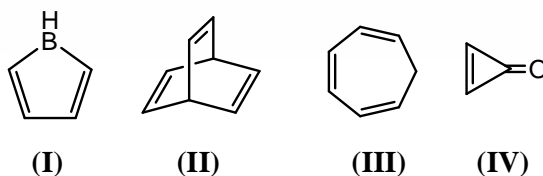


DEC. 2014 (II)
CHEMICAL SCIENCES
BOOKLET [A]

PART – B

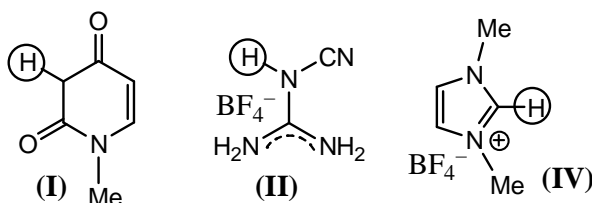
21. The reaction between SbF_5 and two equivalents of HF leads to the formation of
 (a) $\text{H}_2\text{SbF}_3 + 2\text{F}_2$ (b) $\text{HSbF}_2 + 3\text{F}_2$ (c) $\text{SbF}_3 + \text{H}_2 + 2\text{F}_2$ (d) $[\text{SbF}_6]^- [\text{H}_2\text{F}]^+$
22. The δ -bond is formed via the overlap of
 (a) $d_x^2 - y^2$ and $d_x^2 - y^2$ orbitals (b) d_{xz} and d_{xz} orbitals
 (c) d_{xy} and d_{xy} orbitals (d) d_{yz} and d_{yz} orbitals
23. Among F^- , Na^+ , O^{2-} and Mg^{2+} ions, those having the highest and the lowest ionic radii respectively are
 (a) O^{2-} and Na^+ (b) F^- and Mg^{2+} (c) O^{2-} and Mg^{2+} (d) Mg^{2+} and O^{2-}
24. The extent of π -electron conjugation in macrocyclic rings of (1) heme, (2) coenzyme B_{12} and (3) chlorophyll follows the order
 (a) (1) > (3) > (2) (b) (1) > (2) > (3) (c) (3) > (1) > (2) (d) (2) \approx (1) > (3)
25. The correct order of the retention of cations on a sulfonated cation exchange resin column is
 (a) $\text{Ag}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ (b) $\text{K}^+ > \text{Na}^+ > \text{Ag}^+ > \text{Li}^+$
 (c) $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Ag}^+$ (d) $\text{Li}^+ > \text{Na}^+ > \text{Ag}^+ > \text{K}^+$
26. In a polarographic measurement, (aqueous KCl solution used as supporting electrolyte) an applied potential more than +0.4 V, results mainly in the formation of
 (a) Hg^{I} (b) Hg^{II} (c) Cl_2 (d) O_2
27. The correct order of the isomeric shift in Mossbauer spectra (^{57}Fe source) of iron compounds is
 (a) $\text{Fe(II)} > \text{Fe(III)} > \text{Fe(IV)}$ (b) $\text{Fe(III)} > \text{Fe(II)} > \text{Fe(IV)}$
 (c) $\text{Fe(IV)} > \text{Fe(III)} > \text{Fe(II)}$ (d) $\text{Fe(IV)} > \text{Fe(II)} > \text{Fe(III)}$
28. The hapticities 'x' and 'y' of the arene moieties in the diamagnetic complex $[(\eta^x - \text{C}_6\text{H}_6)\text{Ru}(\eta^y - \text{C}_6\text{H}_6)]$ respectively are
 (a) 6 and 6 (b) 4 and 4 (c) 4 and 6 (d) 6 and 2
29. The rate of the reaction $\text{Ni(CO)}_4 + \text{PPh}_3 \xrightarrow{h\nu} [\text{Ni(CO)}_3(\text{PPh}_3)] + \text{CO}$ depends on
 (a) Concentration of both the reactants (b) Concentration of Ni(CO)_4 only
 (c) Concentration of PPh_3 only (d) The steric bulk of PPh_3
30. The product of the reaction of propene, CO and H_2 in the presence of $\text{CO}_2(\text{CO})_8$ as a catalyst is
 (a) Butanoic acid (b) Butanal (c) 2-butanone (d) Methylpropanoate
31. The S and L values for ^{15}N atom respectively, are
 (a) $\frac{1}{2}$ and 1 (b) $\frac{1}{2}$ and 0 (c) 1 and 0 (d) $\frac{3}{2}$ and 0

32. The point group symmetries for $trans\text{-}[\text{Cr}(\text{en})_2\text{F}_2]^+$ and $[\text{TiCl}_6]^{3-}$, respectively, are
 (a) D_{4d} and D_{3d} (b) D_{3d} and D_{4d} (c) D_{4h} and D_{3h} (d) D_{3h} and D_{4h}
33. $\text{Co}_4(\text{CO})_{12}$ adopts the
 (a) *closo*-structure (b) *nido*-structure (c) *arachno*-structure (d) *hypho*-structure
34. Reductive elimination step in hydrogenation of alkenes by Wilkinson catalyst results in (neglecting solvent in coordination sphere of Rh)
 (a) T-shaped $[\text{Rh}(\text{PPh}_3)_2\text{Cl}]$ (b) Trigonal-planar $[\text{Rh}(\text{PPh}_3)_2\text{Cl}]^{2+}$
 (c) T-shaped $[\text{Rh}(\text{H})(\text{PPh}_3)\text{Cl}]^+$ (d) Trigonal-planar $[\text{Rh}(\text{H})(\text{PPh}_3)_2]$
35. In the following reaction $[\text{PtCl}_4]^{2-} + \text{NO}_2^- \rightarrow \text{A} \xrightarrow{\text{NH}_3} \text{B}$, compound B is
 (a) *trans*- $[\text{PtCl}_2(\text{NO}_2)(\text{NH}_3)]^-$ (b) *cis*- $[\text{PtCl}_2(\text{NO}_2)(\text{NH}_3)]^-$
 (c) *trans*- $[\text{PtCl}_2(\text{NH}_3)_2]$ (d) *cis*- $[\text{PtCl}_2(\text{NO}_2)_2]^{2-}$
36. The number of histidine amino acid nitrogen atoms coordinated to bimetallic active site of oxyhemocyanin, and oxyhemerythrin, respectively, are
 (a) 2, 3 and 3, 3 (b) 3, 3 and 2, 3 (c) 3, 3 and 2, 2 (d) 2, 4 and 3, 2
37. Identify correct statements for mercury as an environment pollutant.
 A. Carbanionic biomethylation converts it to MeHg^+
 B. Thiol group of cysteine has strong affinity for mercury
 C. Mercury containing industrial catalyst release caused Minamata disaster
 The correct answer is
 (a) A and B (b) A and C (c) B and C (d) A, B and C
38. The configurations of carbon atoms C3 and C4 in D-ribose, respectively, are
 (a) R and S (b) S and R (c) R and R (d) S and S
39. The compound that is antiaromatic is



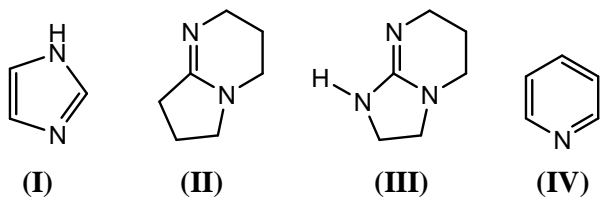
- (a) I (b) II (c) III (d) IV

40. The increasing order of pK_a values of the circled hydrogens in the following compounds is



- (a) $\text{I} < \text{II} < \text{III}$ (b) $\text{I} < \text{III} < \text{II}$ (c) $\text{II} < \text{I} < \text{III}$ (d) $\text{II} < \text{III} < \text{I}$

41. The decreasing order of basicity of the following compounds is



- (a) I > II > III > IV (b) IV > I > II > III (c) III > II > I > IV (d) IV > III > II > I

42. In the most stable conformation of neomenthol, stereochemical orientation of the three substituents on the cyclohexane ring are

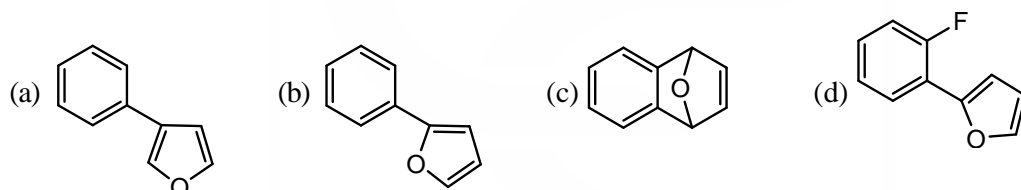
- (a) OH : equatorial; *i*-Pr : equatorial and Me : equatorial
 (b) OH : axial; *i*-Pr : equatorial and Me : equatorial
 (c) OH : equatorial; *i*-Pr : equatorial and Me : axial
 (d) OH : equatorial; *i*-Pr : axial and Me : equatorial

43. The absolute configurations of the chiral centres of starting ketone in the following reaction is

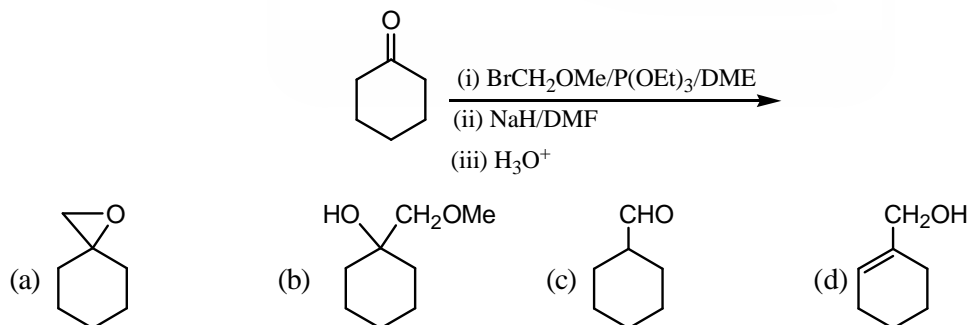


- (a) 3R, 6S (b) 3S, 6S (c) 3R, 6R (d) 3S, 6R

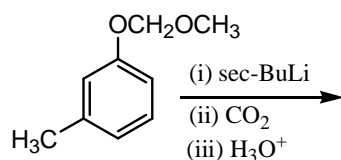
44. The reaction of 1-bromo-2-fluorobenzene with furan in the presence of one equivalent of Mg gives

