2H), 1.73-1.62 (m, 2H)  
 $^{13}\text{C NMR}$ :  $\delta$  174.0, 51.0, 32.9, 32.9, 32.8, 31.0, 23.0



99. The major product formed in the reaction of D-glucose with  $\text{ZnCl}_2$  in MeOH is a methyl glucopyranoside (A or B). The structure of this product and the molecular orbital interaction present between ring-oxygen and the anomeric C-O bond responsible for its stability, respectively, are



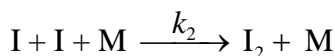
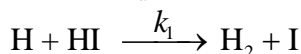
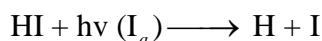
- (a) A and  $n \rightarrow \sigma^*$     (b) A and  $n \rightarrow \sigma$     (c) B and  $n \rightarrow \sigma^*$     (d) B and  $n \rightarrow \sigma$
100. Among the following correct statement for nucleic acids is  
 (a) Uracil is present in DNA  
 (b) Uracil is present in RNA  
 (c) Phosphorylation in RNA is at 2' and 5' positions  
 (d) Normally three hydrogen bonds stabilize A-T base pair
101. The figure below depicts an adsorption isotherm of  $\text{O}_2$  on charcoal at 90 K.



- At a pressure 25 torr, only 10% of charcoal sites are occupied by  $\text{O}_2$ . Therefore, the ratio of adsorption to desorption rate constants (in  $\text{torr}^{-1}$ ) is close to  
 (a) 0.003    (b) 0.004    (c) 0.006    (d) 0.015
102. Polonium is the only metal known to exist in a simple cubic lattice form. The density of polonium at  $0^\circ\text{C}$  is measured to be  $10.00\text{ g/cm}^3$ . The atomic radius of polonium would then be (assume the mass of a polonium atom =  $2.7 \times 10^{-22}\text{ g}$ )  
 (a)  $1.1\text{ \AA}$     (b)  $1.9\text{ \AA}$     (c)  $1.5\text{ \AA}$     (d)  $2.3\text{ \AA}$
103. The specific conductance of a solution is  $0.176\text{ }\Omega^{-1}\text{cm}^{-1}$ . If the cell constant is  $0.255\text{ cm}^{-1}$ , the conductance ( $\Omega^{-1}$ ) of that solution is  
 (a) 1.449    (b) 0.690    (c) 0.045    (d) 0.431



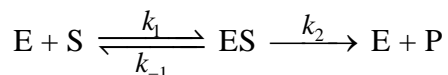
104. Photochemical decomposition of HI takes place with the following mechanism



Considering hydrogen (H) and iodine (I) atoms as intermediates, the rate of removal of HI is

- (a)  $I_a/2$                       (b)  $I_a$                       (c)  $2I_a$                       (d)  $I_a^2$

105. In an enzyme-catalysed reaction



$k_2 = 3.42 \times 10^4 \text{ s}^{-1}$ . If  $[E]_0 = 1 \times 10^{-2} \text{ mol dm}^{-3}$ , the magnitude of maximum velocity and turn over number using Michaelis-Menten kinetics are

- (a)  $3.42 \times 10^2 \text{ mol dm}^{-3} \text{ s}^{-1}; 3.42 \times 10^4 \text{ s}^{-1}$       (b)  $3.42 \times 10^6 \text{ mol dm}^{-3} \text{ s}^{-1}; 3.42 \times 10^4 \text{ s}^{-1}$   
 (c)  $3.42 \times 10^4 \text{ mol dm}^{-3} \text{ s}^{-1}; 3.42 \times 10^6 \text{ s}^{-1}$       (d)  $3.42 \times 10^4 \text{ mol dm}^{-3} \text{ s}^{-1}; 3.42 \times 10^2 \text{ s}^{-1}$

106. Arrhenius equations for two chemical reactions are:  $k_1 = A_1 e^{-E_1/RT}$ ,  $k_2 = A_2 e^{-E_2/RT}$ . If  $E_1 > E_2$ , then at a given temperature  $T$ ,

- (a)  $\frac{k_1}{k_2} < \frac{A_1}{A_2}$                       (b)  $\frac{k_2}{k_1} < \frac{A_2}{A_1}$                       (c)  $k_1 k_2 > A_1 A_2$                       (d)  $k_1 + k_2 > A_1 + A_2$

107. The fugacity of a real gas is less than the pressure (P) of an ideal gas at the same temperature (T) only when ( $T_b$  is the Boyle temperature of the real gas)

- (a) high  $P, T < T_b$       (b) low  $P, T < T_b$       (c) high  $P, T > T_b$       (d) low  $P, T > T_b$

108. For the reaction  $\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ , the equilibrium constant  $K_p$  depends on the degree of dissociation  $\alpha$  ( $\alpha \ll 1$ ) and total pressure P as

- (a)  $K_p \propto \alpha^2 P$       (b)  $K_p \propto \alpha^{3/2} P^{1/2}$       (c)  $K_p \propto \alpha^{1/2} P^{3/2}$       (d)  $K_p \propto \alpha P^2$

109. The minimum work required by an engine to transfer 5 J of heat from a reservoir at 100 K to one at 300 K is

- (a) 5 J                      (b) 10 J                      (c) 15 J                      (d) 20 J

110. The correct relation involving symmetry operations

- (a)  $S_4^2 = S_2$                       (b)  $\sigma(xz)\sigma(yz) = C_2(x)$   
 (c)  $S_4^3 = C_4^3$                       (d)  $S_6^3 = S_2$

