

PAPER : CSIR-UGC-NET/JRF Dec. 2012
CHEMICAL SCIENCES BOOKLET-[A]

Part-B

21. For an odd nucleon in 'g' nuclear orbital and parallel to I, spin and parity are
(a) 9/2 and (+) (b) 7/2 and (+) (c) 9/2 and (-) (d) 7/2 and (-)
22. For the deposition of Pb by electroplating, the best suited compound among the following is
(a) PbCl_2 (b) PbSO_4 (c) $\text{Pb}(\text{Et})_4$ (d) $\text{Pb}(\text{BF}_4)_2$.
23. Appropriate reasons for the deviation from the Beer's law among the following are
(A) Monochromaticity of light (C) Very high concentration of analyte
(B) Association of analyte (D) Dissociation of analyte.
(a) A, B and D (b) B, C and D (c) A, C and D (d) A, B and C
24. Which one of the following shows the highest solubility in hot concentrated aqueous NaOH?
(a) $\text{La}(\text{OH})_3$ (b) $\text{Nd}(\text{OH})_3$ (c) $\text{Sm}(\text{OH})_3$ (d) $\text{Lu}(\text{OH})_3$.
25. In the vibrational spectrum of CO_2 , the number of fundamental vibrational modes common in both infrared and Raman are
(a) Three (b) Two (c) One (d) Zero
26. The light pink color of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and the deep blue color of $[\text{CoCl}_4]^{2-}$ are due to
(a) MLCT transition in the first and d-d transition in the second
(b) LMCT transition in both
(c) d-d transitions in both
(d) d-d transition in the first and MLCT transition in the second.
27. In $[\text{Mo}_2(\text{S}_2)_6]^{2-}$ cluster the number of bridging S_2^{2-} and coordination number of Mo respectively, are
(a) 2 and 8 (b) 2 and 6 (c) 1 and 8 (d) 1 and 6
28. ^1H NMR spectrum of HD would show
(a) a singlet (b) a doublet
(c) a triplet with intensity ratio 1:2:1 (d) a triplet with intensity ratio 1:1:1
29. The number of possible isomers of $[\text{Ru}(\text{PPh}_3)_2(\text{acac})_2]$ (acac = acetylacetonate) is:
(a) 2 (b) 3 (c) 4 (d) 5
30. The total number of Cu-O bonds present in the crystalline copper(II) acetate monohydrate is:
(a) 10 (b) 6 (c) 8 (d) 4
31. The electronegativity differences is the highest for the pair
(a) Li, Cl (b) K, F (c) Na, Cl (d) Li, F
32. Which ones among CO_3^{2-} , SO_3 , XeO_3 and NO_3^- have planar structure?
(a) CO_3^{2-} , SO_3 and XeO_3 (b) SO_3 , XeO_3 and NO_3^-
(c) CO_3^{2-} , XeO_3 and NO_3^- (d) CO_3^{2-} , SO_3 and NO_3^-
-

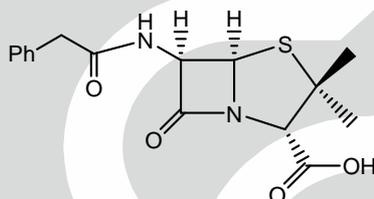
33. The substitution of $\eta^5 - \text{Cp}$ group with nitric oxide is the easiest for
 (a) $\eta^5 - \text{Cp}_2\text{Fe}$ (b) $\eta^5 - \text{Cp}_2\text{CoCl}$ (c) $\eta^5 - \text{Cp}_2\text{Ni}$ (d) $\eta^5 - \text{Cp}_2\text{Co}$

34. The molecule $(\text{CO})_5\text{M}=\text{C} \begin{array}{l} \diagup \text{OCH}_3 \\ \diagdown \text{Ph} \end{array}$
 obeys 18 electron rule. The two 'M' satisfying the condition are