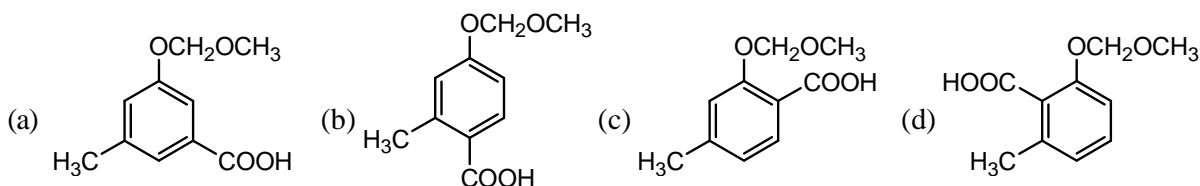


45. The product for the following sequence of reactions is

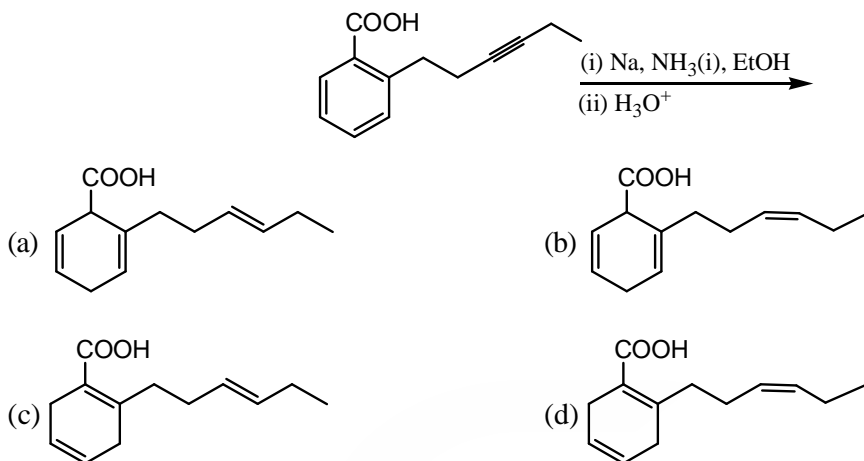


46. The major product formed in the following reaction is

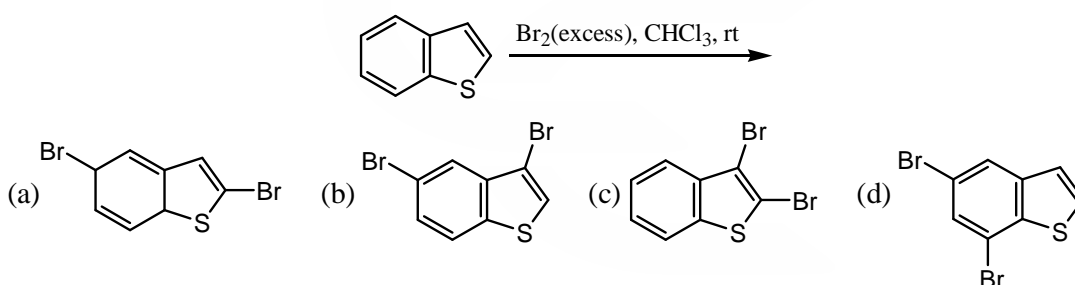




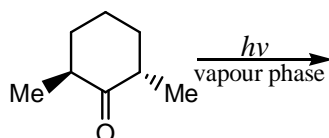
47. The major product of the following reaction is



48. The major product of the following reaction is

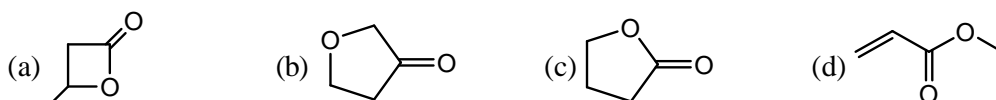


49. The cyclic product(s) of the following photochemical reaction is(are)

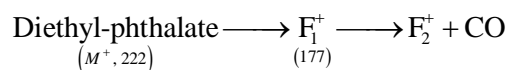


- (a) only *cis*-1, 2-dimethylcyclopentane
 (b) only *trans*-1, 2-dimethylcyclopentane
 (c) a mixture of *cis*- and *trans*-1, 2-dimethylcyclopentanes
 (d) only 2, 6-dimethylcyclohexanol

50. A compound with molecular formula $C_4H_6O_2$ shows band at 1770 cm^{-1} in IR spectrum and peaks at 178, 68, 28 and 22 ppm in ^{13}C NMR spectrum. The correct structure of the compound is

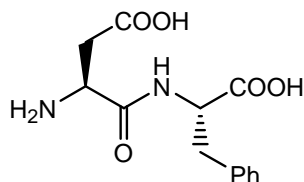


51. The mass of metastable ion produced due to decomposition of F_1^+ in the following mass fragmentation sequence is



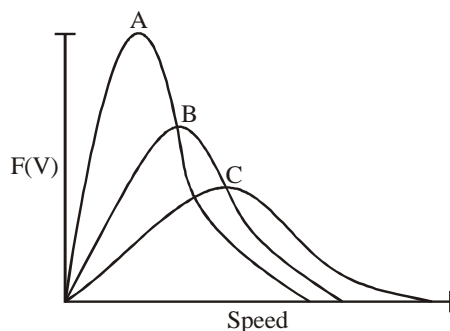
- (a) 141.2 (b) 125.4 (c) 45.0 (d) 210.2

52. The ratio of the relative intensities of the carbon signals in the first order ^{13}C NMR spectrum of CD_3Cl is
 (a) 1:4:6:4:1 (b) 1:3:3:1 (c) 1:6:15:20:15:6:1 (d) 1:3:6:7:6:3:1
53. The biosynthetic precursor of abietic acid is
 (a) Shikimic acid (b) Mevalonic acid (c) Chorismic acid (d) Cinnamic acid
54. The amino acid constituents of artificial sweetener given below are



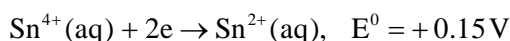
- (a) D-Glutamic acid and L-phenylglycine (b) L-Glutamic acid and L-phenylalanine
 (c) L-Aspartic acid and L-phenylalanine (d) L-Aspartic acid and L-tyrosine
55. Bond lengths of homonuclear diatomic molecules can be determined with the help of both
 (a) Rotational and vibrational spectroscopy.
 (b) Rotational and rotational Raman spectroscopy.
 (c) Rotational Raman and electronic spectroscopy.
 (d) Vibrational and electronic spectroscopy.
56. If the component of the orbital angular momentum along the molecular axis of a heteronuclear diatomic molecule is non-zero, the rotational-vibrational spectrum will show
 (a) P and R branches only. (b) P and Q branches only.
 (c) Q and R branches only. (d) All the P, Q and R branches.
57. For a particle of mass m confined in a box of length L , assume $\Delta x = L$. Assume further that $\Delta p(\text{min}) = \langle p^2 \rangle^{1/2}$. Use the uncertainty principle to obtain an estimate of the energy of the particle. The value will be
 (a) $\frac{h^2}{(8mL^2)}$ (b) $\frac{\hbar^2}{(8mL^2)}$ (c) $\frac{h^2}{(32mL^2)}$ (d) $\frac{h^2}{(2mL^2)}$

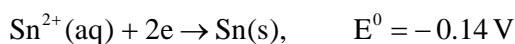
58.



Identify the speed distribution functions of Ne, Ar, and Kr with the curves in the figure above

- (a) Ne-A, Ar-B, Kr-C (b) Ne-B, Ar-C, Kr-A
 (c) Ne-C, Ar-B, Kr-A (d) Ne-C, Ar-A, Kr-B
59. For the cell reaction, $\text{Sn}(s) + \text{Sn}^{4+}(\text{aq}) \rightleftharpoons 2\text{Sn}^{2+}(\text{aq})$, separate electrode reactions could be written with the respective standard electrode potential data at 25°C as

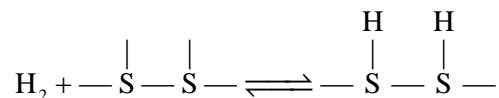




When RT/F is given as 25.7 mV, logarithm of the equilibrium constant ($\ell n K$) is

- (a) 22.6 (b) 226 (c) 2.26 (d) 2.26×10^{-1}

60. Hydrogen is adsorbed on many metal surfaces by dissociation (S represents a surface site):



If the pressure of H_2 (p) is small, the fraction of the surface covered by hydrogen is proportional to

- (a) p (b) p^2 (c) $p^{1/2}$ (d) $p^{3/2}$

61. For a process in a closed system, temperature is equal to

- (a) $\left(\frac{\partial H}{\partial P}\right)_S$ (b) $-\left(\frac{\partial A}{\partial V}\right)_T$ (c) $\left(\frac{\partial G}{\partial P}\right)_T$ (d) $\left(\frac{\partial H}{\partial S}\right)_P$

62. The exact differential df of a state function $f(x, y)$, among the following is

- (a) $x dy$ (b) $dx - \frac{x}{y} dy$ (c) $y dx - x dy$ (d) $\frac{1}{y} dx - \frac{x}{y^2} dy$

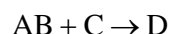
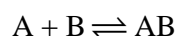
63. The angular momentum operator $L_z = -i\hbar \frac{\partial}{\partial \phi}$ has eigen functions of the form $\exp[iA\phi]$. The condition that a full rotation leaves such an eigen function unchanged is satisfied for all the values of A .

- (a) $0, \pm \frac{1}{3}, \pm \frac{2}{3}, \pm 1, \pm \frac{4}{3}, \dots$ (b) $0, \pm 1, \pm 2, \pm 3, \dots$
(c) $0, \pm \frac{1}{2}, \pm 1, \pm \frac{3}{2}, \dots$ (d) $0, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$

64. X-ray diffraction does not give any structural information for

- (a) Metallic solids (b) Ionic solids (c) Molecular solids (d) Amorphous solids

65. A reaction $A + B + C \rightarrow D$ follows the mechanism



in which first step remains essentially in equilibrium. If ΔH is the enthalpy change for the first reaction and E_0 is the activation energy for the second reaction, the activation energy of the overall reaction will be given by

- (a) E_0 (b) $E_0 - \Delta H$ (c) $E_0 + \Delta H$ (d) $E_0 + 2\Delta H$

66. Wavelength (λ in nm) of the Lyman series for an one-electron ion is in the range $24 \leq \lambda \leq 30$. The ionization

energy of the ion will be closest to $\left(1 \int = \frac{10^{19}}{1.6} \text{ eV} \right)$

- (a) 32 eV (b) 42 eV (c) 52 eV (d) 62 eV

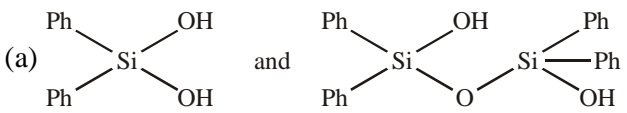
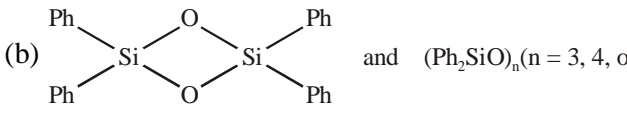
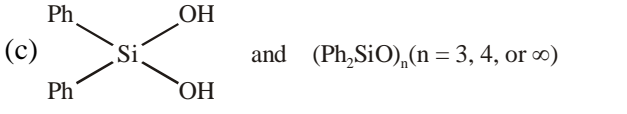
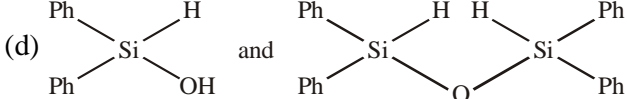
67. A sample experiment revealed that PVC formed in the medium has $\langle M_n \rangle = 13$, and $\langle M_w \rangle = 16$, where $\langle M_n \rangle$ stands for the number average molar mass and $\langle M_w \rangle$ for the weight average molar mass. The variance of M_n will then be

