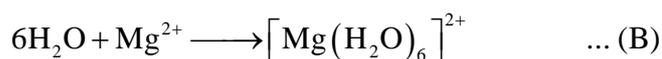


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CHEMICAL SCIENCES BOOKLET - [C]

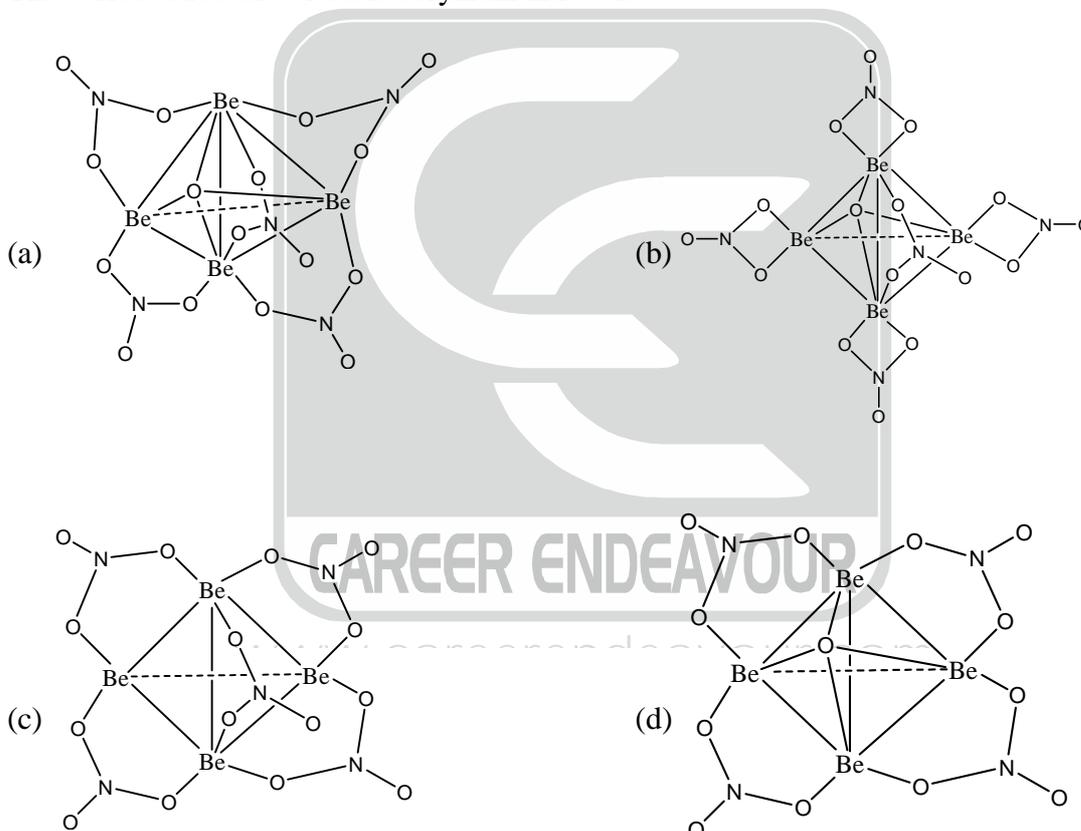
Part - B

21. In the reactions (A) and (B),



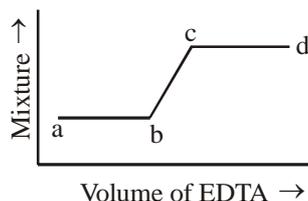
water behaves as

- (a) An acid in both (A) and (B) (b) An acid in (A) and a base in (B)
 (c) A base in (A) an acid in (B) (d) A base in both (A) and (B)
22. The size of the d orbitals in Si, P, S and Cl follows the order.
 (a) $\text{Cl} > \text{S} > \text{P} > \text{Si}$ (b) $\text{Cl} > \text{P} > \text{S} > \text{Si}$ (c) $\text{P} > \text{S} > \text{Si} > \text{Cl}$ (d) $\text{Si} > \text{P} > \text{S} > \text{Cl}$
23. The correct structure of basic beryllium nitrate is:



24. The total number of lone pairs of electrons in I_3^- is:
 (a) Zero (b) Three (c) Six (d) Nine
25. If Mössbauer spectrum of $\text{Fe}(\text{CO})_5$ is recorded in the presence of a magnetic field, the original spectrum with two lines changes into the one with
 (a) Three lines (b) Four lines (c) Five lines (d) Six lines

26. The spectrophotometric response for the titration of a mixture of Fe^{3+} and Cu^{2+} ions against EDTA is given below.

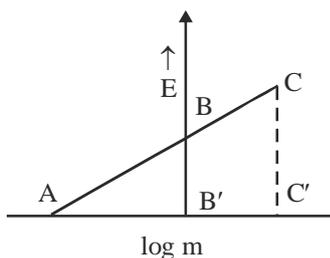


The correct statement is:

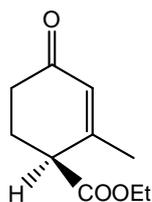
- (a) Volume $ab \equiv [\text{Fe}^{3+}]$ and volume $cd \equiv [\text{Cu}^{2+}]$
 (b) Volume $ab \equiv [\text{Cu}^{2+}]$ and volume $cd \equiv [\text{Fe}^{3+}]$
 (c) Volume $ab \equiv [\text{Fe}^{3+}]$ and volume $ab \equiv$ excess EDTA
 (d) Volume $ab \equiv [\text{Cu}^{2+}]$ and volume $cd \equiv$ excess EDTA
27. In 'carbon-dating' application of radioisotopes, ^{14}C emits
 (a) β - particle (b) α - particle (c) γ - radiation (d) Positron.
28. The actual base pairs present in the double helical structure of DNA containing adenine (A), thymine (T), cytosine (C) and guanine (G), are
 (a) AG and CT (b) AC and GT (c) AG and AC (d) AT and GC
29. The oxidation state of iron in met-hemoglobin is
 (a) Three (b) Two (c) Four (d) Zero
30. The reactions of $\text{Ni}(\text{CO})_4$ with the ligand ($\text{L} = \text{PMe}_3$ or $\text{P}(\text{OMe})_3$) L yields $\text{Ni}(\text{CO})_3\text{L}$. The reaction is
 (a) Associative (b) Dissociative (c) Interchange (I_a) (d) Interchange (I_d)
31. As a ligand Cl^- is:
 (a) Only a σ -donor (b) Only a π -donor
 (c) Both a σ -donor and a π -donor (d) A σ -donor and a σ -acceptor
32. The correct d-electron configuration showing spin-orbit coupling is
 (a) $t_{2g}^4 e_g^2$ (b) $t_{2g}^6 e_g^0$ (c) $t_{2g}^4 e_g^0$ (d) $t_{2g}^3 e_g^2$
33. The correct statement for the aggregating nature of alkyl lithium (RLi) reagent is:
 (a) The carbanion nucleophilicity increases with aggregation.
 (b) The observed aggregation arises from its electron deficient nature.
 (c) Carbanion nucleophilicity does not depend on aggregation.
 (d) The extent of aggregation is maximum in polar dative solvents.
34. For the reaction, $\text{trans} - [\text{IrCl}(\text{CO})(\text{PPh}_3)_2] + \text{Cl}_2 \rightarrow \text{trans} - [\text{IrCl}_3(\text{CO})(\text{Phh}_3)_2]$, the correct observation
 (a) $\nu_{\text{CO}}(\text{product}) > \nu_{\text{CO}}(\text{reactant})$ (b) $\nu_{\text{CO}}(\text{product}) < \nu_{\text{CO}}(\text{reactant})$
 (c) $\nu_{\text{CO}}(\text{product}) = \nu_{\text{CO}}(\text{reactant})$ (d) $\nu_{\text{CO}}(\text{product}) = \nu_{\text{CO}}(\text{free CO})$

35. The nucleophilic attack on olefins under mild conditions:
(a) Is always facile (b) Is more facile than electrophilic attack on olefins
(c) Is facile for electron-rich olefins (d) Requires activation by coordination to metal.
36. Among the following the strongest oxidizing agent is:
(a) $[\text{WO}_4]^{2-}$ (b) $[\text{CrO}_4]^{2-}$ (c) $[\text{MoO}_4]^{2-}$ (d) $[\text{ReO}_4]^{-2}$
37. The least basic among the following is:
(a) $\text{Al}(\text{OH})_3$ (b) $\text{La}(\text{OH})_3$ (c) $\text{Ce}(\text{OH})_3$ (d) $\text{Lu}(\text{OH})_3$
38. For any operator A and its adjoint A^\dagger , the **INCORRECT** statement is:
(a) AA^\dagger is hermitian (b) $AA^\dagger + A^\dagger A$ is hermitian.
(c) $A + A^\dagger$ is hermitian (d) $A - A^\dagger$ is hermitian.
39. For hydrogen-like atom with a nuclear charge Z, the energy of orbital with principal quantum number 'n' follows the relation.
(a) $E_n \propto n^2 Z^2$ (b) $E_n \propto -\frac{Z^2}{n}$ (c) $E_n \propto -\frac{Z}{n}$ (d) $E_n \propto -\frac{Z^2}{n^2}$
40. The average value of the radius $\langle r \rangle$ in the 1s state of the hydrogen atom is (a_0 is Bohr radius)
(a) a_0 (b) $1.5 a_0$ (c) $0.75 a_0$ (d) $0.5 a_0$.
41. Among the following, the **CORRECT** statement is:
(a) The number of irreducible representations is equal to classes of symmetry operations.
(b) The number of irreducible representations is equal to the order of the symmetry point group.
(c) The irreducible representations contained in any point group are always of one dimension.
(d) A symmetry point group may not contain a totally symmetric irreducible representation.
42. For a diatomic molecule AB, the energy for the rotational transition from $J = 0$ to $J = 1$ state is 3.9 cm^{-1} . The energy for the rotational transition from $J = 3$ to $J = 4$ state would be
(a) 3.9 cm^{-1} (b) 7.8 cm^{-1} (c) 11.7 cm^{-1} (d) 15.6 cm^{-1}
43. For the vibrational Raman spectrum of a homonuclear diatomic molecule, the selection rule under harmonic approximation is
(a) $\Delta v = 0$ only (b) $\Delta v = \pm 1$ only (c) $\Delta v = \pm 2$ only (d) $\Delta v = 0, \pm 1$
44. With increase in temperature, the Gibbs free energy for the adsorption of a gas on to a solid surface
(a) Becomes more positive from a positive value
(b) Becomes more negative from a positive value
(c) Becomes more positive from a negative value.
(d) Becomes more negative from a negative value
45. The vapour of a pure substance, when cooled under a pressure less than its triple-point pressure,
(a) Liquifies (b) Liquifies first and then solidifies
(c) Solidifies directly (d) Remains unchanged.
46. The quantities, which are held fixed in a canonical ensemble are
(a) N, T and P (b) V, T and N (c) N, V and E (d) μ , V and P