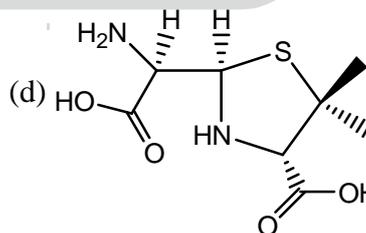
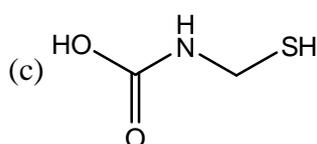
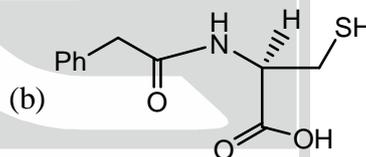
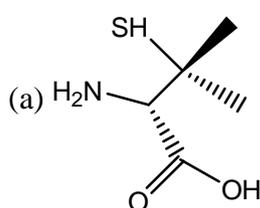
- (a) Cr, Re^+ (b) Mo, V (c) V, Re^+ (d) Cr, V
35. The correct set of the biologically essential elements is,
 (a) Fe, Mo, Cu, Zn (b) Fe, Cu, Co, Ru (c) Cu, Mn, Zn, Ag (d) Fe, Ru, Zn, Mg

36. The number of lines exhibited by a high resolution EPR spectrum of the species, $[\text{Cu}(\text{ethylenediamine})_2]^{2+}$ is [Nuclear spin (I) of Cu = 3/2 and that of N = 1]
 (a) 12 (b) 15 (c) 20 (d) 36

37. Degradation of penicillin G



gives penicillamine that can utilize nitrogen, oxygen or sulfur atoms as donors to bind with lead(II), mercury (II) or copper(II). The structure of penicillamine is



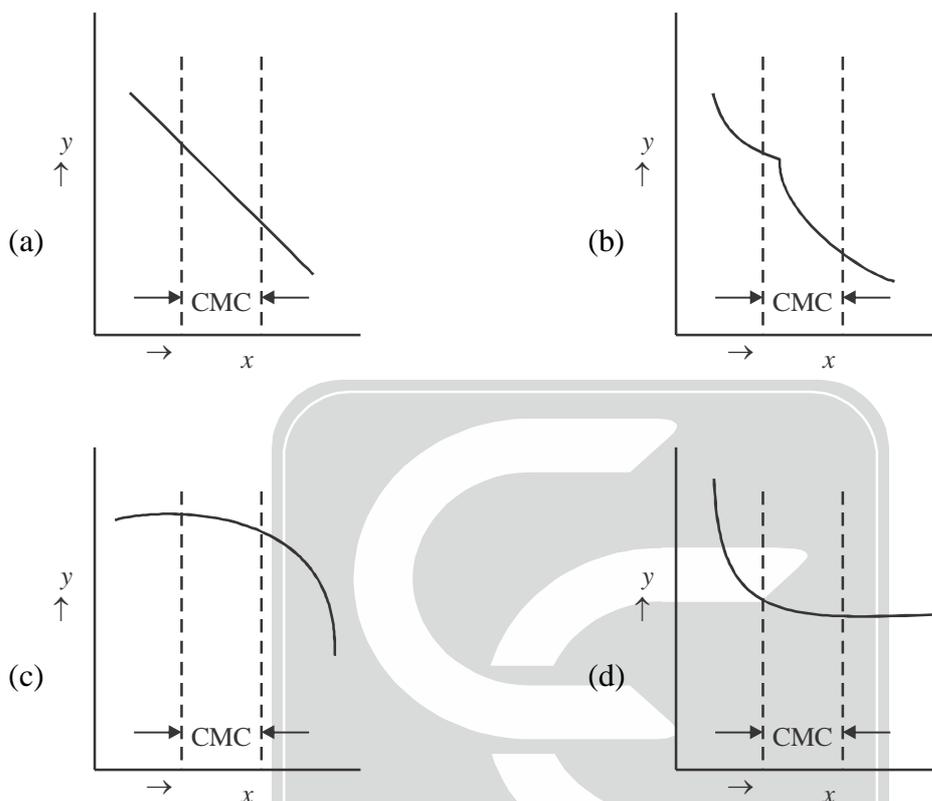
38. The molecular that has an S_6 symmetry element is
 (a) B_2H_6 (b) CH_4 (c) PH_5 (d) SF_6