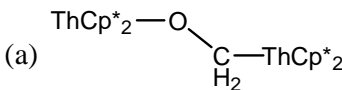
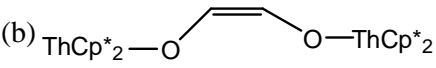
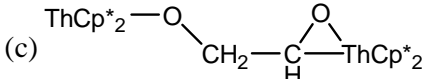
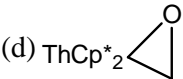
- (a) 39 (b) 3 (c) 1 (d) 87

68. For an enzyme-substrate reaction, a plot between $\frac{1}{v}$ and $\frac{1}{[S]_0}$ yields a slope of 40s. If the enzyme concentration is 2.5 μM , then the catalytic efficiency of the enzyme is
 (a) 40 $\text{Lmol}^{-1}\text{s}^{-1}$ (b) 10^{-4} $\text{Lmol}^{-1}\text{s}^{-1}$ (c) 10^7 $\text{Lmol}^{-1}\text{s}^{-1}$ (d) 10^4 $\text{Lmol}^{-1}\text{s}^{-1}$
69. For a polydispersed macromolecular colloid, osmometry gives
 (a) Weight-average molecular weight
 (b) Number-average molecular weight
 (c) Both weight-average and number average molecular weights
 (d) Viscosity-average molecular weight
70. 10 ml of 0.02 M NaOH is added to 10 ml of 0.02 M acetic acid ($\text{pK}_a = 4.75$). The pH of the solution will be closest to
 (a) 7.0 (b) 8.4 (c) 5.6 (d) 9.6

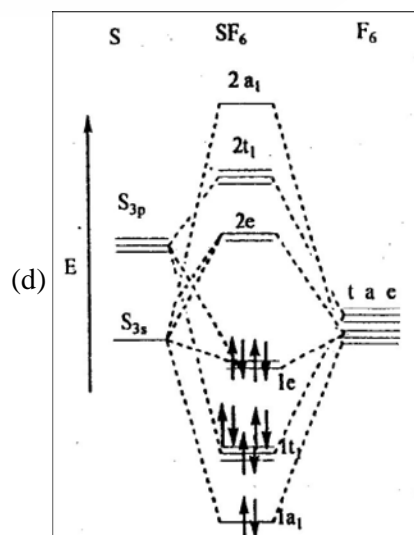
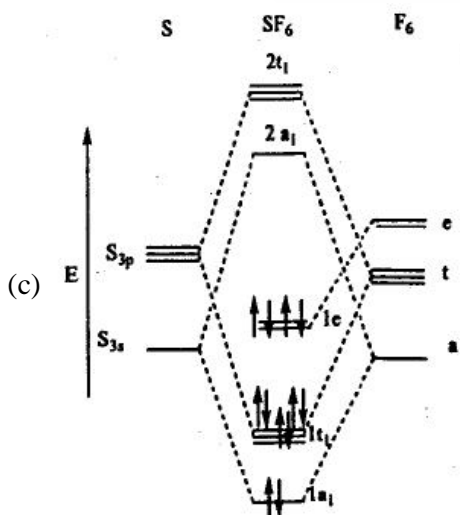
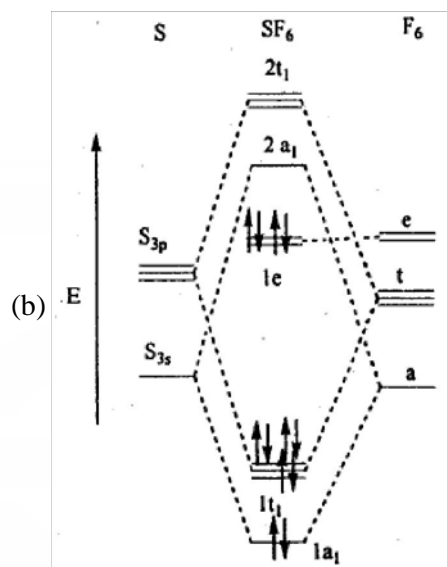
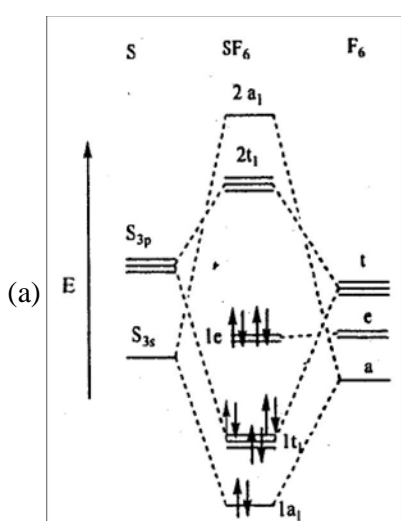
PART – C

71. Which of the following will result in deviation from Beer's law:
 (A) Change in refractive index of medium,
 (B) Dissociation of analyte on dilution,
 (C) Polychromatic light
 (D) Path length of cuvette
 (a) A, B and C (b) B, C and D (c) A, C and D (d) A, B and D
72. The gas commonly used in generating plasma in Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES) is
 (a) Argon (b) Carbon dioxide (c) Nitrous oxide (d) hydrogen
73. The geometric cross-section (in barn) of a nucleus $A = 125$, $r_0 = 1.4 \times 10^{-15}$ m approximately is
 (a) 1.05 (b) 1.54 (c) 2.05 (d) 2.54
74. The number of stereoisomers of *trans*- $[\text{CoCl}_2(\text{triethylenetetramine})]\text{Br}$ is
 (a) One (b) Two (c) Three (d) Four
75. Under physiological condition, oxygen is binding to deoxyhemoglobin and deoxymyoglobin, the binding curve and its pH dependence, respectively, are
 (a) Sigmoidal and pH dependent; hyperbolic and pH independent
 (b) Hyperbolic and pH independent; sigmoidal and pH dependent
 (c) Sigmoidal and pH independent; hyperbolic and pH dependent
 (d) Hyperbolic and pH dependent; sigmoidal and pH independent
76. Match the metalloproteins in column-A with their function in column-B
- | Column-A | Column-B |
|----------------------------------|-----------------------------------------------------------|
| I. Oxyhemocyanin | A. hydrolysis of C-terminal peptide bond |
| II. Carbonic anhydrase | B. methylation |
| III. Cytochrome P ₄₅₀ | C. Conversion of CO_2 to H_2CO_3 |
| IV. Carboxy-peptidase A | D. oxidation of alkene |
| | E. oxygen storage |
| | F. oxygen transport |
- The correct answer is
 (a) I – F; II – C; III – D; IV – A (b) I – E; II – C; III – A; IV – F
 (c) I – F; II – B; III – C; IV – A (d) I – E; II – D; III – C; IV – A

77. $\text{Na}[(\eta^5 - \text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ reacts with Br_2 to give A. Reaction of A with LiAlH_4 results in B. The proton NMR spectrum of B consists of two singlets of relative intensity 5:1. Compounds A and B, respectively, are
- (a) $(\eta^5 - \text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ and $(\eta^5 - \text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}$
 (b) $(\eta^4 - \text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}_2$ and $(\eta^4 - \text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{HBr}$
 (c) $(\eta^5 - \text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ and $(\eta^4 - \text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{H})_2$
 (d) $(\eta^5 - \text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ and $(\eta^5 - \text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{HBr}$
78. The compound that undergoes oxidative addition reaction in presence of H_2 is
- (a) $[\text{Mn}(\text{CO})_5]^-$
 (b) $[(\eta^5 - \text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]^-$
 (c) $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$
 (d) $[(\eta^5 - \text{C}_5\text{H}_5)_2\text{ReH}]$
79. ^1H NMR spectrum of free benzene shows a peak at ~ 7.2 ppm. The expected chemical shift (in ppm) of C_6H_6 ligand in ^1H NMR spectrum of $[(\eta^6 - \text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3]$ and the reason for it, if an, is/are
- (a) 4.5 ; disruption of ring current
 (b) 9.0 ; inductive effect
 (c) 7.2
 (d) 2.5 ; combination of inductive effect and disruption of ring current
80. An aqueous solution of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ complex is pale pink in colour. The probable reasons for it are
- (A) Presence of $^6\text{A}_{1g}$ ground state
 (B) Disallowed transition by spin selection rule
 (C) Presence of $^2\text{T}_{2g}$ ground state
 (D) Charge transfer transition
- The correct answer is
- (a) A and B (b) A and C (c) B and C (d) C and D
81. The reaction of phosphorus trichloride with phenyllithium in 1:3 molar ratio yields product 'A', which on further treatment with methyl iodide produces 'B'. The reaction of B with $^n\text{BuLi}$ gives product 'C'. The products A, B and C, respectively, are
- (a) $[\text{PPh}_4]\text{Cl}$, $[\text{Ph}_2\text{P}=\text{CH}_2]\text{I}$, $\text{Ph}_2\text{P}(^n\text{Bu})$
 (b) PPh_3 , $[\text{Ph}_3\text{PI}]\text{Me}$, $\text{Ph}_2\text{P}(^n\text{Bu})_3$
 (c) PPh_3 , $[\text{Ph}_3\text{PMe}]\text{I}$, $\text{Ph}_3\text{P}=\text{CH}_2$
 (d) $[\text{PPh}_4]\text{Cl}$, $[\text{Ph}_3\text{P}=\text{CH}_2]\text{I}$, $[\text{Ph}_3\text{P}(^n\text{Bu})]\text{Li}$
82. The reaction between diphenyldichlorosilane and water in 1:2 molar ratio gives product A which on heating above 100°C yields a cyclic or polymeric product B. The products A and B respectively, are
- (a) 
 (b) 
 (c) 
 (d) 

83. According to Wade's rule, anion $C_2B_9H_{12}^-$ adopts
 (a) *closo*-structure (b) *nido*-structure (c) *arachno*-structure (d) *hypho*-structure
84. The final product in the reaction of $[Cp^*_2 ThH]$ with CO in an equimolar ratio is
 (a)  (b) 
 (c)  (d) 
85. Hindered β -diketonates like dpmH (dpmH = dipivaloylmethane) are used for the separation of lanthanides because complexes formed with dpmH can be separated by
 (a) Gel permeation chromatography (b) Gas chromatography
 (c) Gel filtration chromatography (d) Ion exchange chromatography
86. Base hydrolysis of $[CoCl(NH_3)_5]^{2+}$ is an overall second order reaction, whereas that of $[Co(CN)_6]^{3-}$ is of first order. The rates depend in both cases solely on the concentrations of the cobalt complex. This may be due to
 (A) Presence of ionizable proton in $[CoCl(NH_3)_5]^{2+}$ but not in $[Co(CN)_6]^{3-}$
 (B) $S_N^1_{CB}$ mechanism in the case of $[CoCl(NH_3)_5]^{2+}$ only
 (C) $S_N^1_{CB}$ mechanism in the case of $[Co(CN)_6]^{3-}$ only
 (D) $S_N^1_{CB}$ mechanism in both the complexes
 Correct explanation(s) is/are
 (a) A and B (b) A and C (c) B only (d) A and D
87. A borane (X) is reacted with ammonia to give a salt of borohydride (Y). The ^{11}B NMR spectrum of Y consists of a triplet and a quintet. The borane X is
 (a) B_2H_6 (b) B_3H_9 (c) B_4H_8 (d) B_5H_9
88. The main products of the reaction of equimolar quantities of XeF_6 with $NaNO_3$ are
 (a) $XeOF_4$, NaF and NO_2F (b) XeO_2F_2 , NaF, NOF and F_2
 (c) $XeOF_4$, $NaNO_2$ and F_2 (d) XeF_4 , $NaNO_2$ and F_2O
89. The spin-only magnetic moment and the spectroscopic ground state term symbol of manganese center in $[MnF_6]^{3-}$ ion respectively, are
 (a) 4.9 BM and 5D (b) 4.9 BM and 4F (c) 3.9 BM and 3D (d) 4.9 BM and 3F
90. The three dimensional structure of compound $[Co(Co(NH_3)_4(OH)_2)_3]Br_6$ has
 (a) Twelve Co–O and twelve Co–N bonds (b) Ten Co–O and ten Co–N bonds
 (c) Fourteen Co–O and ten Co–N bonds (d) Twelve Co–O and ten Co–N bonds
91. The spin-only (μ_s) and spin plus orbital (μ_{s+L}) magnetic moments of $[CrCl_6]^{3-}$ are
 (a) 3.87 BM and 5.20 BM (b) 2.84 BM and 5.20 BM
 (c) 3.87 BM and 6.34 BM (d) 2.84 BM and 6.34 BM