47. The correct value of E° , of a half cell in the following graph of E vs $\log m$ (molality) is:

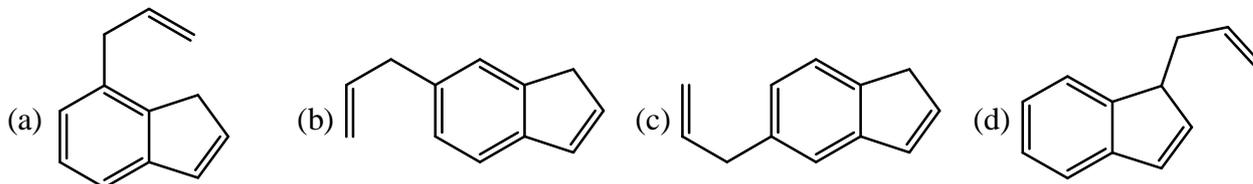
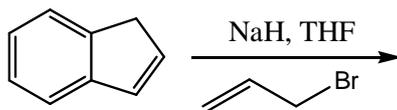


- (a) CC'/AC' (b) AB' (c) BB' (d) CC'
48. One of the assumptions made in the conventional activated complex theory is:
 (a) Equilibrium is maintained between reactants and the activated complex
 (b) Equilibrium is maintained between the reactants and the products.
 (c) Equilibrium is maintained between the products and the activated complex
 (d) Equilibrium is maintained between the reactants, the activated complex and the products.
49. For a reaction, the rate constant k at 27°C was found to be $k = 5.4 \times 10^{11} e^{-50}$
 The activation energy of the reaction is
 (a) 50 J mol^{-1} (b) 415 J mol^{-1} (c) $15,000 \text{ J mol}^{-1}$ (d) $125,000 \text{ J mol}^{-1}$
50. During the addition polymerisation, the reaction proceeds via
 (a) Step-growth process (b) Free-radical chain reaction
 (c) Cascade process (d) Addition reaction
51. How many atoms are there in an element packed in a fcc structure
 (a) 1 (b) 2 (c) 4 (d) 8
52. The structure obtained when all the tetrahedral holes are occupied in a fcc structure is of the type
 (a) NaCl (b) CsCl (c) CaF_2 (d) ZnS
53. Dispersion of a solid in a liquid, a liquid in a gas and a liquid in a liquid are respectively known as
 (a) Aerosol, emulsion, sol (b) Sol, aerosol, emulsion
 (c) Emulsion, sol, aerosol (d) Aerosol, sol, emulsion
54. The data obtained from two sets of experiments A and B have the following characteristics
- | Experiment | A | B |
|--------------------|----------|-----------|
| Mean | 50 units | 100 units |
| Standard deviation | 2 units | 2 units |
- It may be concluded that
 (a) A is more precise than B (b) A is less precise than B
 (c) A and B are of the same precision (d) Relative precision of A and B cannot be assessed.
55. The IUPAC name of the compound given below is:



- (a) ethyl (R)-2-methyl-4-oxocyclohex-2-enecarboxylate
 (b) ethyl (S)-2-methyl-4-oxocyclohex-2-enecarboxylate
 (c) (R)-4-ethoxycarbonyl-3-methylcyclo-hex-2-enone
 (d) (S)-4-ethoxycarbonyl-3-methylcyclo-hex-2-enone

56. The major product formed in the following reaction is:



57. The number of signals that appear in the broadband decoupled ^{13}C NMR spectrum of phenanthrene and anthracene, respectively are

- (a) ten and four (b) ten and ten (c) seven and four (d) seven and seven.

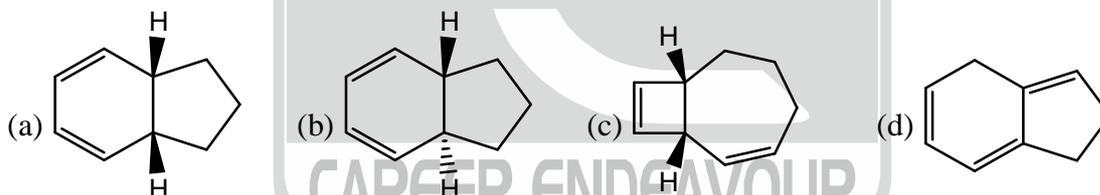
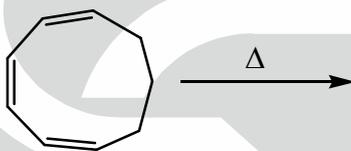
58. The co-enzyme that is involved in the reduction of a double bond in fatty acid biosynthesis is:

- (a) NADH (b) Biotin (c) Pyridoxal (d) FADH_2 .

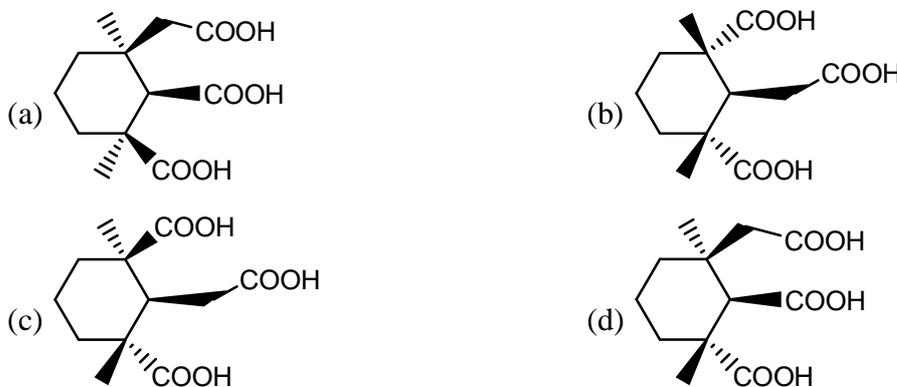
59. Epoxidation of (R)-cyclohex-2-enol with peracetic acid yields a 95:5 mixture of compounds A and B. Compounds A and B are

- (a) Enantiomers (b) Diastereomers (c) Constitutional isomers (d) Homomers

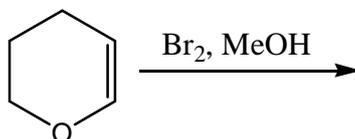
60. The major product formed in the following concerted reaction is

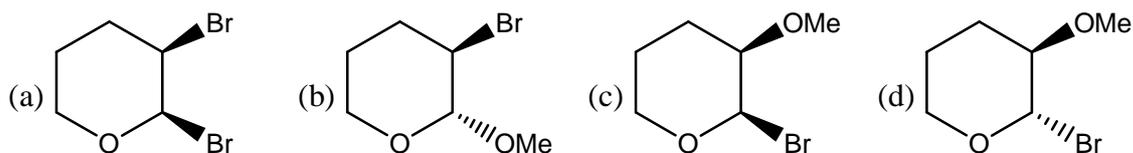


61. The structure of meso-tricarboxylic acid that is formed on potassium permanganate oxidation of abietic acid is:

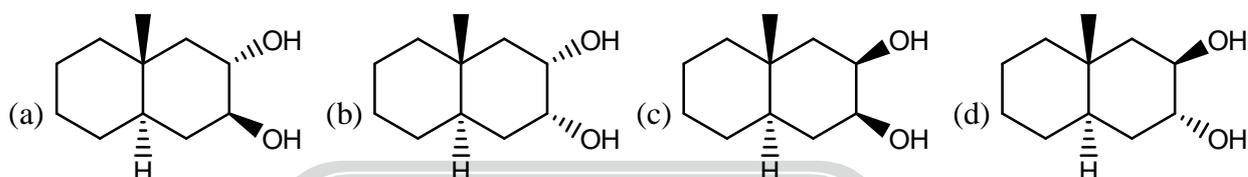
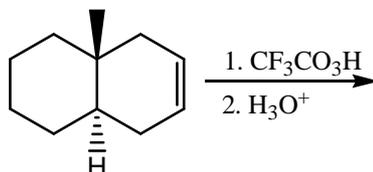


62. The major product formed in the following reaction is:





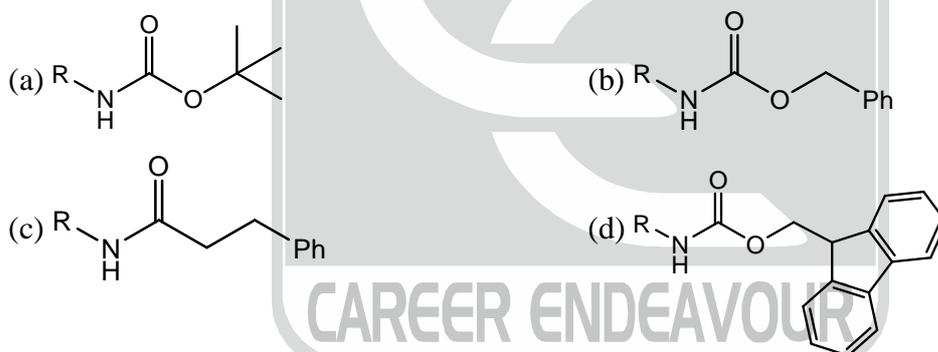
63. The major product formed in the following reaction is:



64. Among the following, the synthetic equivalent for acyl anion is:



65. Among the following, the compound that undergoes deprotection easily on treatment with hydrogen in the presence of 10% Pd/C to generate RNH_2 is:



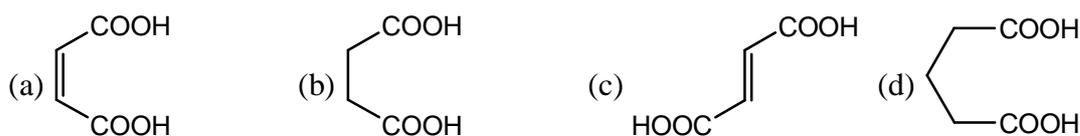
66. Among the following, the amino acid which is basic in nature is:



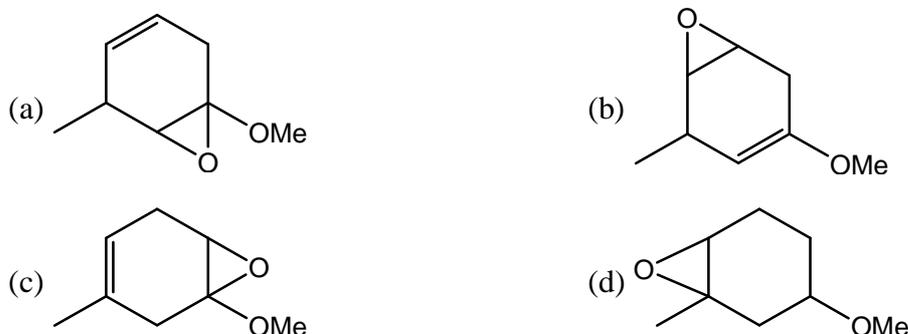
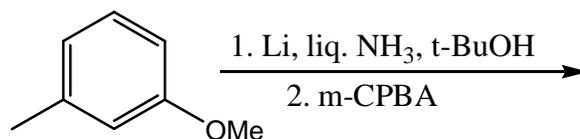
67. "Phosphorescence" is represented as



68. Among the following diacids, the one that forms an anhydride fastest on heating with acetic anhydride is:



69. The major product formed in the following reaction sequence is:



70. In the 400 MHz ^1H NMR spectrum, of organic compound exhibited a doublet. The two lines of the doublet are at δ 2.35 and 2.38 ppm. The coupling constant (J) value is
 (a) 3 Hz (b) 6 Hz (c) 9 Hz (d) 12 Hz

Part - C

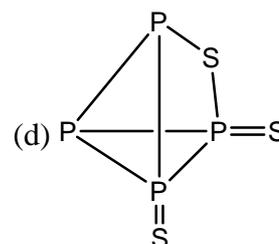
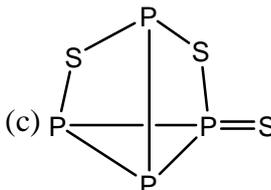
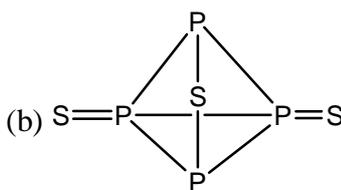
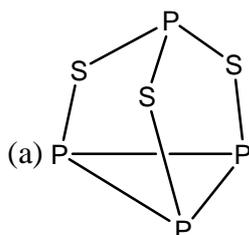
71. The strength of $p_\pi - d_\pi$ bonding in E-O (E = Si, P, S and Cl) follows the order
 (a) Si - O > P - O > S - O > Cl - O (b) P - O > Si - O > S - O > Cl - O
 (c) S - O > Cl - O > P - O > Si - O (d) Cl - O > S - O > P - O > Si - O
72. In the following reactions carried out in liquid NH_3 .

$$\text{Zn}(\text{NH}_2)_2 + 2 \text{KNH}_2 \longrightarrow \text{K}_2[\text{Zn}(\text{NH}_2)_4]$$

$$\text{K}_2[\text{Zn}(\text{NH}_2)_4] + 2 \text{NH}_4\text{NO}_3 \longrightarrow \text{Zn}(\text{NH}_2)_2 + 2 \text{KNO}_3 + 4 \text{NH}_3$$
 KNH_2 and NH_4NO_3 act respectively as
 (a) Solvo-acid and solvo-base (b) Solvo-base and solvo-acid
 (c) Conjugate acid and conjugate base (d) Conjugate base and conjugate acid
73. The pair of lanthanides with the highest third-ionization energy is:
 (a) Eu, Gd (b) Eu, Yb (c) Dy, Yb (d) Lu, Yb
74. The lanthanide(III) ion having the highest partition coefficient between tri-n-butylphosphate and concentrated HNO_3 is:
 (a) La(III) (b) Eu(III) (c) Nd(III) (d) Lu(III)
75. The quantitative determination of N_2H_4 with KIO_3 proceeds in a mixture of $\text{H}_2\text{O}/\text{CCl}_4$ as follows

$$\text{N}_2\text{H}_4 + \text{KIO}_3 + 2\text{HCl} \longrightarrow \text{N}_2 + \text{KCl} + \text{ICl} + 3\text{H}_2\text{O}$$
 The end point for the titrimetric reaction is:
 (a) Consumption of N_2H_4
 (b) ICl formation
 (c) Disappearance of the Yellow color due to Cl_2 in CCl_4 layer.
 (d) Displacement of the Red color due to I_2 in CCl_4 layer.

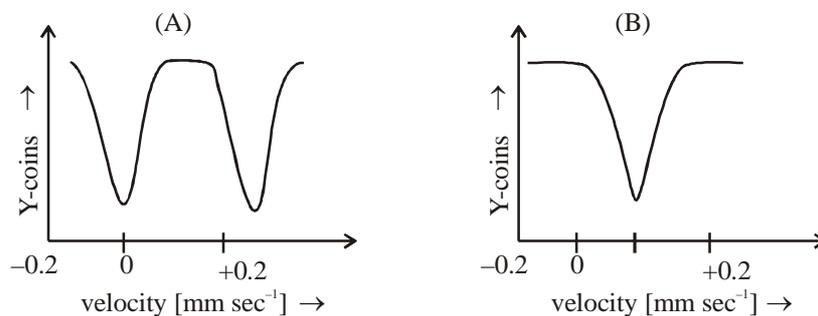
76. Among the halides, NCl_3 (A), PCl_3 (B) and AsCl_3 (C), those which produce two different acids.
 (a) A and B (b) A and C (c) B and C (d) A, B and C
77. The decreasing order of dipole moment of molecules is
 (a) $\text{NF}_3 > \text{NH}_3 > \text{H}_2\text{O}$ (b) $\text{NH}_3 > \text{NF}_2 > \text{H}_2\text{O}$ (c) $\text{H}_2\text{O} > \text{NH}_3 > \text{NF}_3$ (d) $\text{H}_2\text{O} > \text{NF}_3 > \text{NH}_3$
78. The cluster having arachno type structure is:
 (a) $[\text{Os}_5(\text{CO})_{16}]$ (b) $[\text{Os}_3(\text{CO})_{12}]$ (c) $[\text{Ir}_4(\text{CO})_{12}]$ (d) $[\text{Rh}_6(\text{CO})_{16}]$
79. The carbonyl resonance in ^{13}C NMR spectrum of $[(\eta^5 - \text{C}_5\text{H}_5)\text{Rh}(\text{CO})]_3$ (^{103}Rh , nuclear spin, $I=1/2$, 100%) shows a triplet at -65°C owing to the presence of
 (a) Terminal CO (b) $\mu_2 - \text{CO}$ (c) $\mu_3 - \text{CO}$ (d) $\eta^5 - \text{C}_5\text{H}_5$
80. Low oxidation state complexes are often air-sensitive, but are rarely water sensitive because
 (a) Air is reducing in nature while water is inert
 (b) Both air and water are oxidizing in nature
 (c) Both air and water are not π -acceptors
 (d) Complexes with low oxidation states will easily lose electrons to O_2 but will not bind to a π -donor molecule like H_2O .
81. The metal complex that exhibits a triplet as well as doublet in its ^{31}P NMR spectrum is
 (a) $\text{mer} - [\text{IrCl}_3(\text{PPh}_3)_3]$ (b) $\text{trans} - [\text{IrCl}(\text{Co})(\text{PPh}_3)_2]$
 (c) $\text{fac} - [\text{IrCl}_3(\text{PPh}_3)_3]$ (d) $[\text{Ir}(\text{PPh}_3)_4]^+$
82. The complex that **DOES NOT** obey 18- electron rule is:
 (a) $[(\eta^5 - \text{C}_5\text{H}_5)\text{RuCl}(\text{CO})(\text{PPh}_3)]$ (b) $[\text{W}(\text{CO})_3(\text{SiMe}_3)(\text{Cl})(\text{NCMe})_2]$
 (c) $[\text{IrCl}_3(\text{PPh}_3)_2(\text{AsPh}_2)]$ (d) $[\text{Os}(\text{N})\text{Br}_2(\text{PMe}_3)(\text{NMe}_2)]^-$
83. The number of spin-allowed ligand field transitions for octahedral $\text{Ni}(\text{II})$ complexes with $^3\text{A}_{2g}$ ground state is:
 (a) Two (b) Three (c) One (d) Four
84. The correct structure of P_4S_3 is:



85. The final product of the reaction $[\text{Mn}(\text{CO})_6]^+ + \text{MeLi} \longrightarrow$ is:
- (a) $[\text{Mn}(\text{CO})_6]^+ \text{Me}^-$ (b) $[\text{Mn}(\text{CO})_5 \text{Me}]$
 (c) $[\text{Mn}(\text{CO})_6]$ (d) $[(\text{MeCO})\text{Mn}(\text{CO})_5]$
86. The reaction that yields $\text{Li}[\text{AlH}_4]$ is:
- (a) $\text{HCl}(\text{excess}) + \text{AlCl}_3 + \text{Li} \rightarrow$ (b) $\text{H}_2 + \text{Al} + \text{Li} \rightarrow$
 (c) $\text{LiH}(\text{excess}) + \text{AlCl}_3 \rightarrow$ (d) $\text{LiH}(\text{excess}) + \text{Al} \rightarrow$
87. The number of microstates for d^5 electron configuration is:
- (a) 21×6^3 (b) 14×6^3 (c) 7×6^2 (d) 28×6^3
88. The carbon-14 activity of an old wood sample is found to be $14.2 \text{ disintegrations min}^{-1}\text{g}^{-1}$. Calculate age of old wood sample, if for a fresh wood sample carbon-14 activity is $15.3 \text{ disintegrations min}^{-1}\text{g}^{-1}$ ($t_{1/2}$ carbon-14 is 5730 years), is:
- (a) 5, 000 years (b) 4, 000 years (c) 877 years (d) 617 years
89. The reaction $3[\text{Rh}_4(\text{CO})_{12}] \rightarrow 2[\text{Rh}_6(\text{CO})_{16}] + 4\text{CO}$ [25°C , 500 atm CO] is:
- (a) Exothermic as more metal-metal bonds are formed.
 (b) Endothermic as stronger metal-carbonyl bonds are cleaved while weaker metal-metal bonds are formed.
 (c) Is entropically favorable but enthalpically unfavorable such that $\Delta G = 0$
 (d) Thermodynamically unfavourable ($\Delta G > 0$).
90. A column is packed with 0.5 g of a strongly acidic ion exchange resin in H^+ form. A 1.0 M NaCl solution is passed through the column until the eluant coming out becomes neutral. The collected eluant is completely neutralized by 17 ml. of 0.5 M NaOH. The ion exchange capacity of the resin is:
- (a) 1.00 meq/g (b) 1.25 meq/g (c) 1.50 meq/g (d) 1.75 meq/g
91. The molar extinction coefficient of B (MW = 180) is $4 \times 10^3 \text{ lit mol}^{-1} \text{ cm}^{-1}$. One liter solution of C which contains 0.1358 g pharmaceutical preparation of B, shows an absorbance of 0.411 in a 1 cm quartz cell. The percentage (w/w) of B in the pharmaceutical preparation is:
- (a) 10.20 (b) 14.60 (c) 20.40 (d) 29.12
92. The changes (from A-D given below) which occur when O_2 binds to hemerythrin are
- (A) One iron atoms is oxidized
 (B) Both the iron atoms are oxidized
 (C) O_2 binds to one iron atom and is also hydrogen bonded.
 (D) O_2 binds to both the iron atoms and is also hydrogen bonded.
- (a) B and C (b) B and D (c) A and D (d) A and C
93. In photosynthetic systems the redox metalloproteins involved in electron transfer are cytochrome (cyt, b), cytochrome bf complex (cyt bf) and plastocyanin (PC). The pathway of electron flow is
- (a) $\text{PC} \rightarrow \text{cyt b} \rightarrow \text{cyt bf}$ (b) $\text{cyt bf} \rightarrow \text{cyt b} \rightarrow \text{PC}$
 (c) $\text{cyt b} \rightarrow \text{cyt bf} \rightarrow \text{PC}$ (d) $\text{PC} \rightarrow \text{cyt bf} \rightarrow \text{cyt b}$
94. The total numbers of fine and hyperfine EPR lines expected for octahedral high-spin $\text{Mn}(\text{II})$ complexes are respectively ($I = 5/2$ for Mn)
- (a) 3 and 30 (b) 5 and 33 (c) 5 and 30 (d) 4 and 24



95. The Mossbauer spectra of two iron complexes are shown below. They may arise from (i) high-spin iron(III), (ii) high-spin iron(II) and (iii) low-spin iron(III)



The correct matches of spectra (A) and (B) with the iron complexes are

- (a) A with (i) and B with (ii) (b) A with (ii) and B with (i)
 (c) A with (iii) and B with (ii) (d) A with (ii) and B with (iii)
96. The probability of finding the particle in a one dimensional box of length 'L' in the region between $\frac{L}{4}$ and $\frac{3L}{4}$ for quantum number $n = 1$ is:
- (a) $\frac{1}{2}$ (b) $\frac{1}{2} + \frac{1}{\pi}$ (c) $\frac{1}{2} - \frac{1}{\pi}$ (d) $\frac{2}{3}$
97. A particle in three dimensional cubic box of length L has energy of $\frac{14h^2}{8mL^2}$. The degeneracy of the state is
- (a) 2 (b) 3 (c) 6 (d) 9
98. The following are the three statements about perturbation theory
- (A) Second order perturbation correction to the ground state energy is ALWAYS negative.
 (B) Sum of the zeroth order and the first order corrections to the ground state energy is ALWAYS greater than the exact ground state energy.
 (C) Sum of the zeroth order and first order corrections to the ground state energy is less than the exact state energy.
- From the following which one is correct?
- (a) Only A is true (b) Both A and B are true (c) Only C is true (d) Both B and C are true
99. Using Hückel molecular orbital approximation, the two roots of secular equation of ethene are
- (a) $\alpha + \sqrt{2}\beta, \alpha - \sqrt{2}\beta$ (b) $\alpha + \beta, \alpha$ (c) $\alpha + \beta, \alpha - \beta$ (d) $\alpha + 2\beta, \alpha - 2\beta$
100. For H_2 molecule in the excited state $\sigma_g^1 \sigma_s^1$, the spin part of the triplet state with $m_s = 0$ is proportional to
- (a) $\alpha(1)\beta(2)$ (b) $[a(1)\beta(2) - \beta(1)\alpha(2)]$
 (c) $\alpha(1)\alpha(2)$ (d) $[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$
101. A square pyramidal, MX_4 , molecule belongs to C_{4v} point group. The symmetry operations are: E, $2C_4, C_2, 2\sigma_v$ and $2\sigma_d$. The trace for the reducible representation, when symmetry operations of C_{4v} applied to MX_4 , is:
- (a) 5 1 1 1 3 (b) 1 1 1 1 1 (c) 5 1 1 1 1 (d) 4 1 1 1 3

102. Character table of C_{2v} point group is:

C_{2v}	E	C_2	σ_v	$\sigma_{v'}$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	1
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

If the initial and final states belong to A_1 and B_1 irreducible representation respectively, the allowed electronic transition from A_1 to B_1 is:

- (a) z-polarized (b) y-polarized (c) x-polarized (d) x, z-polarized

103. Using cuvettes of 0.5 cm path length, a 10^{-4} M solution of a chromophore shows 50% transmittance at certain wave length. The molar extinction coefficient of the chromophore at this wave length is ($\log 2 = 0.301$)

- (a) $1500 \text{ M}^{-1} \text{ cm}^{-1}$ (b) $3010 \text{ M}^{-1} \text{ cm}^{-1}$ (c) $5000 \text{ M}^{-1} \text{ cm}^{-1}$ (d) $6020 \text{ M}^{-1} \text{ cm}^{-1}$.

104. The set of allowed electronic transitions among the following is:

- (A) $^4\Sigma \rightarrow ^2\Pi$ (B) $^3\Sigma \rightarrow ^3\Pi$ (C) $^1\Delta \rightarrow ^1\Delta$ (D) $^2\Pi \rightarrow ^2\Pi$ (E) $^3\Sigma \rightarrow ^3\Delta$
 (a) A, B, E (b) A, C, E (c) B, C, D (d) C, D, E

105. The following data were obtained from the vibrational fine structure in the vibronic spectrum of a diatomic molecule:

$$\omega_e = 512 \text{ cm}^{-1}, \omega_e x_e = 8 \text{ cm}^{-1}$$

where ω_e is the energy associated with the natural frequency of vibration and x_e is the anharmonicity constant. The dissociation energy (D_e) of the molecule is:

- (a) 4096 cm^{-1} (b) 6144 cm^{-1} (c) 8192 cm^{-1} (d) 16384 cm^{-1} .

106. An ideal gas was subjected to a reversible, adiabatic, expansion and then its initial volume was restored by a reversible, isothermal compression. If 'q' denotes the heat added to the system and 'w' the work done by the system, then

- (a) $w < 0, q < 0$ (b) $w > 0, q < 0$ (c) $w < 0, q > 0$ (d) $w > 0, q > 0$

107. The gas phase reaction $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$ is an exothermic process. In an equilibrium mixture of NO_2 and N_2O_4 , the decomposition of N_2O_4 can be induced by

- (a) Lowering the temperature (b) Increasing the pressure
 (c) Introducing an inert gas at constant volume (d) Introducing an inert gas at constant pressure.

108. Indicate which one of the following relations is NOT correct.

- (a) $-\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V$ (b) $-\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
 (c) $-\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ (d) $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$



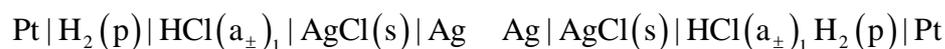
109. The energy levels of the harmonic oscillator (neglecting zero point energy) are $\epsilon_n = nh\nu$ for $n = 0, 1, 2, \dots, \infty$. Assuming $h\nu = k_B T$, the partition function is:

(a) e (b) $\frac{1}{e}$ (c) $1 - \frac{1}{e}$ (d) $\frac{1}{1 - \frac{1}{e}}$

110. The correct entropy for 6 identical particles with their occupation number $\{0, 1, 2, 3\}$ in four states is

(a) $k_B \ln 6$ (b) $k_B \ln 12$ (c) $k_B \ln 60$ (d) $k_B \ln 720$

111. The correct Nernst equation for the concentration cell:



without liquid junction would be

(a) $E = \frac{2RT}{F} \ln \frac{(\text{a}_{\pm})_1}{(\text{a}_{\pm})_2}$ (b) $E = \frac{RT}{F} \ln \frac{(\text{a}_{\pm})_2}{(\text{a}_{\pm})_1}$ (c) $E = \frac{2RT}{F} \ln \frac{(\text{a}_{\pm})_2}{(\text{a}_{\pm})_1}$ (d) $E = \frac{RT}{2F} \ln \frac{(\text{a}_{\pm})_2}{(\text{a}_{\pm})_1}$

112. Main assumption(s) involved in the derivation of Debye-Hückel equation is(are) the validity of

(a) Only Poission equation (b) Poission equation and Boltzmann distribution

(c) Poission equation, Boltzmann distribution and $|\pm Z e \phi| \gg k_B T$

(d) Poission equation Boltzmann distribution and $|\pm Z e \phi| \ll k_B T$

113. In the base (OH^-) hydrolysis of a transition metal complex $[\text{ML}_6]^{Z+}$, the slope between $\log(k/k_0)$ and \sqrt{I} is found to be -2.1 . The charge on the complex is:

(a) +1 (b) +2 (c) +3 (d) +4

114. The rate law for one of the mechanism of the pyrolysis of CH_3CHO at 520°C and 0.2 bar is

$$\text{Rate} = - \left| k_2 \left(\frac{k_1}{2k_4} \right)^{1/2} \right| [\text{CH}_3\text{CHO}]^{3/2}$$

The overall activation energy E , in terms of the rate law is:

(a) $E_a(2) + E_a(1) + 2E_a(4)$ (b) $E_a(2) + \frac{1}{2}E_a(1) - E_a(4)$

(c) $E_a(2) + \frac{1}{2}E_a(1) - \frac{1}{2}E_a(4)$ (d) $E_a(2) - \frac{1}{2}E_a(1) + \frac{1}{2}E_a(4)$

115. In the Michaelis-Menten mechanism for enzyme kinetics, the expression obtained is:

$$\frac{v}{[\text{E}]_0 [\text{S}]} = 1.4 \times 10^{12} - \frac{10^4 v}{[\text{E}]_0}$$

The values of k_3 (k_{exp} , $\text{mol L}^{-1}\text{s}^{-1}$) and K (Michaelis constant, mol L^{-1}), respectively are

(a) $1.4 \times 10^{12}, 10^4$ (b) $1.4 \times 10^8, 10^4$ (c) $1.4 \times 10^8, 10^{-4}$ (d) $1.4 \times 10^{12}, 10^{-4}$

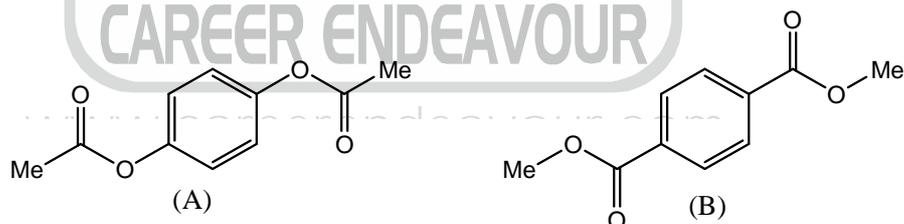
116. The most used acid catalyst in oil industry and the relevant process are respectively
 (a) Aluminophosphate and reforming (b) Aluminosilicate and cracking
 (c) Aluminosilicate and reforming (d) Aluminophosphate and cracking.
117. The wavelength and the spectral region for a single electron transfer across the band gap in a semiconductor ($E_x - 1.98 \times 10^{-19}$) are [$h = 6.626 \times 10^{-34}$ Js, $c = 3 \times 10^8$ ms $^{-1}$]
 (a) 1000 nm, UV (b) 1000 nm, IR (c) 500 nm, visible (d) 500 nm, FAR IR
118. The lattice parameter of an element stabilized in a fcc structure is 4.04 Å. The atomic radius of the element is:
 (a) 2.86 Å (b) 1.43 Å (c) 4.29 Å (d) 5.72 Å
119. The number-average molar mass (\bar{M}_n) and weight-average molar mass (\bar{M}_w) of a polymer are obtained respectively by
 (a) Osmometry and light scattering measurements
 (b) Osmometry and viscosity measurements
 (c) Light scattering and sedimentation measurements
 (d) Viscosity and light scattering measurements

120. Two data sets involving the same variables X and Y are given below

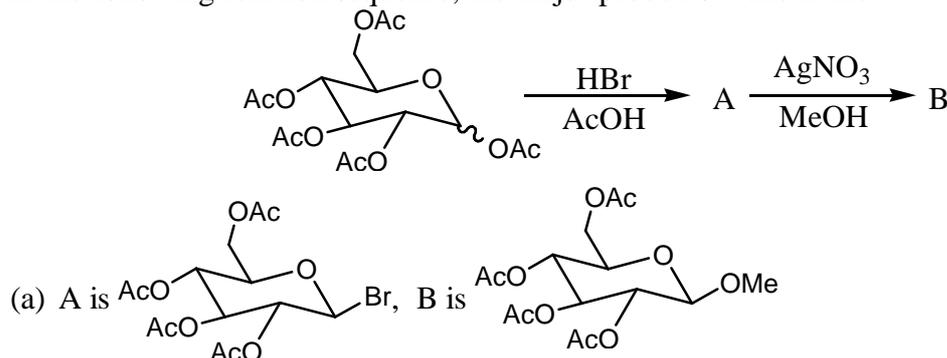
X	4.1	4.2	4.3	4.4	4.5	4.6
Y(set A)	10.2	10.6	10.9	11.5	11.8	12.2
Y(set B)	10.2	10.6	11.1	11.3	11.8	12.2

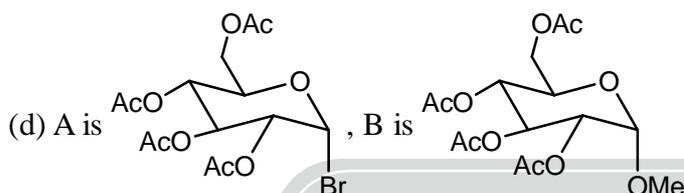
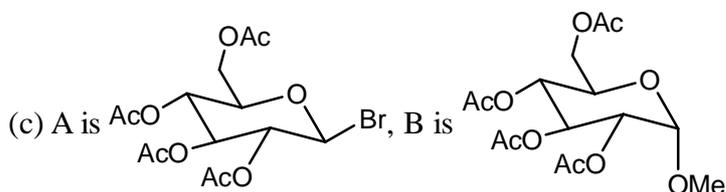
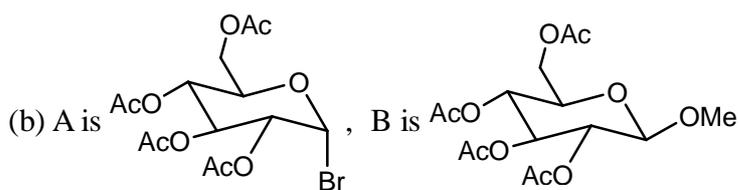
If the slopes and intercepts of the regression lines for the two sets are denoted by (m_A, m_B) and (C_A, C_B), respectively, then

- (a) $m_A > m_B, C_A > C_B$ (b) $m_A < m_B, C_A > C_B$
 (c) $m_A > m_B, C_A < C_B$ (d) $m_A < m_B, C_A < C_B$
121. Compounds A and B exhibit two singlets, each in their ^1H NMR spectra. The expected chemical shifts are at δ

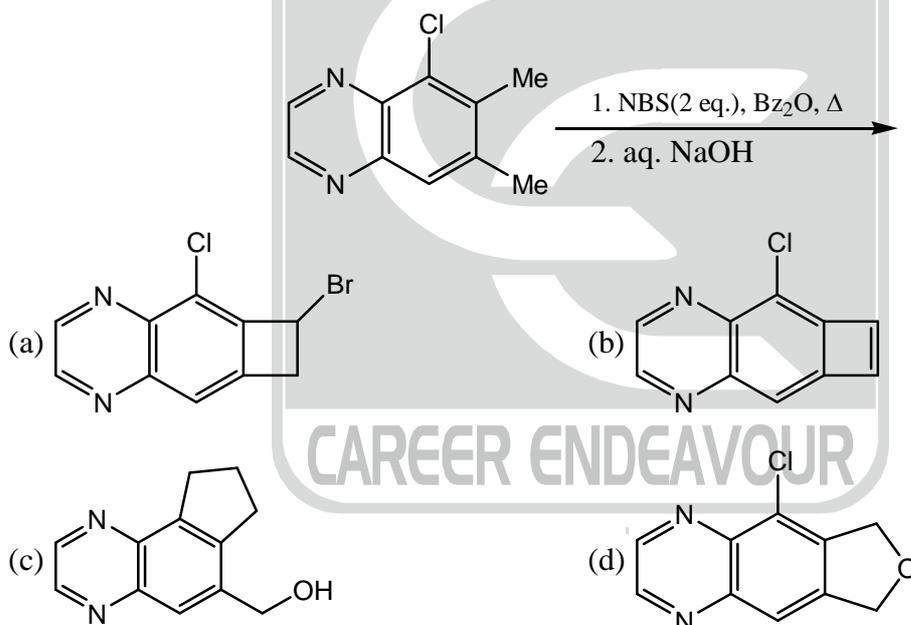


- (a) 6.9 and 2.1 for A; 7.7 and 3.9 for B (b) 7.7 and 3.9 for A; 6.9 and 2.1 for B
 (c) 6.9 and 3.9 for A; 7.7 and 2.1 for B (d) 7.7 and 2.1 for A; 6.9 and 3.9 for B
122. In the following reaction sequence, the major products A and B are