39. The electric dipole allowed transition in a d^2 atomic system is
 (a) $^3\text{F} \rightarrow ^1\text{D}$ (b) $^3\text{F} \rightarrow ^1\text{P}$ (c) $^3\text{F} \rightarrow ^3\text{D}$ (d) $^3\text{F} \rightarrow ^3\text{P}$

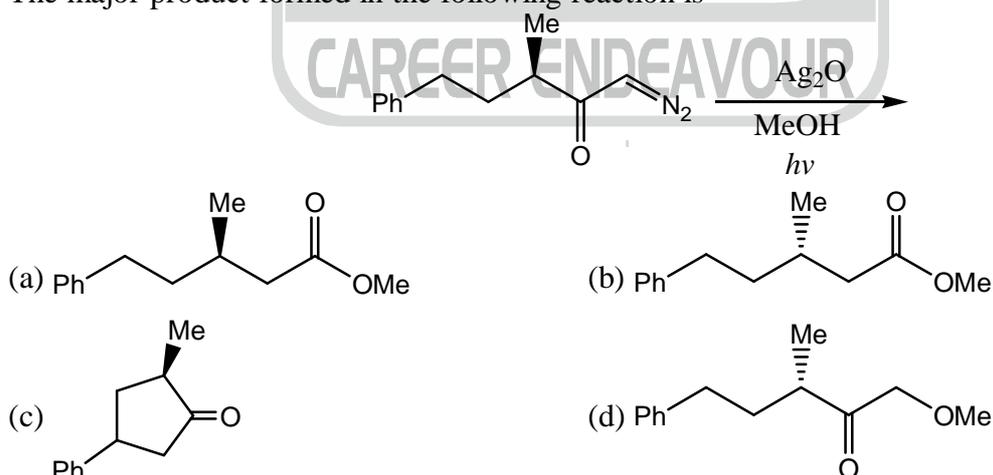
40. When a hydrogen atom is placed in an electric field along the y-axis, the orbital that mixes most with the ground state 1s orbital is
 (a) 2s (b) $2p_x$ (c) $2p_y$ (d) $2p_z$

41. For water, $\Delta H_{\text{vap}} \approx 41 \text{ kJ mol}^{-1}$. The molar entropy of vaporization at 1 atm pressure is approximately
 (a) $410 \text{ J K}^{-1} \text{ mol}^{-1}$ (b) $110 \text{ J K}^{-1} \text{ mol}^{-1}$ (c) $41 \text{ J K}^{-1} \text{ mol}^{-1}$ (d) $11 \text{ JK}^{-1} \text{ mol}^{-1}$.
42. If A and B are non-commuting hermitian operators, all eigenvalues of the operator given by the commutator $[A, B]$ are
 (a) complex (b) real (c) imaginary (d) zero
43. The value of commutator $[x, p_x^2]$ is given by
 (a) $2i$ (b) $2i\hbar$ (c) $2i\hbar x$ (d) $2i\hbar p_x$
44. The correlation coefficient between two arbitrary variables x and y is zero, if
 (a) $\langle xy \rangle = \langle yx \rangle$ (b) $\langle x^2 \rangle = \langle x \rangle^2$ (c) $\langle y^2 \rangle = \langle y \rangle^2$ (d) $\langle xy \rangle = \langle x \rangle \langle y \rangle$
45. A carnot takes up 90 J of heat from the source kept at 300K. The correct statement among the following is
 (a) It transfers 60 J of heat to the sink at 200K
 (b) It transfers 50 J of heat to the sink at 200K
 (c) It transfers 60 J of heat to the sink at 250 K
 (d) It transfers 50 J of heat to the sink at 250 K
46. The relative population in two states with energies E_1 and E_2 satisfying Boltzmann distribution is given by $n_1/n_2 = (3/2)\exp[-(E_1 - E_2)/k_B T]$. The relative degeneracy g_2/g_1 is:
 (a) 2 (b) $2/3$ (c) $3/2$ (d) 3
47. The Daniel cell is
 (a) $\text{Pt}_I(\text{s}) | \text{Zn}(\text{s}) | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}(\text{s}) | \text{Pt}_{II}(\text{s})$
 (b) $\text{Pt}_I(\text{s}) | \text{Zn}(\text{s}) | \text{Zn}^{2+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}(\text{s}) | \text{Pt}_{II}(\text{s})$
 (c) $\text{Pt}_I(\text{s}) | \text{Fe}(\text{s}) | \text{Fe}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}(\text{s}) | \text{Pt}_{II}(\text{s})$
 (d) $\text{Pt}_I(\text{s}) | \text{H}_2(\text{s}) | \text{H}_2\text{SO}_4(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}(\text{s}) | \text{Pt}_{II}(\text{s})$
48. If the concept of half-life is generalized to quarter-life of a first order chemical reaction, it will be equal to
 (a) $\ln 2/k$ (b) $\ln 4/k$ (c) $4/k$ (d) $1/4k$
49. Kohlrausch's law is applicable to a dilute solution of
 (a) Potassium chloride in hexane (b) Acetic acid in water
 (c) Hydrochloric acid in water (d) Benzoic acid in benzene
50. A dilute silver nitrate solution is added to a slight excess iodide solution. A solution of AgI is formed whose surface adsorbs.
 (a) I^- (b) NO_3^- (c) Na^+ (d) Ag^+
51. The absorption spectrum of O_2 shows a vibrational structure that becomes continuum at 56875 cm^{-1} . At the continuum, it dissociates into one ground state atom (O_g) and one excited state atom (O_e). The energy difference between O_e and O_g is 15125 cm^{-1} . The dissociation energy (in cm^{-1}) of ground state of O_2 is:
 (a) $\frac{56875}{15125}$ (b) $\frac{15125}{56875}$ (c) 72000 (d) 41750