92. Complexes $\text{HM}(\text{CO})_5$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{M}'(\text{CO})_3]_2$ obey the 18-electron rule. Identify M and M' and their ^1H NMR chemical shifts relative to TMS.
- (a) M = Mn, -7.5; M' = Cr, 4.10 (b) M = Cr, 4.10; M' = Mn, -7.5
 (c) M = V, -7.5; M' = Cr, 4.10 (d) M = Mn, 10.22; M' = Fe, 2.80
93. 12-Crown-4 binds with the alkali metal ions in the following order :
 $\text{Li}^+ \gg \text{Na}^+ > \text{K}^+ > \text{Cs}^+$. It is due to the
- (a) Right size of cation (b) Change in entropy being positive
 (c) Conformational flexibility of crown ether (d) Hydrophobicity of crown ether
94. The correct schematic molecular energy diagram for SF_6 molecule is



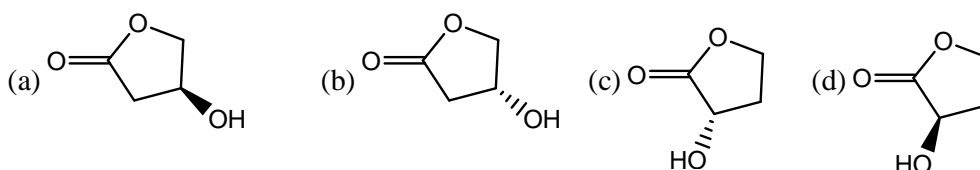
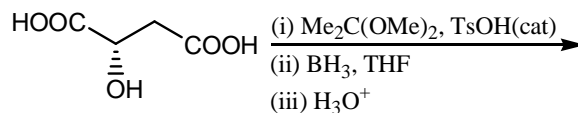
95. Gel permeation chromatography can be used to separate which of the following

- (A) Lanthanides
 (B) Alkaline earths
 (C) Fatty acids
 (D) Low molecular weight peptides

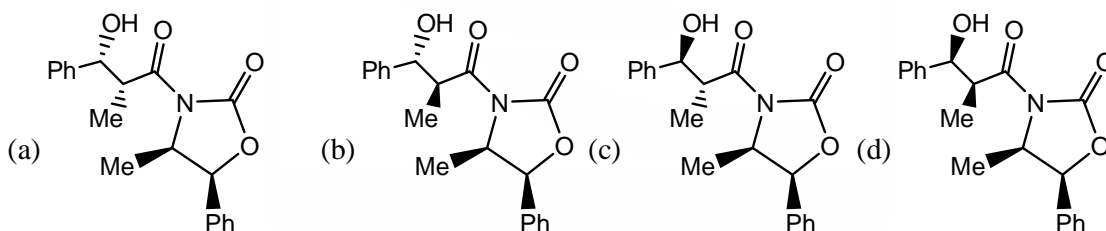
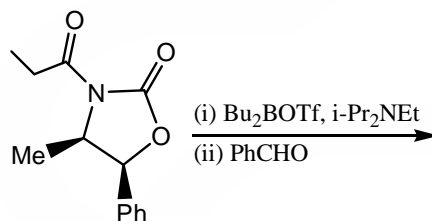
The correct answer is

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

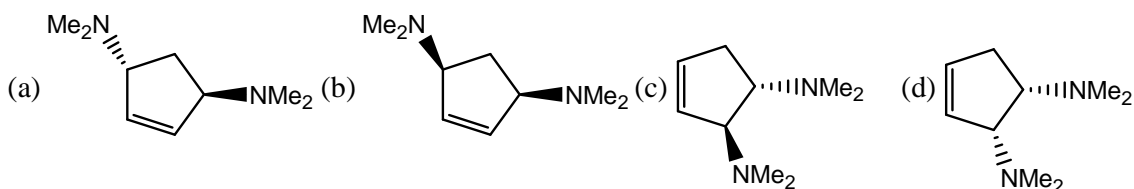
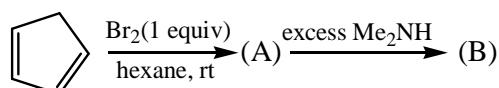
96. The major product formed in the following reaction is



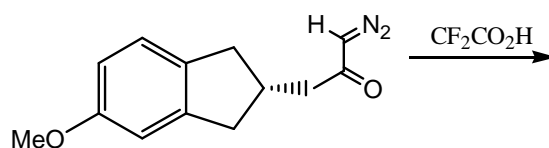
97. The major product formed in the following transformation is

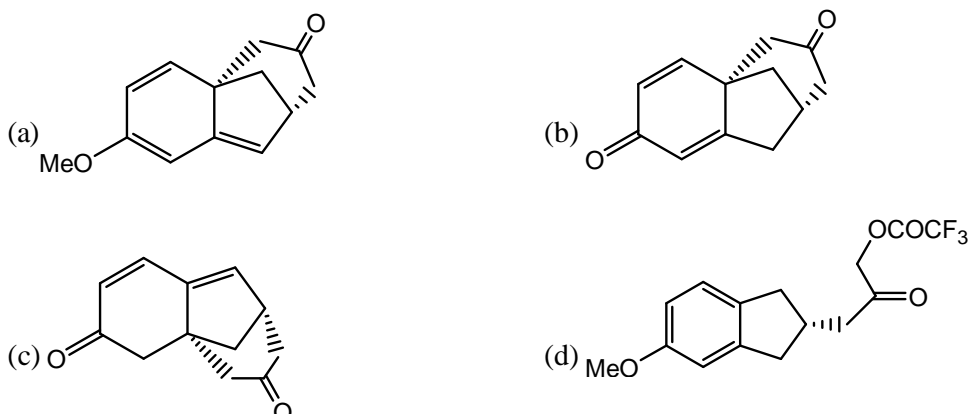


98. The product of B in the following reaction sequence is

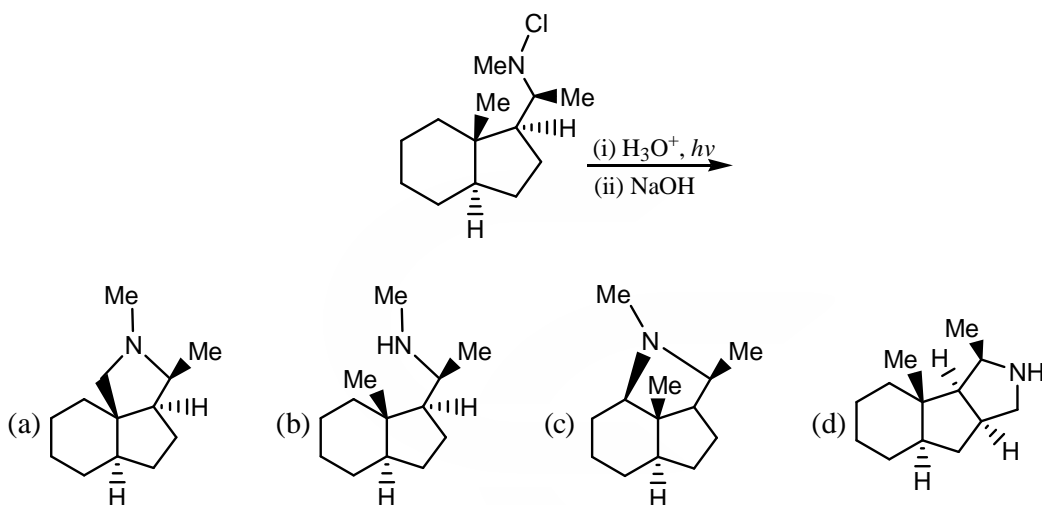


99. The major product of the following reaction is

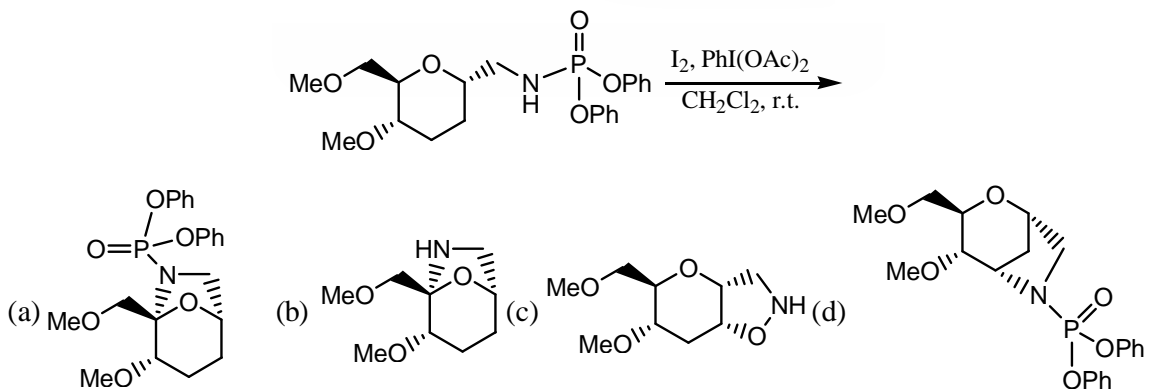




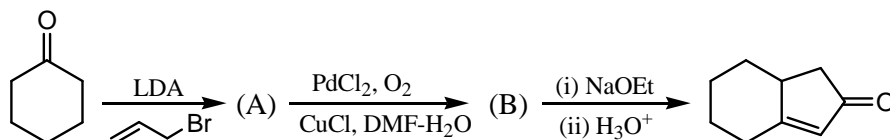
100. The major product of the following reactions is

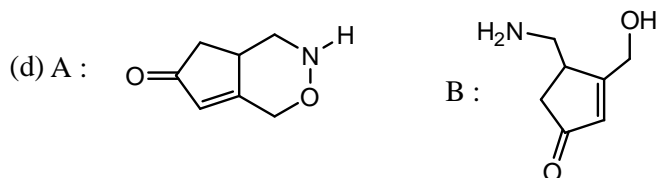


101. The major product for the following reactions is



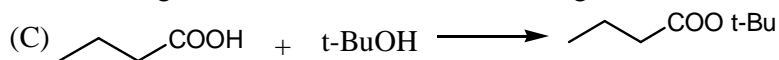
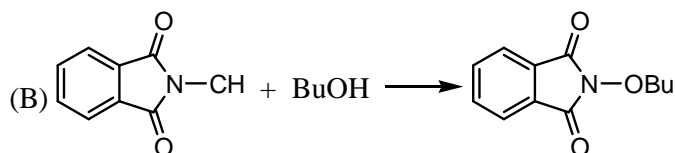
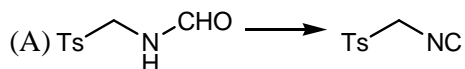
102. The products A and B in the following reaction sequence are