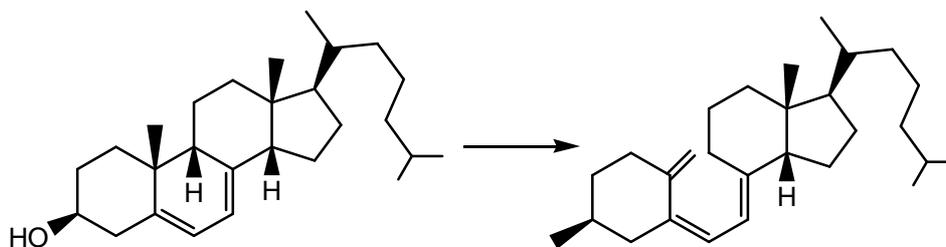




123. The structure of the tricyclic compound formed in the following two step sequence is

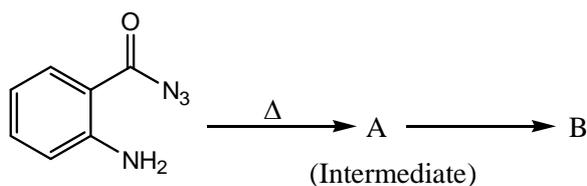


124. The two step conversion of 7-dehydrocholesterol to vitamin D₃ proceeds through



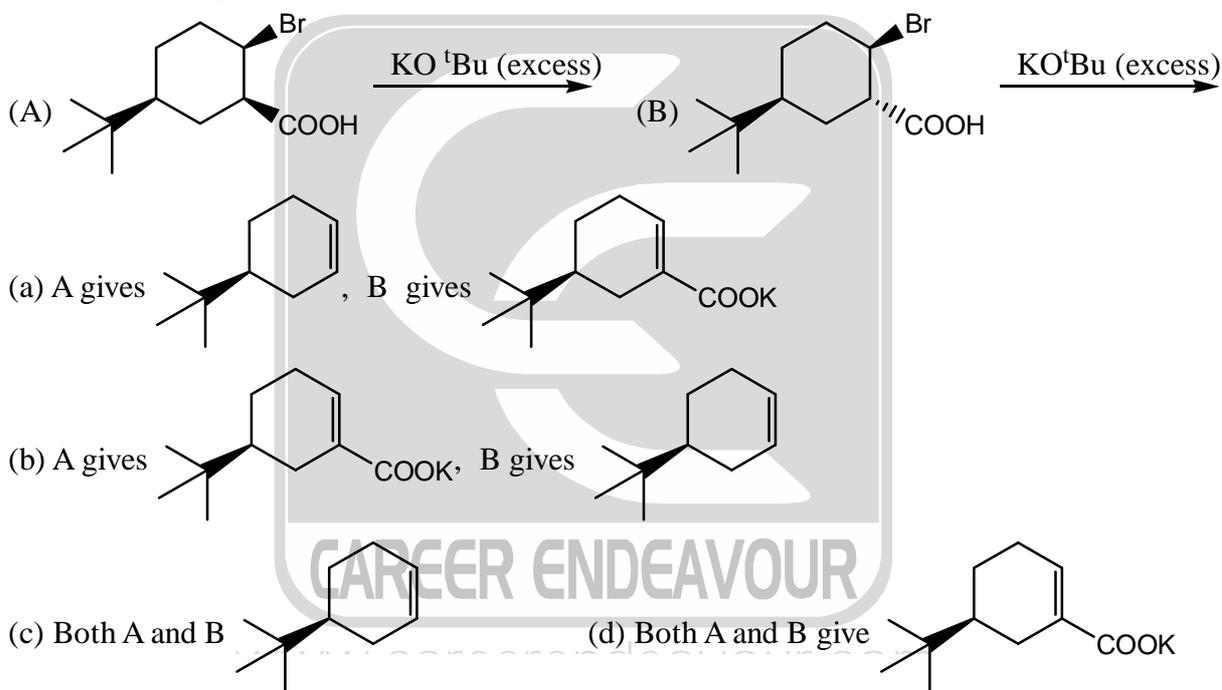
- (a) Photochemical electrocyclic disrotatory ring opening; and thermal antarafacial [1, 7]-H shift.
 (b) Photochemical electrocyclic conrotatory ring opening; and thermal antarafacial [1, 7]-H shift.
 (c) Thermal electrocyclic conrotatory ring opening; and photochemical suprafacial [1, 7]-H shift.
 (d) Thermal electrocyclic disrotatory ring opening; and thermal suprafacial [1, 7]-H shift.

125. The intermediate A and the major product B in the following reaction are

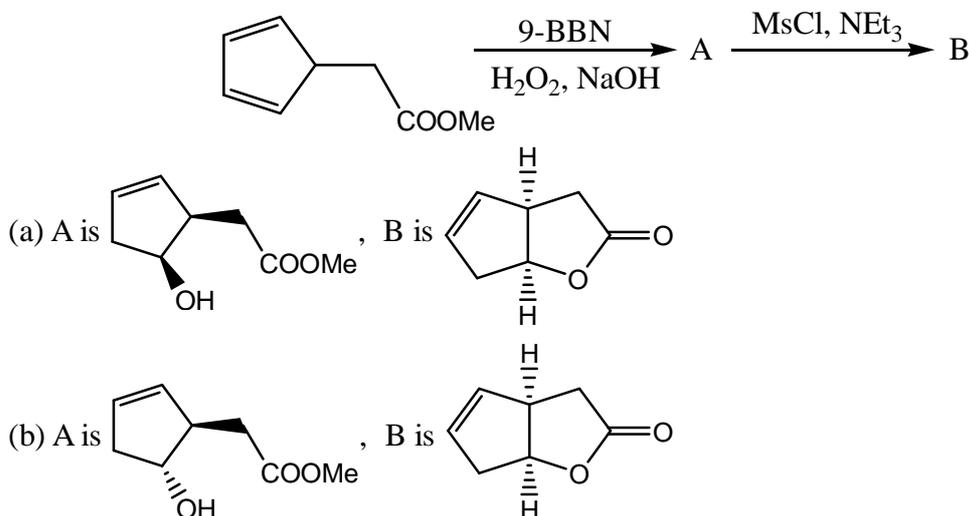


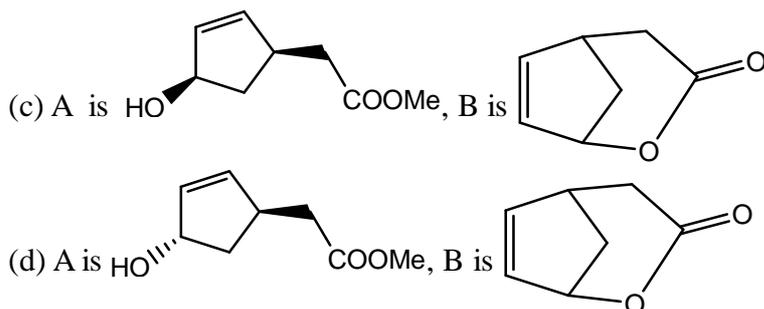
- (a) A is acyl cation; B is
- (b) A is acyl cation; B is
- (c) A is nitrene; B is
- (d) A is acyl nitrene; B is

126. For the following two reactions A and B, the correct statement is:



127. The major compound B formed in the reaction sequence given below exhibited a carbonyl absorption band at 1770 cm^{-1} in the IR spectrum. The structure A and B are

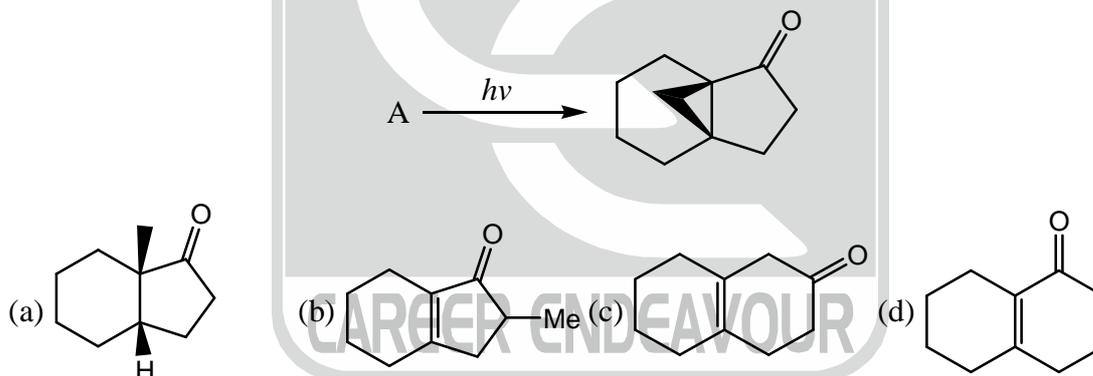




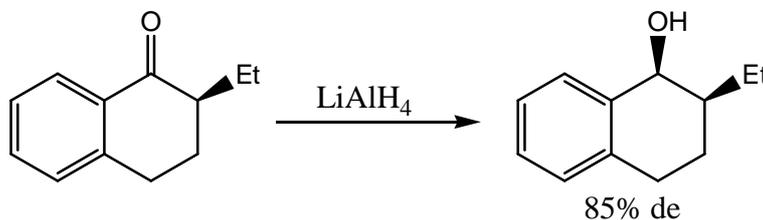
128. Consider the following reaction sequence starting with monoterpene α -pinene. Identify the correct statement



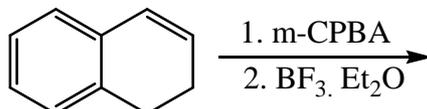
- (a) A has a disubstituted double bond; B and C are dicarboxylic acids.
 (b) A has a trisubstituted double bond; B is a methyl ketone; and C is a dicarboxylic acid.
 (c) A has a disubstituted double bond; B is a methyl ketone; and C is a dicarboxylic acid.
 (d) A has an exocyclic double bond; B and C are monocarboxylic acids.
129. The major product formed when (3R, 4S)-3, 4-dimethylhexa-1, 5-diene is heated at 240° is:
 (a) (2Z, 6Z)-octa-2, 6-diene (b) (2E, 6E)-octa-2, 6-diene
 (c) (2E, 6Z)-octa-2, 6-diene (d) (3Z, 5E)-octa-3, 5-diene
130. Structure of the starting material A in the following photochemical Norrish reaction, is

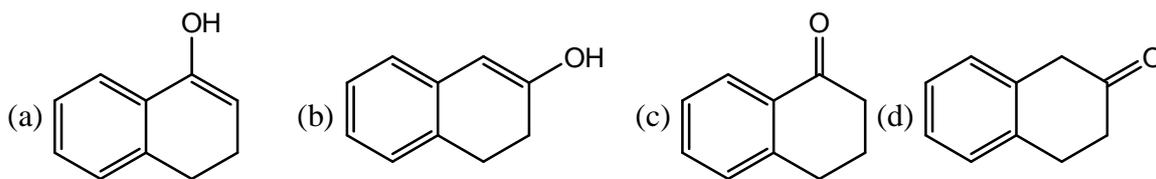


131. Considering the following reaction, among A-C, the correct statements are

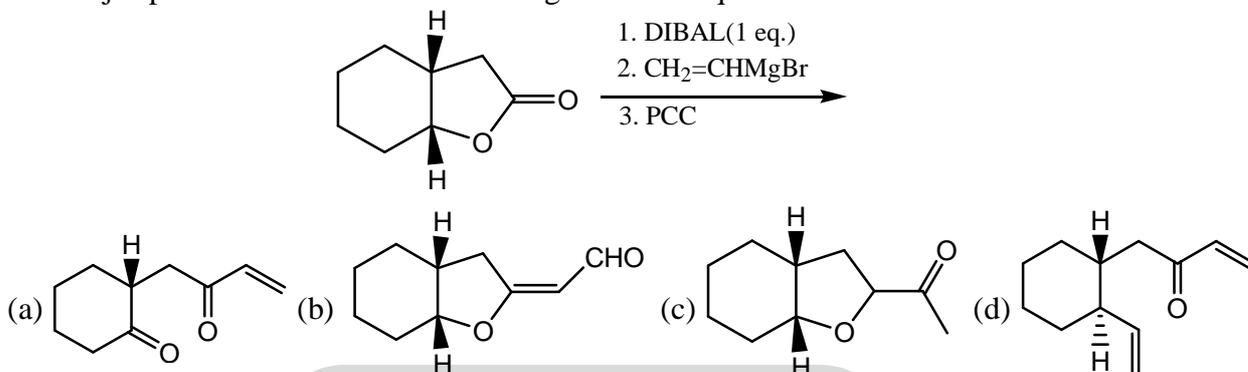


- (A) The carbonyl group has enantiotopic faces;
 (B) The hydride attack is re-facial;
 (C) It is a diastereoselective reduction.
 (a) (A) and (B) only (b) (A) and (C) only (c) (B) and (C) only (d) (A), (B) and (C)
132. The major product formed in the following reaction sequence is