52. The angle between the two planes represented by the Miller indices (1 1 0) and (1 1 1) in a simple cubic lattice is:
 (a) 30° (b) 45° (c) 60° (d) 90°
53. The correct representation of the variation of molar conductivity (y-axis) with surfactant concentration (x-axis) is [CMC = critical micelle concentration].

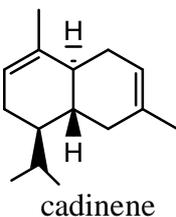


54. The major product formed in the following reaction is



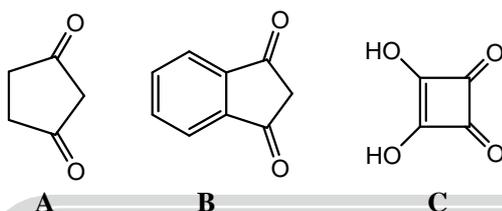
55. If the pK_a value for p-methoxybenzoic acid is 4.46 and that of benzoic acid is 4.19, the σ_{para} for methoxy group is:
 (a) 8.65 (b) 4.32 (c) 0.27 (d) -0.27

56. The biosynthetic precursor of cadinene is:



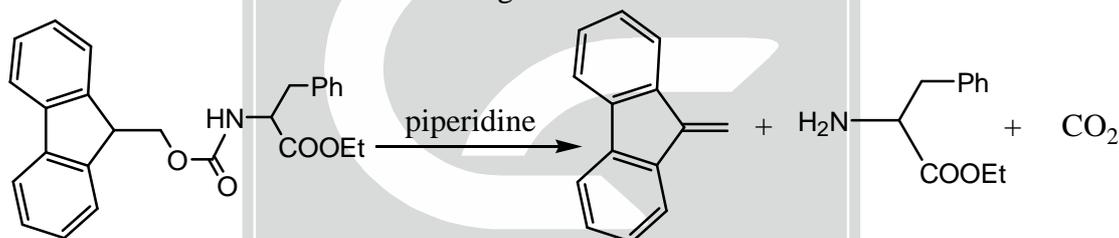
- (a) shikimic acid (b) mevalonic acid (c) arachidonic acid (d) prephenic acid.

57. The correct order of acidity of the compounds A – C is:



- (a) A > B > C (b) B > C > A (c) C > A > B (d) B > A > C

58. The mechanism involved in the following conversion is:



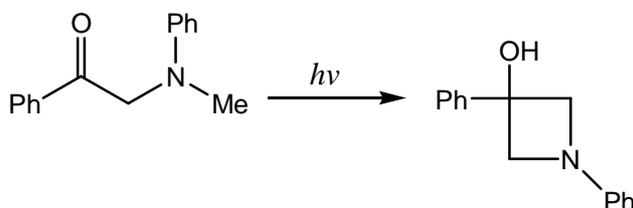
- (a) E₂-elimination (b) E₁-elimination (c) syn-elimination (d) E₁ CB-elimination.