104. The correct combinations of the reactions and the reagents are

Reactions



Reagents

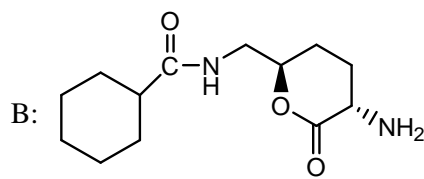
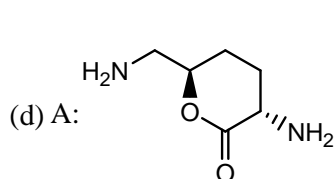
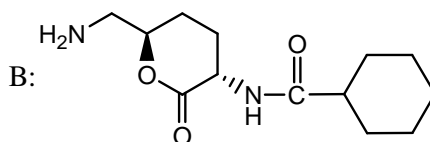
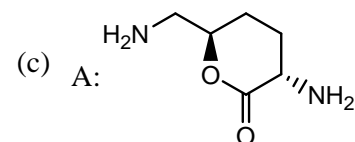
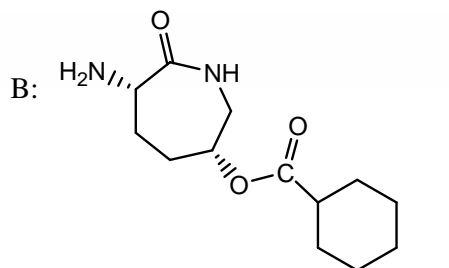
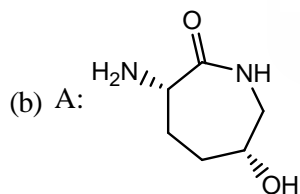
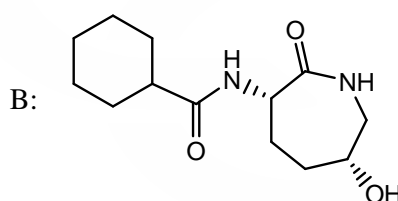
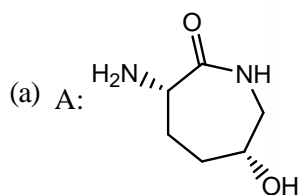
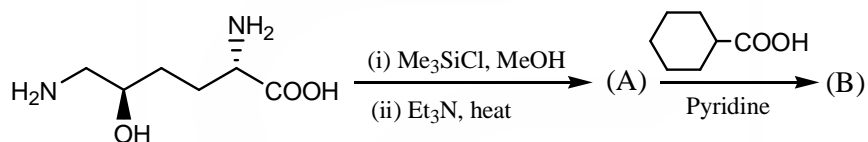
(P) PPh_3 and $\text{O}_2\text{EtNC}=\text{NCO}_2\text{Et}$

(Q) $\text{POCl}_3, \text{Et}_2\text{N}$

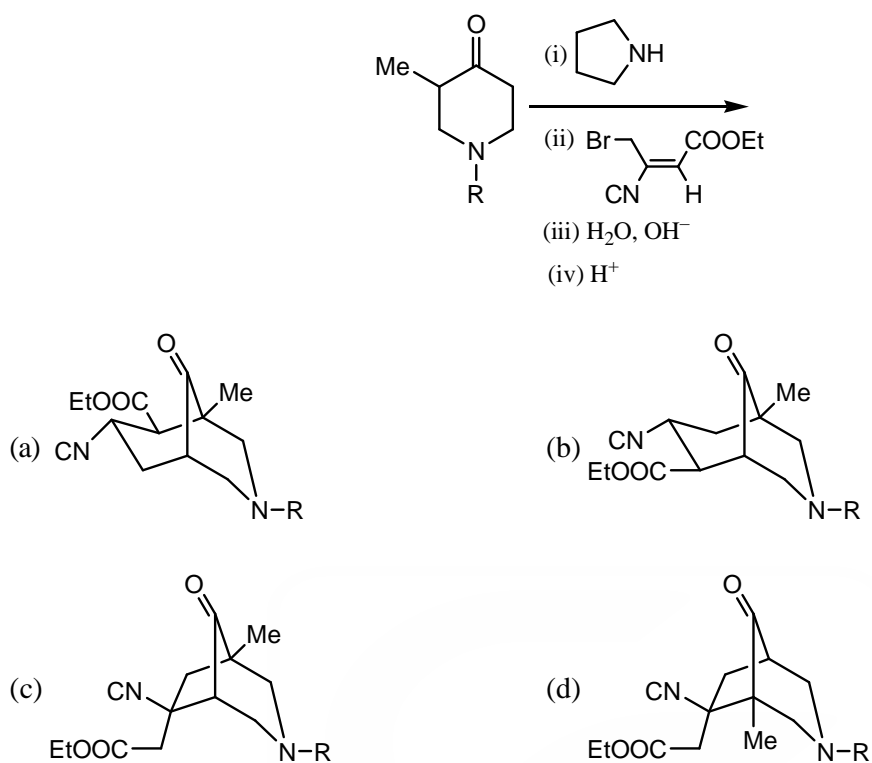
(R) H_2SO_4

(a) A-P, B-Q, C-R (b) A-Q, B-R, C-P (c) A-P, B-R, C-Q (d) A-Q, B-P, C-R

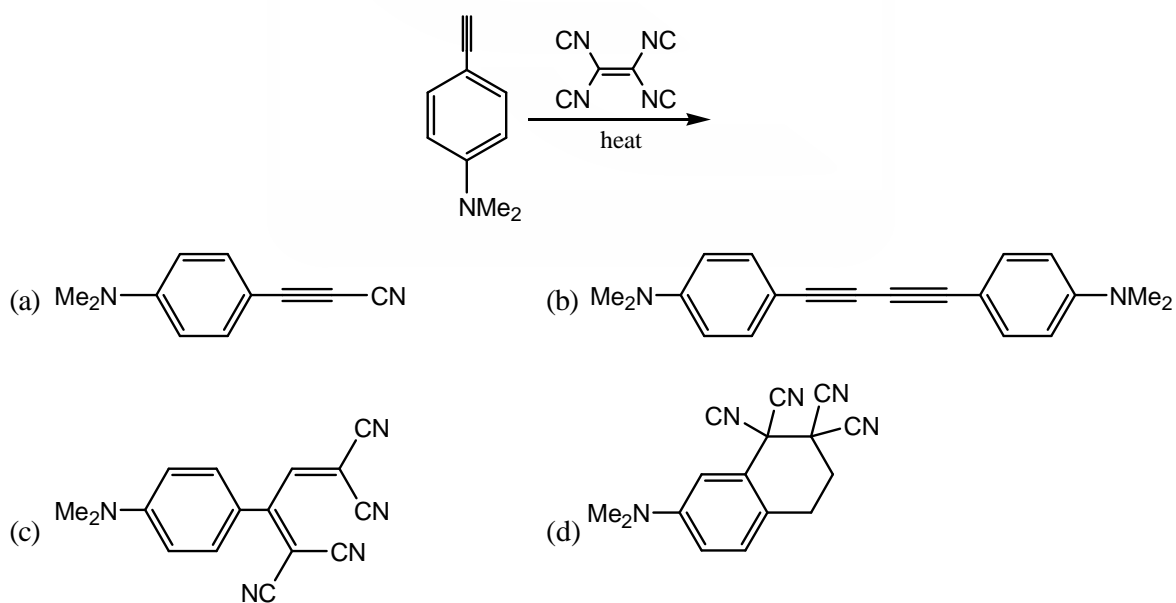
105. The products A and B in the following reaction sequence are



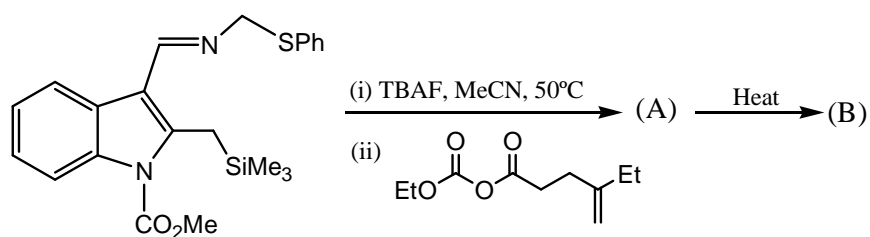
106. The major product of the following reaction is