133. The major product formed in the following reaction sequence is:



134. Match the following

Compound

¹³C NMR chemical shift (δ ppm)

(A) Acetic acid

(i) 95

(B) Acetonitrile

(ii) 115

(C) Acetone

(iii) 175

(D) Carbon tetrachloride

(iv) 205

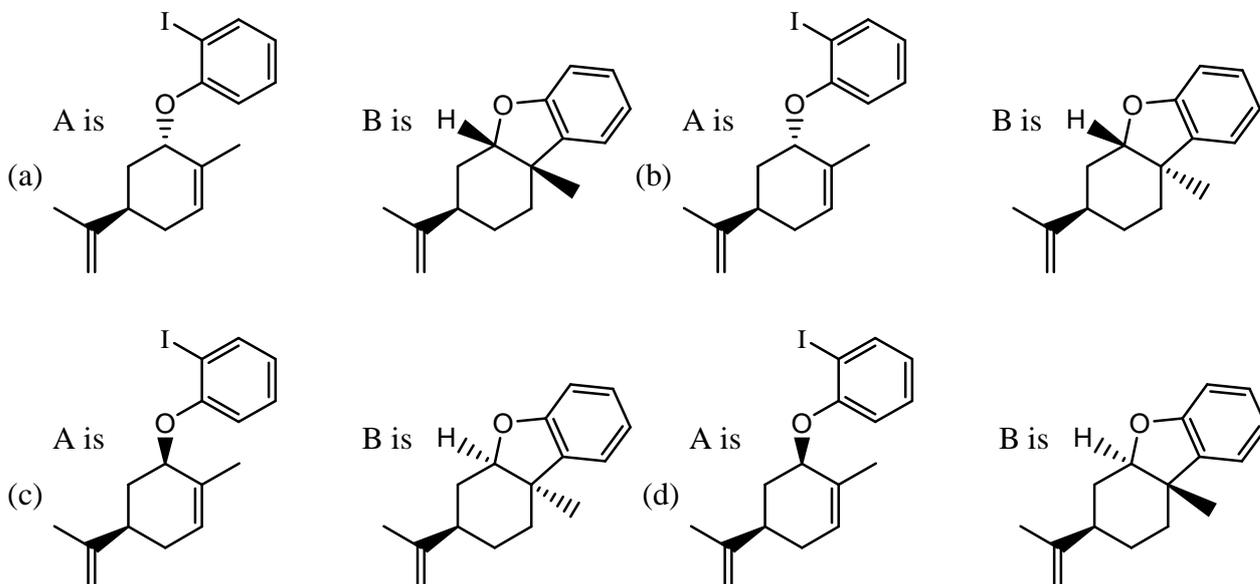
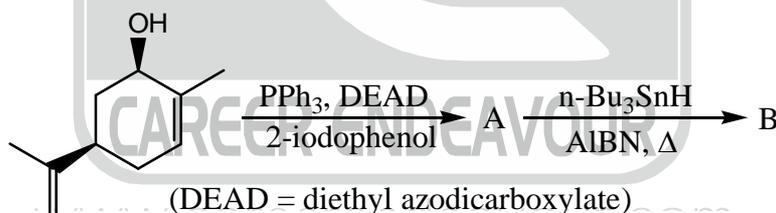
(a) (A)-(iii), (B)-(ii), (C)-(iv), (D)-(i)

(b) (A)-(iii), (B)-(iv), (C)-(i), (D)-(ii)

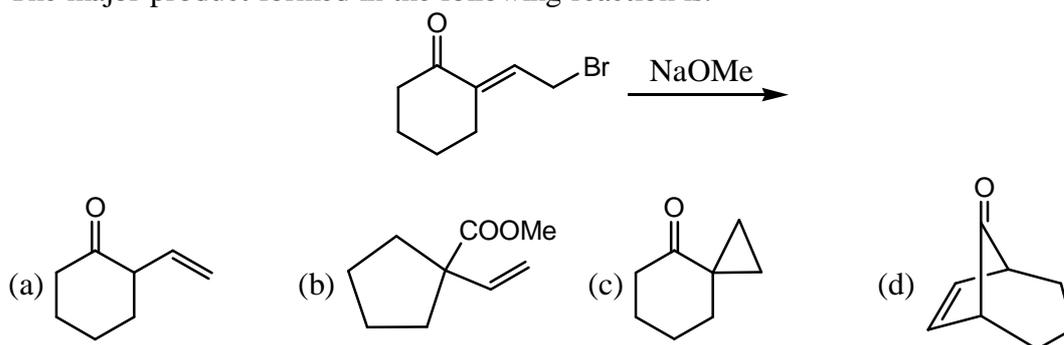
(c) (A)-(i), (B)-(ii), (C)-(iv), (D)-(ii)

(d) (A)-(iii), (B)-(i), (C)-(iii), (D)-(iv)

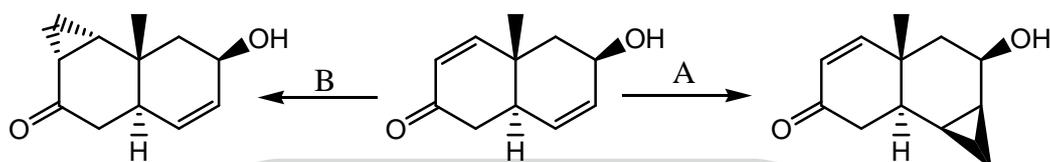
135. The major products A and B in the following reaction sequence are



136. The major product formed in the following reaction is:

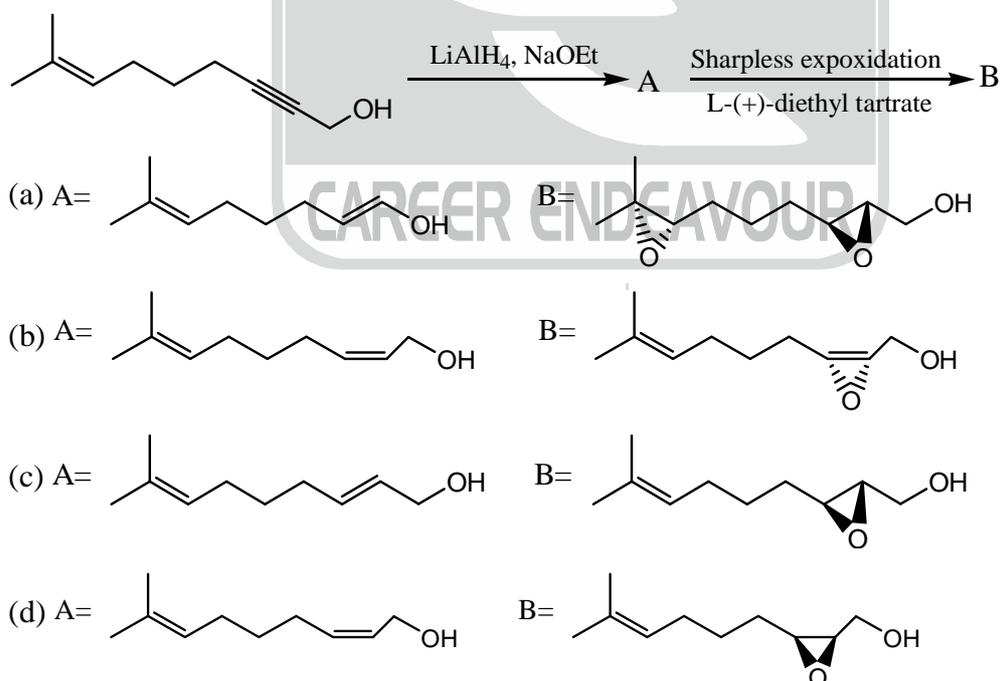


137. The reagents A and B in the following reactions are

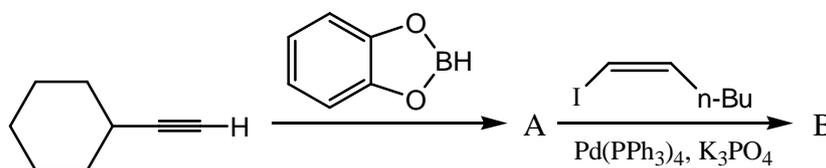


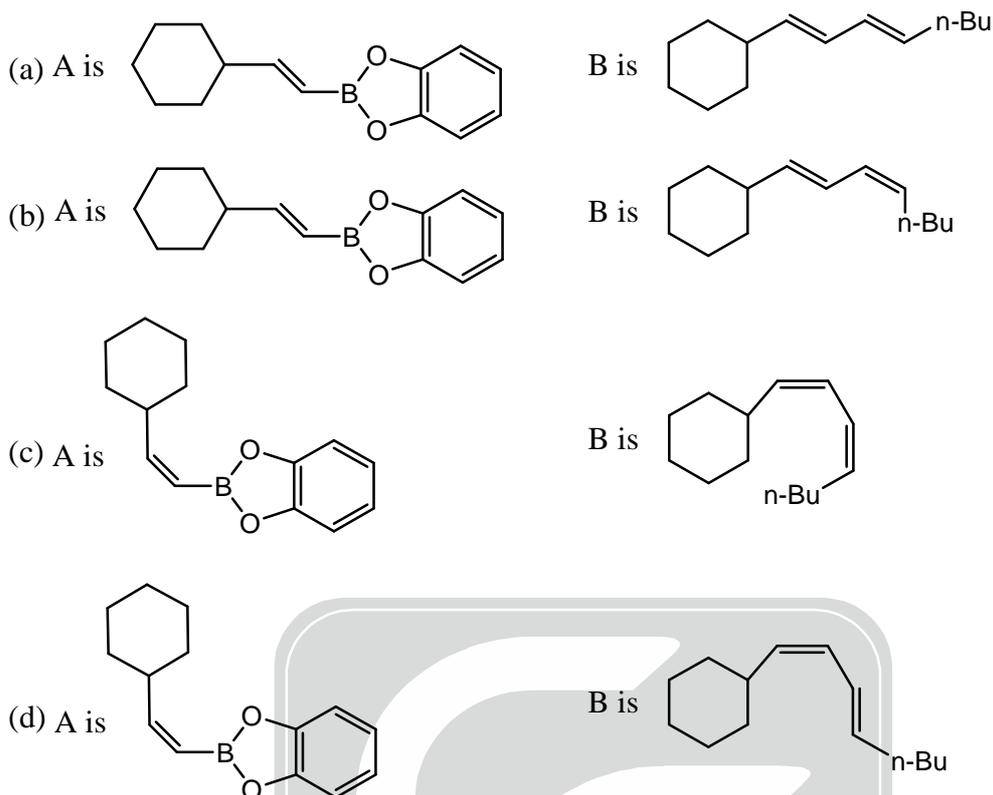
- (a) A = CH_2I_2 , Zn - Cu; B = $\text{Me}_3\text{S}^+\text{I}^-$, NaH
 (b) A = CH_2I_2 , Zn - Cu; B = $\text{Me}_3\text{S}^+(\text{O})\text{I}^-$, NaH
 (c) A = $\text{Me}_3\text{S}^+\text{I}^-$, NaH; B = $\text{Me}_3\text{S}^+(\text{O})\text{I}^-$, NaH
 (d) A = $\text{Me}_3\text{S}^+(\text{O})\text{I}^-$, NaH; B = CH_2I_2 , Zn - Cu