59. The correct statement(s)-A-D are given for the following reaction. The correct one(s) is/are



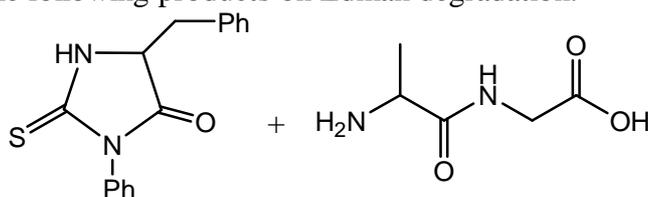
- (a) aromatic ipso substitution reaction (b) aromatic nucleophilic substitution
(c) aromatic electrophilic substitution (d) aromatic free radical substitution.

60. The following photochemical transformation proceeds through



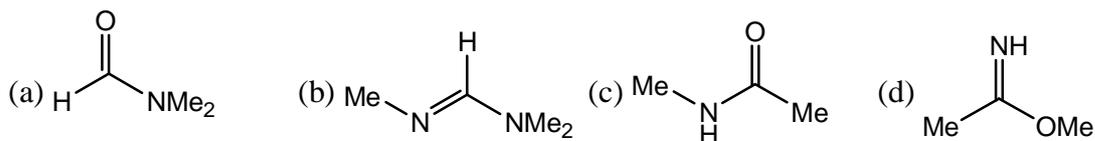
- (a) Norrish type I reaction (b) Norrish type II reaction
(c) Barton reaction (d) Paterno-Buchi reaction

61. A tripeptide gives the following products on Edman degradation.



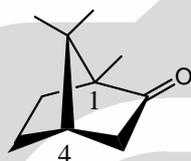
The tripeptide is

- (a) Phe-Ala-Gly (b) Phe-Gly-Ala (c) Ala-Gly-Phe (d) Gly-Ala-Phe
62. In the ^1H NMR spectrum recorded at 293 K, an organic compound ($\text{C}_3\text{H}_7\text{NO}$), exhibited signals at δ 7.8 (1H, s), 2.8 (3H, s) and 2.6 (3H, s). The compound is

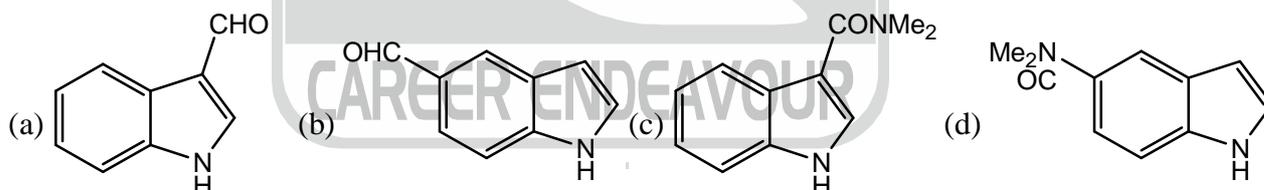
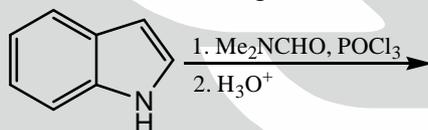


63. In the IR spectrum of p-nitrophenyl acetate, the carbonyl absorption band appears at
(a) 1670 cm^{-1} (b) 1700 cm^{-1} (c) 1730 cm^{-1} (d) 1760 cm^{-1} .

64. The absolute configuration at the two chiral centres of (–)-camphore is:



- (a) 1R, 4R (b) 1R, 4S (c) 1S, 4R (d) 1S, 4S
65. The major product formed in the following reaction is



66. The first person to separate a racemic mixture into individual enantiomers is
(a) J. H van't Hoff (b) Pasteur (c) H.E. Fischer (d) F. Wohler

67. Consider the following statements for [18]-annulene

(A) It is aromatic

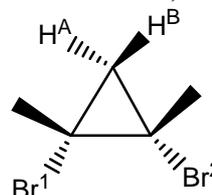
(B) The inner protons resonate at δ 9.28 in its ^1H NMR spectrum

(C) There are six protons in the shielded zone.