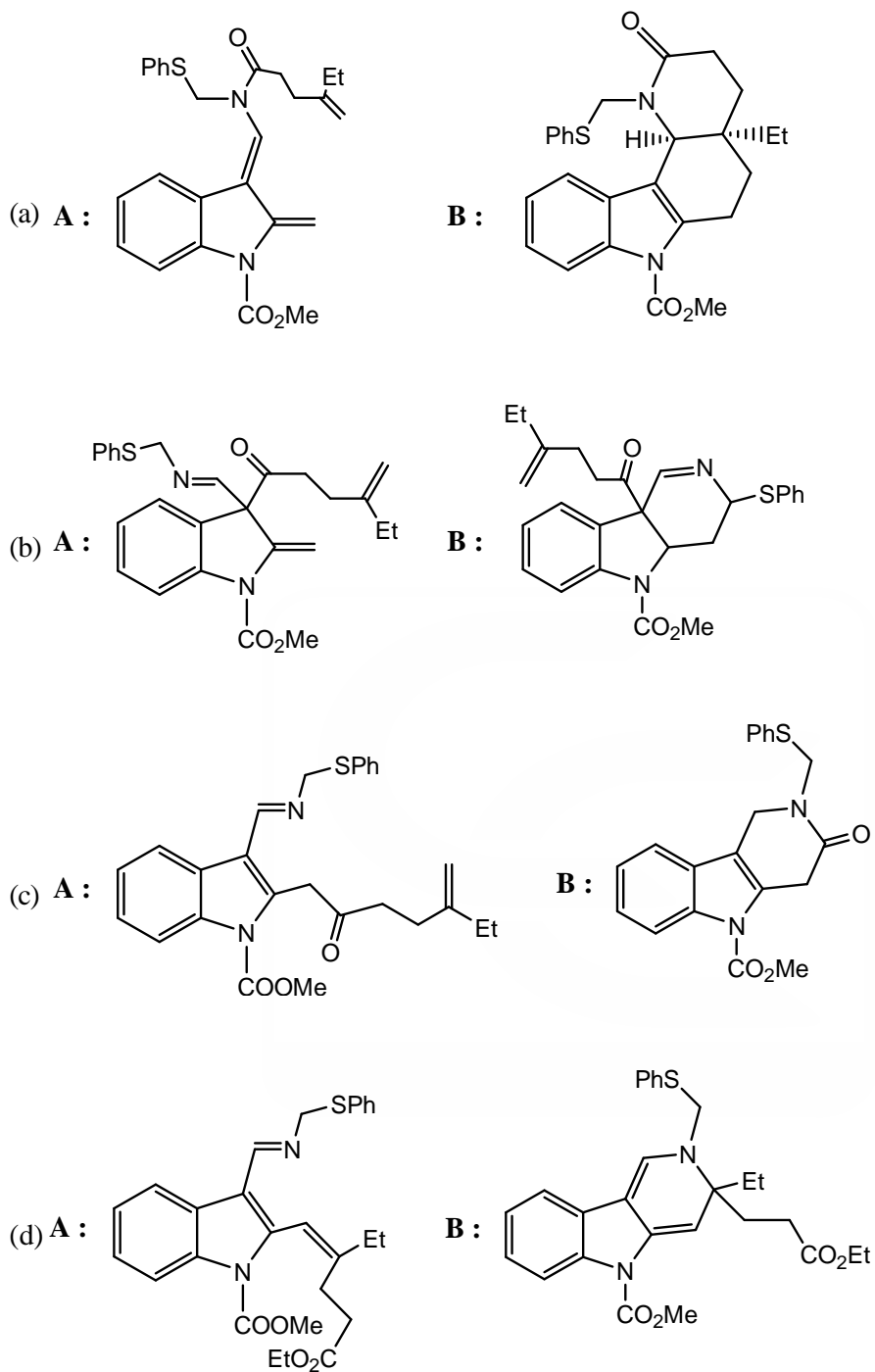


107. The major product of the following reaction is

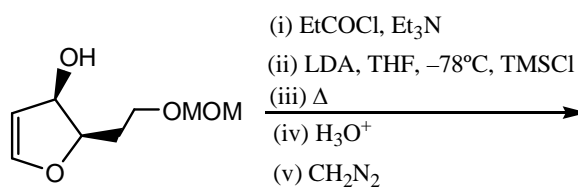


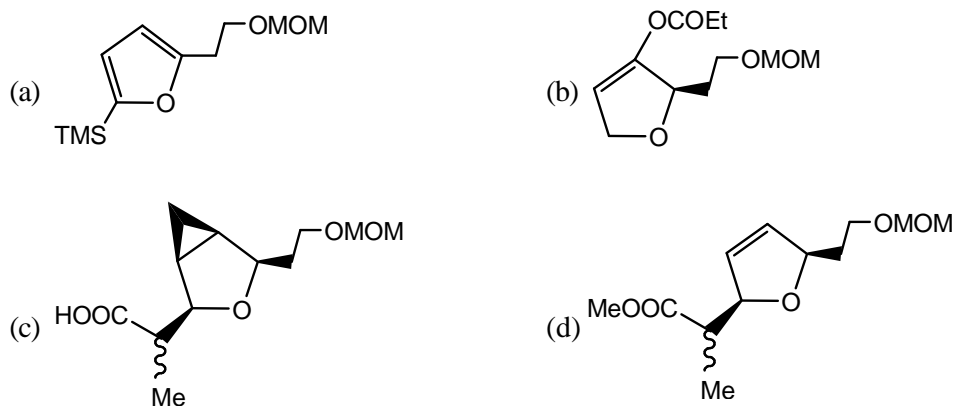
108. The products A and B in the following reaction sequence are



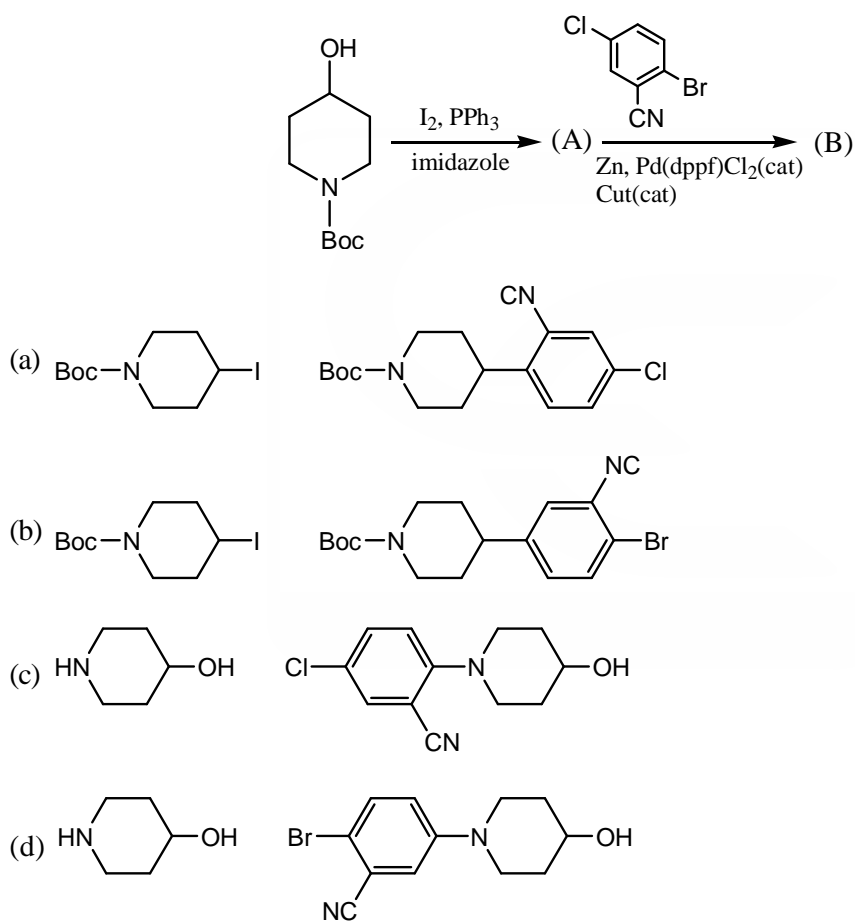


109. The major product formed in the following reaction sequence is

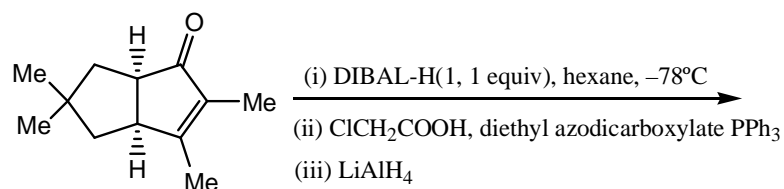


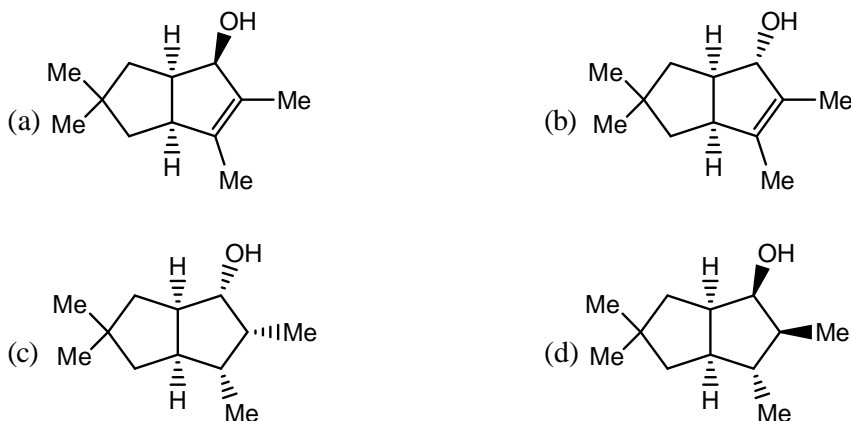


110. In the following reaction sequence, the structures of A and B are, respectively,



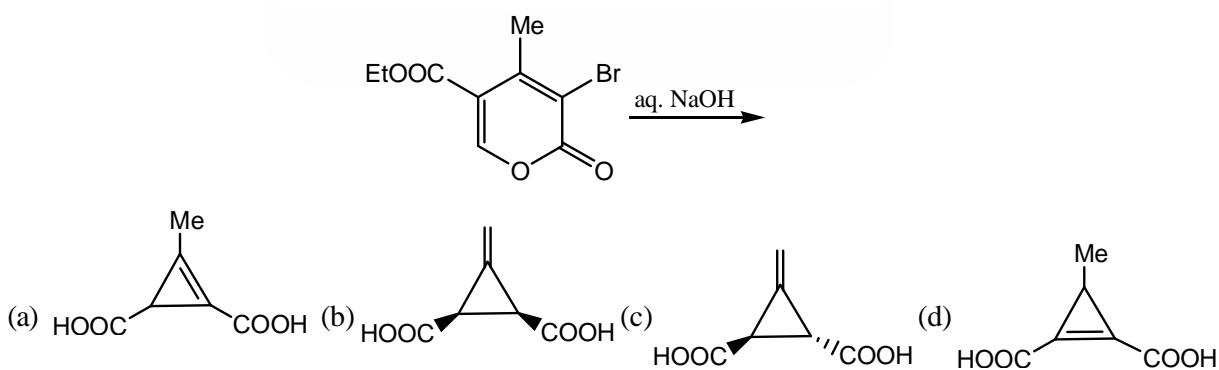
111. In the following reaction sequence, the structure of the product is



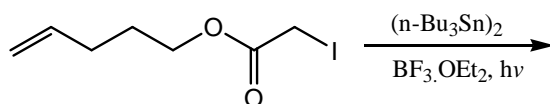


112. The correct combination of the following reactions and their ρ values is
- | Entry | Reaction | Entry | ρ value |
|-------|------------------------------------------------------|-------|--------------|
| A | $\text{ArNH}_2 + \text{PhCOCl}$
in benzene | P | + 2.01 |
| B | $\text{ArO}^- + \text{EtI}$
in EtOH | Q | - 0.99 |
| C | $\text{ArCO}_2\text{Et} + \text{aq}$
NaOH in EtOH | R | - 2.69 |
| | | S | + 0.78 |
- (a) A-P; B-R; C-P (b) A-R; B-Q; C-P (c) A-R; B-P; C-Q (d) A-Q; B-R; C-S

113. The following reactions gives a product (racemic) which exhibits the following NMR data :
 $^1\text{H NMR}$: δ 2.67 (2H, s), 5.60 (2H, s)
ppm; $^{13}\text{C NMR}$: δ 170.3, 129.0, 105.0, 25.4 ppm
The structure of the product (racemic) is