111. A polydisperse polymer sample has ten molecules of molar mass 20,000  $\text{g mol}^{-1}$  and fifteen molecules of molar mass 10,000  $\text{g mol}^{-1}$ . The number-average molar mass ( $\text{g mol}^{-1}$ ) ( $\bar{M}_n$ ) of the sample is

- (a) 13,000                      (b) 14,000                      (c) 15,000                      (d) 16,000

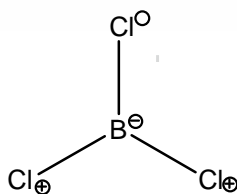
112. Consider a system of three particles which can occupy energy levels with energy 0,  $\epsilon$  and  $2\epsilon$ , such that the total energy  $E = 4\epsilon$ . Cases A, B and C correspond to spin  $\frac{1}{2}$  fermions, spin 0 bosons, and classically distinguishable particles, respectively. The correct ordering of entropy is  
 (a)  $S_A > S_B > S_C$       (b)  $S_B > S_A > S_C$       (c)  $S_C > S_B > S_A$       (d)  $S_C > S_A > S_B$
113. For a point group, an incomplete character table is given below with one irreducible representation missing

	E	$2C_3$	$3\sigma_v$
$A_1$	1	1	1
–	–	–	–
E	2	-1	0

The Mulliken symbol and characters of the missing representation are

- (a)  $A'_1$  1 -1 1      (b)  $B_1$  1 -1 -1      (c)  $A_2$  1 1 -1      (d)  $B_2$  1 -1 1
114. Given below is a specific vibrational mode of  $\text{BCl}_3$  with  $\oplus$  and  $\ominus$  denoting movements of the respective atoms above and below the plane of the molecule respectively. The irreducible representation of the vibrational mode and its *IR* / Raman activity are

$D_{3h}$	E	$2C_3$	$3C_2$	$\sigma_h$	$2S_6$	$3\sigma_v$		
$A_1$	1	1	1	1	1	1		$x^2 + y^2, z^2$
$A_2$	1	1	-1	1	1	-1	$R_z$	
$E'$	2	-1	0	2	-1	0	$(x, y)$	$(x^2 - y^2, xy)$
$A_1''$	1	1	1	-1	-1	-1		
$A_2''$	1	1	-1	-1	-1	1	$z$	
$E''$	2	-1	0	-2	1	0	$(R_x, R_y)$	$(xz, yz)$



- (a)  $A'_2$ ; neither *IR* nor Raman active      (b)  $E'$ ; both *IR* and Raman active  
 (c)  $A'_1$ ; Raman active      (d)  $A''_2$ ; *IR* active
115. The first excited state ( $^2P_{1/2}$ ) of fluorine lies at an energy of  $400 \text{ cm}^{-1}$  above the ground state ( $^2P_{3/2}$ ). The fraction of Fluorine atoms in the first excited state at  $k_B T = 420 \text{ cm}^{-1}$  is close to  
 (a)  $\frac{1}{1+e}$       (b)  $\frac{1}{2+e}$       (c)  $\frac{1}{1+4e}$       (d)  $\frac{1}{1+2e}$

116. The two limiting wavefunctions of the ground state of  $\text{H}_2^+$  molecular ion, as the internuclear separation  $R$  goes to (i)  $\infty$  (infinity) and (ii) 0 (zero) are ( $1s_a, 1s_b$  are  $1s$ -orbital wave functions of hydrogen atoms  $a$  and  $b$  in  $\text{H}_2^+$ , and  $1s_{\text{He}}$  is the wave function of the  $1s$  orbital of  $\text{He}^+$ )
- (a) (i)  $1s_a(r)$ ; (ii)  $1s_b(r)$                                  (b) (i)  $1s_b(r)$ ; (ii)  $1s_a(r)$   
(c) (i)  $1s_a(r_1)1s_b(r_2)$ ; (ii)  $1s_{\text{He}}(r_1)1s_{\text{He}}(r_2)$    (d) (i)  $1s_a(r) + 1s_b(r)$ ; (ii)  $1s_{\text{He}}(r)$
117. For a certain magnetic field strength, a free proton spin transition occurs at 700 MHz. Keeping the magnetic field strength constant the  $^{14}\text{N}$  nucleus will resonate at ( $g(p) \approx 5.6$  and  $g(^{14}\text{N}) \approx 0.4$ )
- (a) 700 MHz                 (b) 400 MHz                 (c) 200 MHz                 (d) 50 MHz
118. The first electronic absorption band maximum of a polar and relatively rigid aromatic molecule appears at 310 nm but its fluorescence maximum in acetonitrile solution appears with a large Stokes shift at 450 nm. The most likely reason for the Stokes shift is
- (a) large change in molecular geometry in the excited state  
(b) increase in dipole moment of the molecule in the excited state  
(c) decrease in polarizability of the molecule in the excited state  
(d) lowered interaction of the excited molecule with polar solvent
119. The un-normalized radial wave function of a certain hydrogen atom eigenstate is  $(6r - r^2)\exp(-r/3)$ . A possible angular part of the eigenstate is
- (a)  $5\cos^3\theta - 3\cos\theta$    (b)  $3\cos^2\theta - 1$    (c)  $\cos\theta$                                  (d) 1
120. Given a trial wave function  $\psi_t = C_1\phi_1 + C_2\phi_2$ , and the Hamiltonian matrix elements,  $\int \phi_1^* H \phi_1 d\nu = 0$ ,  $\int \phi_1^* H \phi_2 d\nu = 2.5$ ,  $\int \phi_2^* H \phi_2 d\nu = 12.0$ , the variationally determined ground state energy is
- (a) -0.52                         (b) -0.50                         (c) 12.50                         (d) 12.52