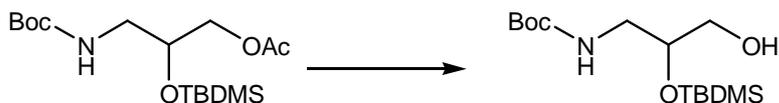
- (a) A, B, C (b) A and B only (c) B and C only (d) A and C only

68. In the compound given below, the relation between H^{A} , H^{B} ; and between Br^1 , Br^2 is:

- (a) H^{A} , H^{B} are enantiotopic; and Br^1 , Br^2 are diastereotopic
(b) H^{A} , H^{B} are diastereotopic; and Br^1 , Br^2 are enantiotopic
(c) H^{A} , H^{B} are diastereotopic; and Br^1 , Br^2 are homotopic
(d) H^{A} , H^{B} are enantiotopic; and Br^1 , Br^2 are homotopic.



69. The most appropriate reagent to effect the following chemoselective conversion is

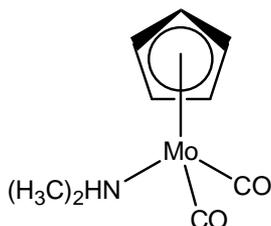


- (a) HCl, EtOH, reflux
 (b) Bu_4NF
 (c) K_2CO_3 , MeOH
 (d) CF_3COOH , EtOH, rt.
70. Among the following, an example of a “Green Synthesis” is
 (a) Synthesis of malachite green
 (b) Friedel-Craft’s acylation of anisole with Ac_2O /anhydrous AlCl_3 .
 (c) Jones’ oxidation of benzyl alcohol to benzoic acid.
 (d) Diels-Alder reaction of furan and maleic acid in water.

Part-C

71. The recoil energy of a Mossbauer nuclide of mass 139 amu is 2.5 MeV. The energy emitted by the nucleus in keV is:
 (a) 12.5 (b) 15.0 (c) 20.5 (d) 25.0
72. Complexes of general formula, $\text{fac}[\text{Mo}(\text{CO})_3(\text{phosphite})_3]$ have the C—O stretching bands as given below.
 Phosphines: PF_3 (A); PCl_3 (B); $\text{P}(\text{Cl})\text{Ph}_2$ (C); PMe_3 (D)
 $\nu(\text{CO})$, cm^{-1} : 2090(i); 2040(ii); 1977(iii); 1945(iv)
 The correct combination of the phosphine and the stretching frequency is,
 (a) (A–i), (B–ii), (C–iii), (D–iv) (b) (A–ii), (B–i), (C–iv), (D–iii)
 (c) (A–iv), (B–iii), (C–ii), (D–i) (d) (A–iii), (B–iv), (C–i), (D–ii)
73. On subjecting 9.5 ml solution of Pb^{2+} of X M to polarographic measurements, I_d was found to be 1 μA . When 0.5 mL of 0.04 M Pb^{2+} was added before the measurement, the I_d was found to be 1.25 μA .
 (a) 0.0035 (b) 0.0400 (c) 0.0067 (d) 0.0080
74. Match each item from the **List-I** (compound in solvent) with that from the **List-II** (its behaviour) and select the correct combination using the codes given below.
- | List-I | List-II |
|--|------------------------------------|
| A. CH_3COOH in pyridine | (i) strong acid. |
| B. CH_3COOH in H_2SO_4 | (ii) weak acid |
| C. HClO_4 in H_2SO_4 | (iii) strong base |
| D. SbF_5 in HF | (iv) weak base |
| (a) (A–i), (B–ii), (C–iii), (D–iv) | (b) (A–ii), (B–i), (C–iii), (D–iv) |
| (c) (A–iii), (B–iv), (C–ii), (D–i) | (d) (A–iv), (B–ii), (C–iii), (D–i) |
75. Structure of a carborane with formula, $\text{C}_2\text{B}_4\text{H}_8$ is formally derived from
 (a) Closo-borane (b) Nido-borane (c) Arachno-borane (d) Conjuncto-borane
76. Boric acid is a weak acid in aqueous solution. But its acidity increases significantly in the presence of ethylene glycol, because
 (a) ethylene glycol releases additional H^+
 (b) $\text{B}(\text{OH})_4^-$ is consumed in forming a compound with ethylene glycol.
 (c) ethylene glycol neutralizes H^+ released by boric acid.
 (d) Boric acid dissociates better in the mixed-solvent.
77. Coordination number of “C” in Be_2C_3 whose structure is correlated with that of CaF_2 , is:
 (a) 2 (b) 4 (c) 6 (d) 8