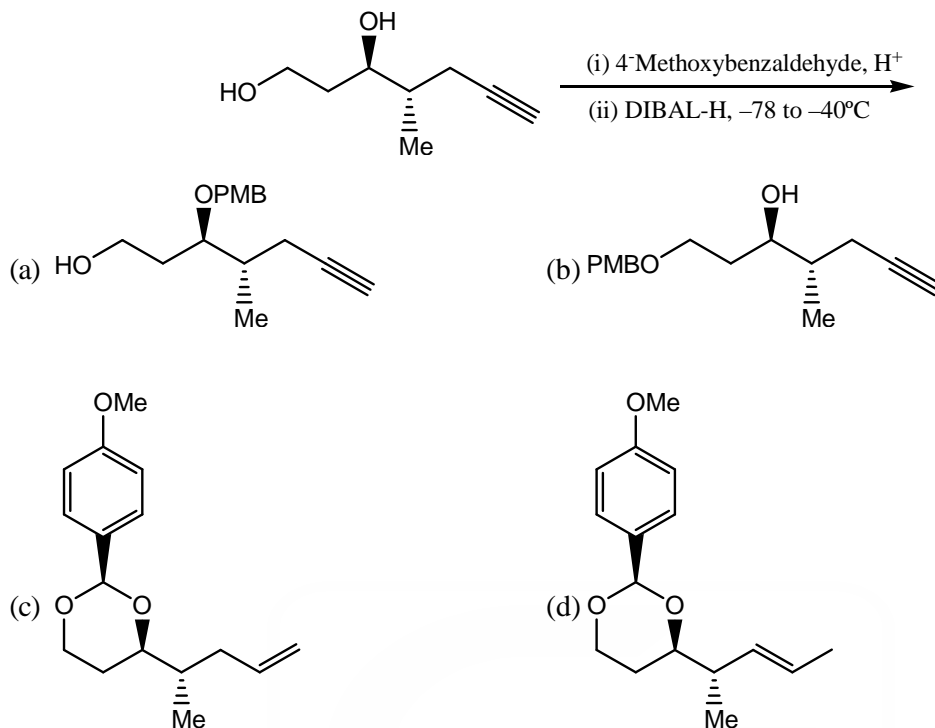


114. The reactive intermediate and the product formed in the following reaction are



- (a) Free radical and 4-iodomethyloxepan-2-one
(b) Free radical and 5-iodooxacan-2-one
(c) Carbene and 3-oxabicyclo[5.1.0]octane-2-one
(d) Carbene and (E)-5-iodopent-3-en-1-yl acetate

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



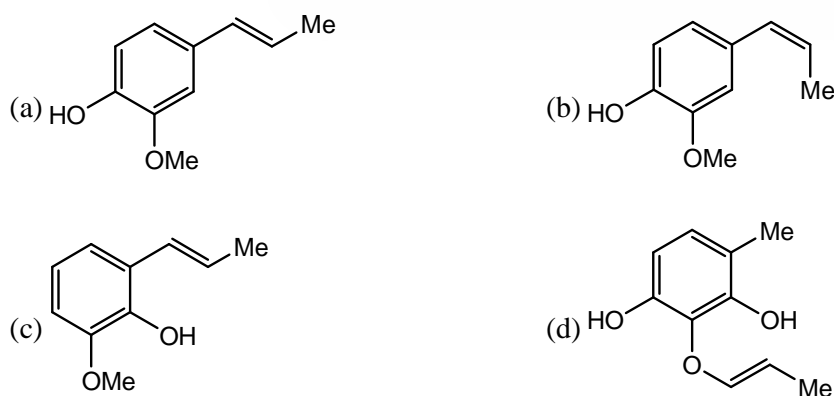
116. An organic compound having molecular formula $C_{10}H_{12}O_2$ exhibits the following spectral data:

IR : 3400 (br), 1600 cm^{-1} .

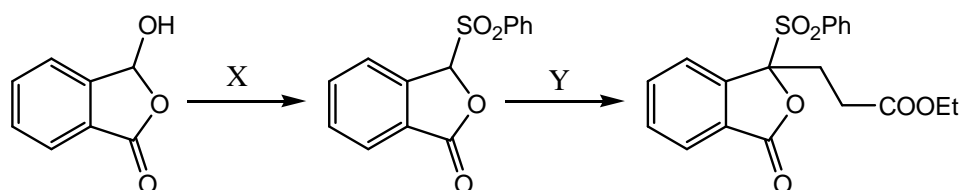
1H NMR : δ 1.85 (3H, d, $J=6$ Hz), 3.8 (3H, s), 5.0 (1H, s, D_2O exchangeable), 6.0 (1H, dq, $J=18, 6$ Hz), 6.28 (1H, d, $J=18$ Hz), 6.75 (1H, d, $J=8$ Hz), 6.8 (1H, s), 6.90 (1H, d, $J=8$ Hz) ppm;

^{13}C NMR : δ 146.5, 144.0, 131.0, 130.5, 123.0, 119.0, 114.0, 108.0, 55.0, 18.0 ppm.

The structure of the compound is

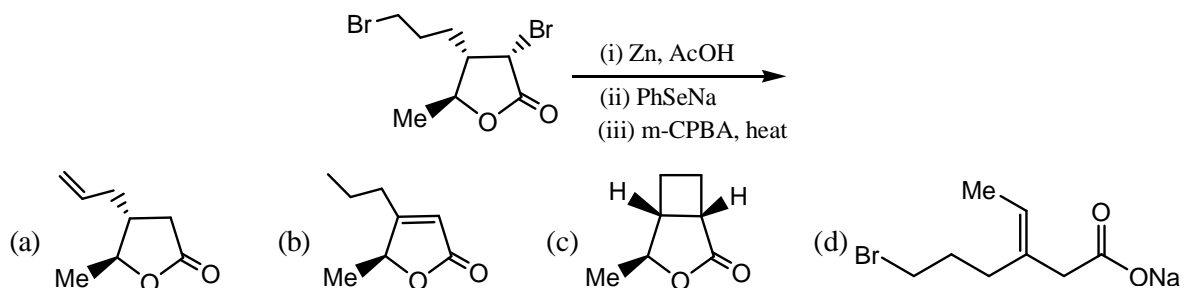


117. In the following reaction sequence, the reagents X and Y are, respectively,

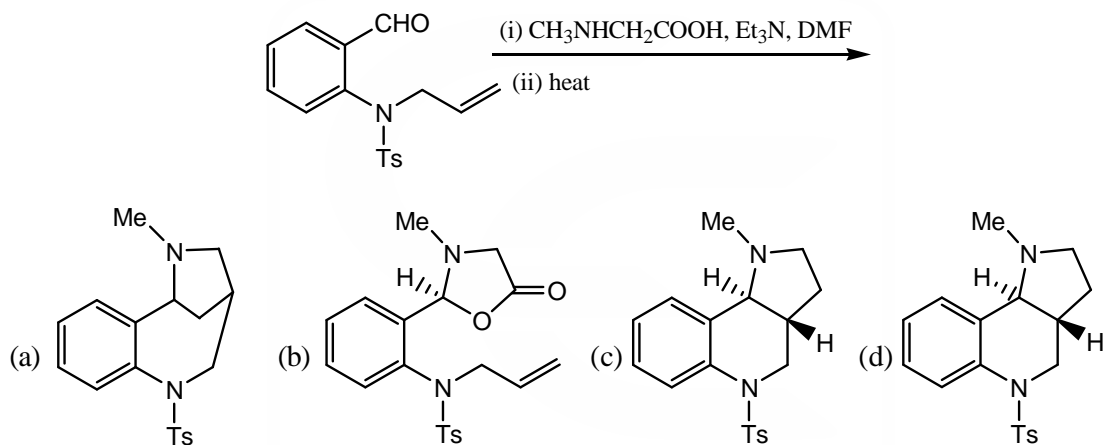


- (a) X = PhSO₂H, BF₃OEt₂ and Y = CH₂ = CHCOOEt, BF₃OEt₂
 (b) X = 1. PhSH, PTSA; 2. m-CPBA and Y = CH₂ = CHCOOEt, BF₃OEt₂
 (c) X = PhSO₃H, BF₃OEt₂ and Y = LDA, CH₂ = CHCOOEt
 (c) X = 1. PhSH, PTSA; 2. m-CPBA and Y = LDA, CH₂ = CHCOOEt

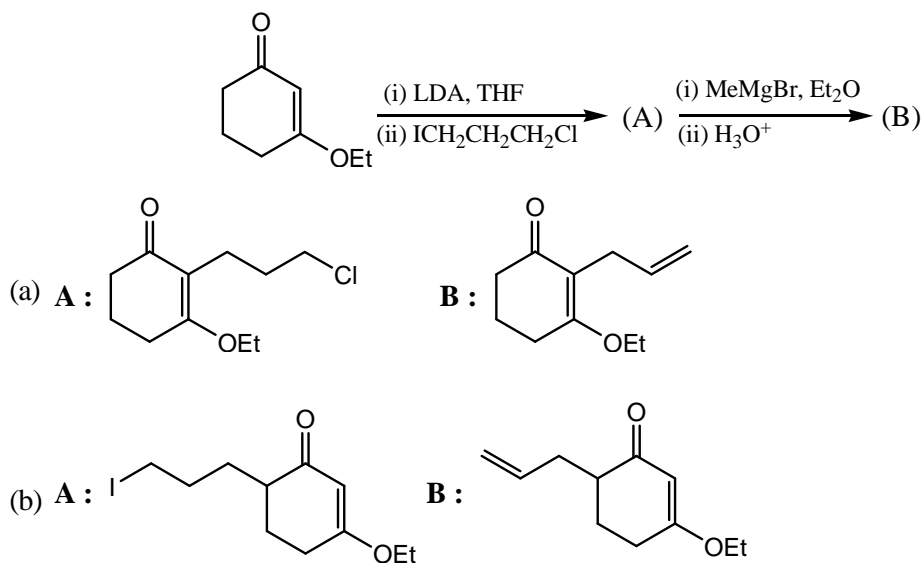
118. The major product of the following reaction is

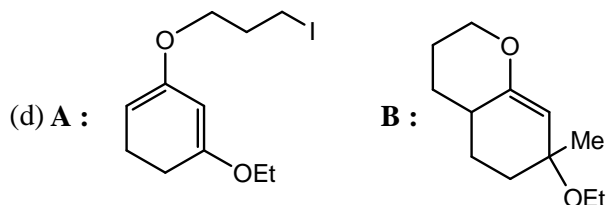
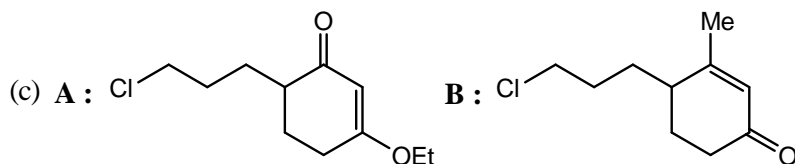


119. The major product of the following reaction is

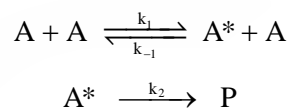


120. The major products A and B formed in the following reaction sequence are

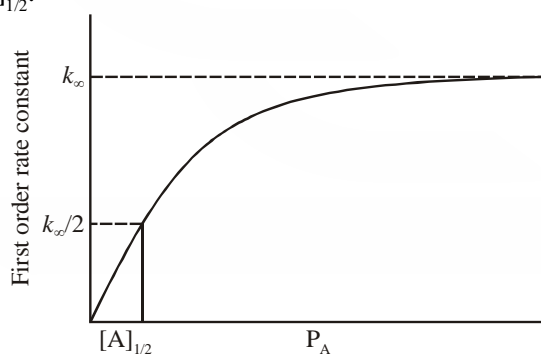




121. For a gaseous reaction, $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{Non-linear T.S.} \rightarrow 2\text{NOCl}$, the pre-exponential factor in the rate constant is proportional to
 (a) $T^{1/2}$ (b) $T^{-1/2}$ (c) $T^{-5/2}$ (d) $T^{-7/2}$
122. Species A undergoes a unimolecular reaction as follows:



For this reaction, the first order rate constant at high pressure is k_∞ . The first order rate constant becomes $\frac{k_\infty}{2}$ when pressure of A is $[\text{A}]_{1/2}$.