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

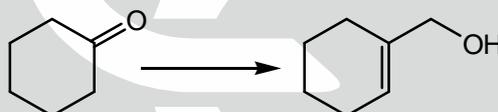


139. The major products A and B formed in the following reaction sequence are



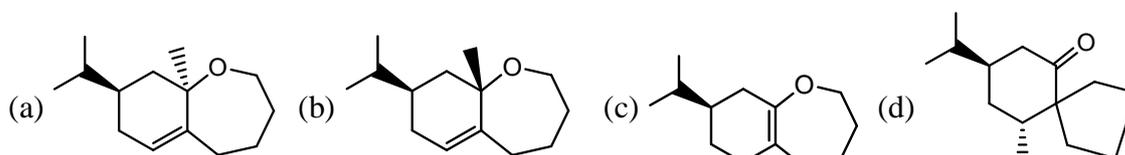
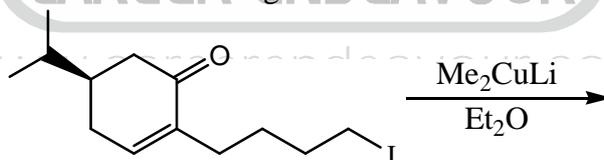


140. The correct reagent combination/reaction sequence for effecting the following conversion is:

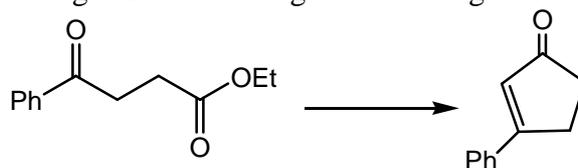


- (a) (1) $\text{Me}_3\text{SiCH}_2\text{OMe}$, BuLi; (2) H_3O^+ ; (3) NaBH_4 , MeOH
 (b) (1) $\text{Ph}_3\text{P}^+\text{CH}_2\text{MeCl}$, BuLi; (2) H_3O^+ ; (3) NaBH_4 , MeOH
 (c) (1) NH_2NHTs ; (2) NaOEt; (3) ClCOOEt
 (d) (1) NH_2NHTs ; (2) 2 eq. BuLi; (3) HCHO

141. The major product formed in the following reaction is:



142. The correct sequence of reagents for effecting the following conversion is:



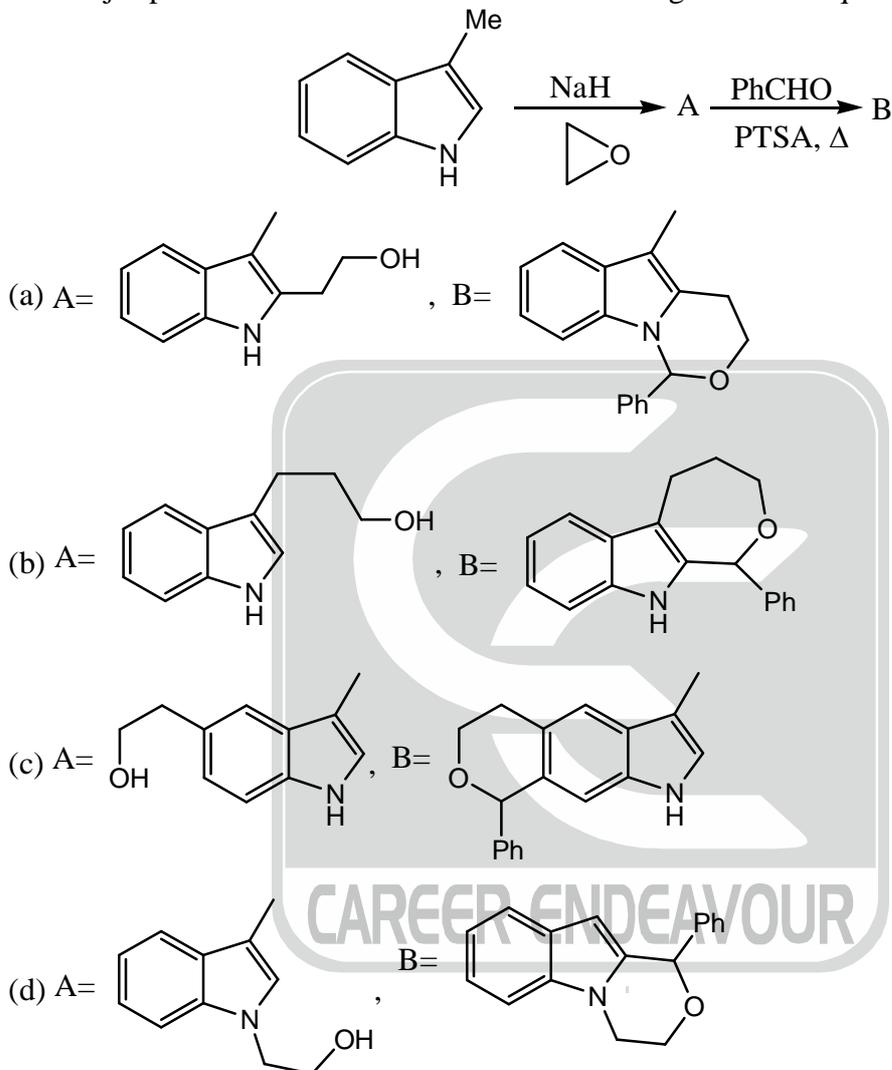
- (a) (1) $(\text{CH}_2\text{OH})_2$, PTSA, Δ ; (2) $\text{Cp}_2\text{Ti} \begin{array}{c} \diagup \\ \text{Cl} \end{array} \text{AlMe}_2$ (Tebbe's reagent) (3) H_3O^+ ; (4) KOH

(b) (1) $(\text{CH}_2\text{OH})_2$, PTSA, Δ ; (2) $\text{Ph}_3\text{P}-\text{CH}_2$; (3) H_3O^+ ; (4) KOH

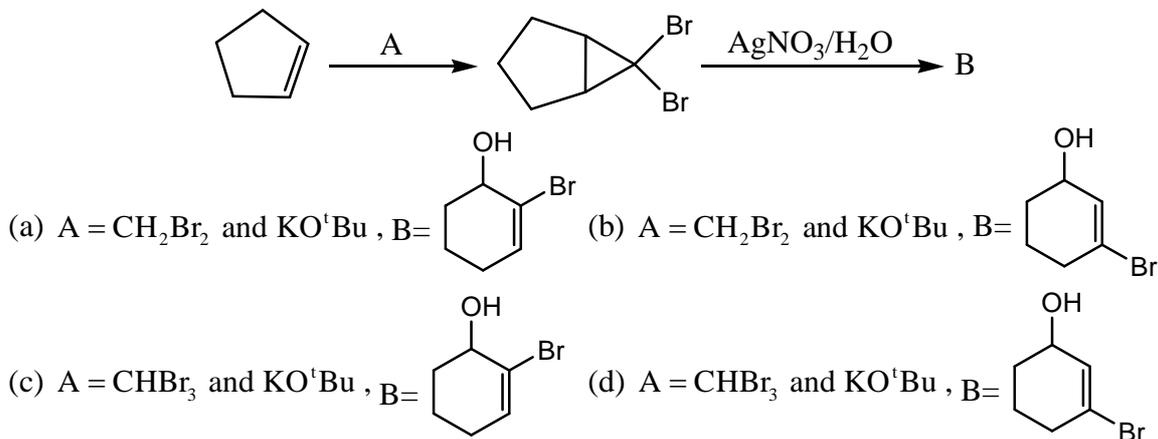
(c) (1) $\text{Cp}_2\text{Ti} \begin{array}{c} \diagup \\ \text{Cl} \\ \diagdown \end{array} \text{AlMe}_2$ (Tebbe's reagent); (2) H_3O^+ ; (3) KOH

(d) $\text{Ph}_3\text{P}=\text{CH}_2$; (2) H_3O^+ ; (3) KOH

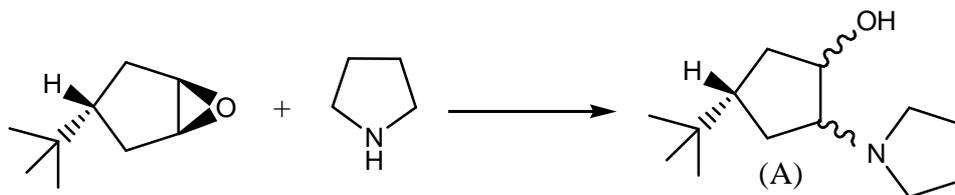
143. The major products A and B formed in the following reaction sequence are



144. The reagent A required, and the major product B formed in the following reaction sequence are



145. Among the choices, the correct statements for A formed in the following reaction.



- (a) A is a single enantiomer (b) A is a racemic mixture
(c) A is a mixture of two diastereomers (d) A is a mixture of two epimers.