78. For the molecule below,



consider the following statements about its room temperature spectral data.

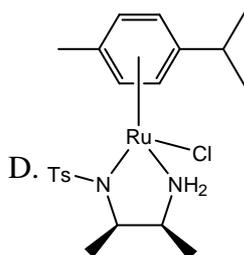
- (A) ^1H NMR has singlets at 5.48 and 3.18 ppm
 (B) ^1H NMR has multiplet at 5.48 and singlet at 3.18 ppm
 (C) IR has CO stretching bands at 1950 and 1860 cm^{-1}
 (D) IR has only one CO stretching band at 1900 cm^{-1} .
 The correct pair of statement is,
 (a) A and C (b) B and C (c) A and D (d) B and D
79. In the cluster $[\text{Co}_3(\text{CH})(\text{CO})_9]$ obeying 18e rule, the number of metal-metal bonds and the bridging ligands respectively, are
 (a) 3 and 1 CH (b) 0 and 3 CO (c) 3 and 1 CO (d) 6 and 1 CH
80. Consider the ions Eu(III), Gd(III), Sm(II) and Lu(III). The observed and calculated magnetic moment values are closest for the pair
 (a) Gd(III), Lu(III) (b) Eu(III), Lu(III) (c) Sm(III), Gd(III) (d) Sm(III), Eu(III)
81. Silicates with continuous 3D frame work are
 (a) Neso-silicates (b) Soro-silicates (c) Phyllo-silicates (d) Tecto-silicates
82. The correct spinel structure of Co_3O_4 is:
 (a) $(\text{Co}^{2+})_t(2\text{Co}^{3+})_o\text{O}_4$ (b) $(\text{Co}^{2+})_t(2\text{Co}^{3+}\text{Co}^{3+})_o\text{O}_4$
 (c) $(\text{Co}^{2+}\text{Co}^{3+})_t(\text{Co}^{3+})_o\text{O}_4$ (d) $(2\text{Co}^{3+})_t(\text{Co}^{2+})_o\text{O}_4$
83. In the solid state, the CuCl_5^{3-} ion has two types of bonds. These are
 (a) Three long and two short (b) Two long and three short
 (c) One long and four short (d) Four long and one short
84. In metalloenzymes, the metal centres are covalently linked through the side chains of the amino acid residues. The correct set of amino acids which are involved in the primary coordinates spheres of metalloenzymes is
 (a) Ala, Leu, His (b) Glu, His, Cys (c) Leu, Glu, Cys (d) Ala, His, Glu
85. Consider the catalyst in **column-I** and reactin in **column-II**

Column-I

- A. $[(\text{R})\text{-BINAP}]\text{Ru}^{2-}$
 B. $[\text{Rh}(\text{CO})_2\text{I}_2]^-$
 C. $\text{Pd}(\text{PPh}_3)_4$

Column-II

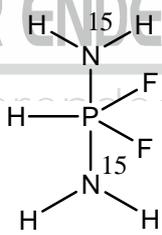
- (i) hydroformylation
 (ii) asymmetric hydrogenation.
 (iii) asymmetric hydrogen transfer



(iv) heck coupling.