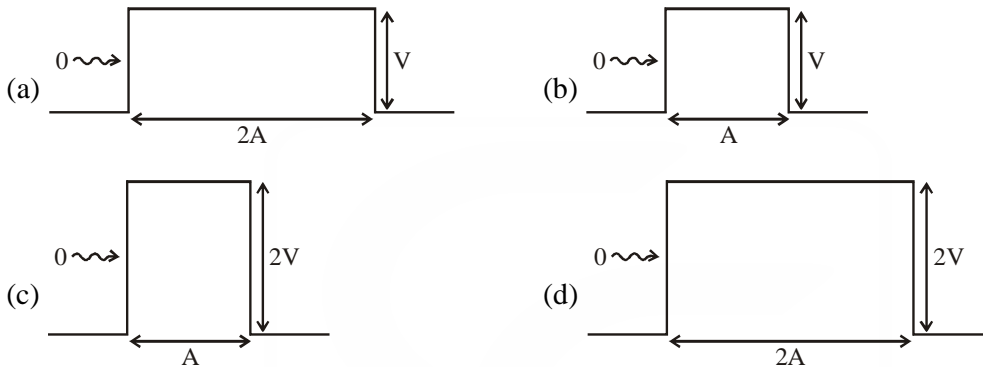
The value of k_1 will be

- (a) $\frac{k_\infty}{[\text{A}]_{1/2}}$ (b) $k_\infty[\text{A}]_{1/2}$ (c) $k_\infty - [\text{A}]_{1/2}$ (d) $\frac{[\text{A}]_{1/2}}{k_\infty}$
123. The low and high temperature limits of vibrational partition function are $\left(\theta = \frac{h\nu}{k}\right)$
 (a) $e^{-\theta/T}$ and $\frac{T}{\theta}e^{-\theta/T}$ (b) $e^{-\theta/2T}$ and $\frac{T}{\theta}e^{-\theta/2T}$
 (c) $e^{-\theta/2T}$ and $\frac{T}{\theta}e^{-\theta/T}$ (d) $e^{-\theta/2T}$ and $\frac{\theta}{T}e^{-\theta/2T}$
124. The probability of finding the harmonic oscillator in the energy level $n = 1$ is (neglect zero point energy and assume $h\nu = k_B T$)
 (a) e (b) e^2 (c) $1 - e^{-2}$ (d) $e^{-2}(e - 1)$

125. A particle in a 1-dimensional box of length L is perturbed by a delta function potential, $\delta(x - L/2)$, in the middle of the box. The first order energy correction to the ground state will be

[Hint : $\int_{-\infty}^{+\infty} f(x)\delta(x-a)dx = f(a)$]

- (a) 0 (b) 1 (c) $L/2$ (d) $2/L$
126. The operators S_{\pm} are defined by $S_{\pm} = S_x \pm iS_y$, where S_x and S_y are components of the spin angular momentum operator. The commutator $[S_z, S_+]$ is
- (a) $\hbar S_+$ (b) $\hbar S_-$ (c) $-\hbar S_+$ (d) $-\hbar S_-$
127. A quantum particle with fixed initial energy $E_0 < V$ is allowed to strike the following four barriers separately. The transmission probability is maximum in



128. Given the following two relations, $x_1 d\mu_1 + x_2 d\mu_2 = 0$ (A)
and $x_1 d\bar{V}_1 + x_2 d\bar{V}_2 = 0$, (B)

for a binary liquid mixture at constant temperature and pressure, the true statement is that,

- (a) Both the relations are correct
(b) Relation A is correct, but B is not
(c) Relation B is correct, but A is not
(d) Both the relations are incorrect, except for very dilute solutions.
129. If the bond length of a heteronuclear diatomic molecule is greater in the upper vibrational state, the gap between the successive absorption lines of P-branch
- (a) Increases non-linearly (b) Decreases non-linearly
(c) Increases linearly (d) Decreases linearly
130. EPR spectrum of a free radical containing nuclei with non-zero nuclear spin is obtained if the following selection rules are observed:
- (a) $\Delta m_s = 0, \Delta m_l = 0$ (b) $\Delta m_s = \pm 1, \Delta m_l = 0$
(c) $\Delta m_s = \pm 1, \Delta m_l = \pm 1$ (d) $\Delta m_s = 0, \Delta m_l = \pm 1$
131. At high pressure, the fugacity coefficient of a real gas is greater than one, because
- (a) Attractive term outweighs the repulsive term
(b) Repulsive term outweighs the attractive term
(c) Repulsive term is equal to the attractive term
(d) The system is independent of both the attractive and repulsive terms

132. If $D_0(A)$ and $I(A)$ refer respectively to the dissociation energy and ionization potential of A (where A is either H, H_2 , or H_2^+ species), the correct relation among the following is

- (a) $D_0(H_2) = D_0(H_2^+) + I(H) - I(H_2)$ (b) $D_0(H_2) = D_0(H_2^+) - I(H) + I(H_2)$
 (c) $D_0(H_2^+) = D_0(H_2) + I(H) + I(H_2)$ (d) $D_0(H_2^+) = D_0(H_2) - I(H) - I(H_2)$

133. The character table of C_{2v} point group is given below. In *cis*-butadiene molecule the vibrational modes belonging to A_2 irreducible representation are *IR* inactive. The remaining *IR* active modes are

C_{2v}	E	C_2	σ_v	σ'_v	
A_1	1	1	1	1	z, x^2, y^2, z
A_2	1	1	-1	-1	R_z, xy
B_1	1	-1	1	-1	x, R_y, xz
B_2	1	-1	-1	1	y, R_x, yz

- (a) $7A_1 + 5B_1 + 8B_2$ (b) $9A_1 + 4B_1 + 7B_2$ (c) $7A_1 + 3B_1 + 7B_2$ (d) $9A_1 + 3B_1 + 8B_2$

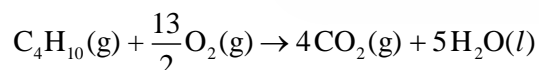
134. The product $\sigma^{xy} \cdot S_4^z$ (S_4^z is the four fold improper axis of rotation around the z -axis, and σ^{xy} is the reflection in the xy plane) is

- (a) C_4^z (b) $C_4 \cdot i$ (c) C_4^y (d) C_2^z

135. A solid consisting of only X-atoms has a close-packed structure with X-X distance of 160 pm. Assuming it to be a closed packed structure of hard spheres with radius equal to half of the X-X bond length, the number of atoms in 1 cm^3 would be

- (a) 6.023×10^{27} (b) 3.45×10^{23} (c) 6.02×10^{21} (d) 3.8×10^{21}

136. Fuel cells provide clean electrical energy to a variety of applications including automobiles and stationary power sources. Normally hydrogen combines with oxygen to give electrical energy and water. If we use butane instead of hydrogen at 1.0 bar and 298 K, the following reaction occurs :



If the change in the Gibbs free energy of this reaction is $2746.06 \text{ kJ mol}^{-1}$, involving 26 electrons, its open circuit voltage is

- (a) 1.55 V (b) 1.09 V (c) 3.15 V (d) 2.06 V

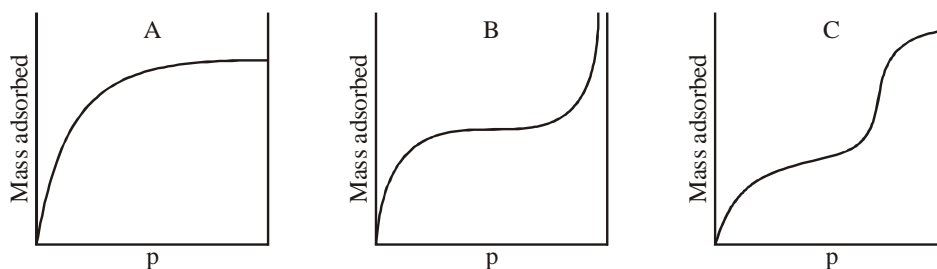
137. The fraction of groups condensed at time t in any stepwise condensation polymerization (overall second order) reaction is

- (a) $1 + kt[A]_0$ (b) $\frac{1}{1 + kt[A]_0}$ (c) $\frac{kt[A]_0}{1 + kt[A]_0}$ (d) $\frac{1 + kt[A]_0}{kt[A]_0}$

138. The configuration $[Ne]2p^13p^1$ has a 3D term. Its levels are

- (a) $^3D_{3/2}, ^3D_{1/2}$ (b) $^3D_{5/2}, ^3D_{3/2}, ^3D_{1/2}$
 (c) $^3D_3, ^3D_2, ^3D_1$ (d) $^3D_3, ^3D_2, ^3D_1, ^3D_0$

139. For some one-electron system with $l = 0$ and $m = 0$, the functions $N_0 e^{-\sigma}$ and $N_1 (2 - \sigma) e^{-\sigma/2}$ refer respectively to the ground (E_0) and first excited (E_1) energy levels. If a variational wave function $N_2 (3 - \sigma) e^{-\sigma}$ yields an average energy \bar{E} , it will satisfy
- (a) $\bar{E} \geq 0$ (b) $0 \leq \bar{E} \leq E_0$ (c) $\bar{E} \geq E_1$ (d) $E_0 \leq \bar{E} \leq E_1$
140. The number of microstates that are possible, when two particles are distributed in four states such that the resulting wave functions are antisymmetric with respect to exchange of the particles, is
- (a) 16 (b) 12 (c) 8 (d) 6
141. A Slater determinant corresponding to the ionic part of the ground state valence bond wave function of H_2 molecule is ($1s_a\alpha, 1s_a\beta, 1s_b\alpha, 1s_b\beta$ are atomic spin-orbitals of hydrogen atoms a and b of the hydrogen molecule)
- (a) $\begin{vmatrix} 1s_a\alpha(1) & 1s_a\beta(1) \\ 1s_a\alpha(2) & 1s_a\beta(2) \end{vmatrix}$ (b) $\begin{vmatrix} 1s_a\alpha(1) & 1s_b\beta(1) \\ 1s_a\alpha(2) & 1s_b\beta(2) \end{vmatrix}$
- (c) $\begin{vmatrix} 1s_a\alpha(1) & 1s_b\alpha(1) \\ 1s_a\alpha(2) & 1s_b\alpha(2) \end{vmatrix}$ (d) $\begin{vmatrix} 1s_a\alpha(1) & 1s_b\beta(1) \\ 1s_a\alpha(1) & 1s_b\beta(2) \end{vmatrix}$
142. When $T \rightarrow \infty$, value of the single-particle partition function will be (given : degeneracy of level $j = g_j$)
- (a) 1 (b) g_0 (c) $\sum_j g_j$ (d) $\frac{1}{\sum_j g_j}$
143. The rate constant for a reaction $A^{1+} + B^{n+} \rightarrow P$ is measured in two different aqueous solutions of ionic strengths 0.01 M and 0.04 M. If $\log \frac{k_{0.04}}{k_{0.01}} = 0.3$, the charge n on B is closest to
- (a) 1 (b) 2 (c) 3 (d) 6
144. According to Huckel theory, the π electron charge on the central carbon atom in propenyl cation $(CH_2CHCH_2)^+$ is (in units of electronic charge)
- (a) $\frac{1}{2}$ (b) $\frac{1}{\sqrt{2}}$ (c) 1 (d) 2
145. Among the following figures, the variations of mass adsorbed with pressure for a monolayer and a multilayer are represented by



- (a) A and C respectively (b) A and B respectively
- (c) C and A respectively (d) B and A respectively