The best match of a catalyst of column-I with the reaction nuclear column-II is

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

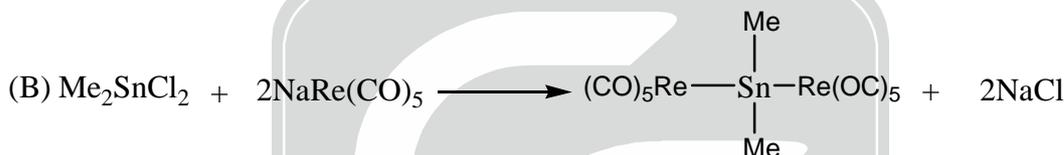
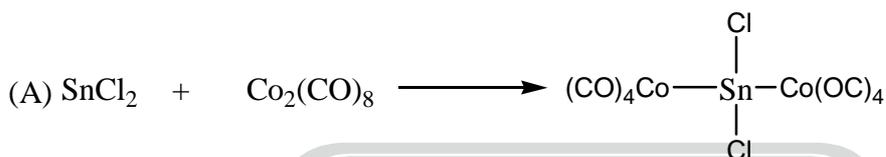
86. A solution of 2.0 g of brass was analysed for Cu electrogravimetrically using Pt-gauze as electrode. The weight of Pt-gauze changed from 14.5g to 16.0 g. The percentage weight of Cu in brass is
 (a) 50 (b) 55 (c) 60 (d) 75
87. The platinum complex of NH_3 and Cl^- ligands is an anti-tumour agent. The correct isomeric formula of the complex and its precursor are
 (a) $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ and PtCl_4^{2-} (b) $\text{trans-Pt}(\text{NH}_3)_2\text{Cl}_2$ and PtCl_4^{2-}
 (c) $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ and $\text{Pt}(\text{NH}_3)_4^{2+}$ (d) $\text{trans-Pt}(\text{NH}_3)_2\text{Cl}_2$ and $\text{Pt}(\text{NH}_3)_4^{2+}$
88. Successive addition of NaCl , H_3PO_4 , KSCN and NaF to a solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ gives yellow, colourless, red and again colorless solutions due to the respective formation of:
 (a) $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_5(\text{PO}_4)]$, $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_5\text{F}]^{2+}$
 (b) $[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}(\text{OH})]^+$, $[\text{Fe}(\text{H}_2\text{O})_5(\text{PO}_4)]$, $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2-}$, $[\text{Fe}(\text{H}_2\text{O})_5\text{F}]^{2+}$
 (c) $[\text{Fe}(\text{H}_2\text{O})_5(\text{Cl})]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_5\text{F}]^{2+}$
 (d) $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_5(\text{PO}_4)]$, $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_4(\text{SCN})\text{F}]^+$
89. Which one of the following will NOT undergo oxidative addition by methyl iodide?
 (a) $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ (b) $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$
 (c) $[\eta^2 - \text{CpRh}(\text{CO})_2]$ (d) $[\eta^5 - \text{Cp}_2\text{Ti}(\text{Me})\text{Cl}]$
90. In hydrofomylation reaction using $[\text{Rh}(\text{PPh}_3)_3(\text{CO})(\text{H})]$ as the catalyst, addition of excess PPh_3 would
 (a) increase the rate of reaction (b) decrease the rate of reaction.
 (c) not influence of the rate of reaction (d) stop the reaction.
91. Find out the number of lines in the ^{31}P NMR signal for
- 
- (a) 3 (b) 6 (c) 18 (d) 90
92. The rate of exchange of OH_2 present in the coordination sphere by $^{18}\text{OH}_2$ of, (i) $[\text{Cu}(\text{OH})_2]_6^{2+}$, (ii) $[\text{Mn}(\text{OH})_2]_6^{2+}$, (iii) $[\text{Fe}(\text{OH})_2]_6^{2+}$, (iv) $[\text{Ni}(\text{OH})_2]_6^{2+}$, follows an order
 (a) (i) > (ii) > (iii) > (iv) (b) (i) > (iv) > (iii) > (ii)
 (c) (ii) > (iii) > (iv) > (i) (d) (iii) > (i) > (iv) > (ii)
93. Based on the behaviour of the metalloenzymes, consider the following statements
 (A) In the enzymes, the zinc activates O_2 to form peroxide species.
 (B) In the enzymes, the zinc activates H_2O and provides a zinc bound hydroxide.
 (C) In the oxidases, the iron activates O_2 to break the bonding between the two oxygens
 (D) Zinc ion acts as a nucleophile and attacks at the peptide carbonyl
 The set of correct statements is,
 (a) A and B (b) B and C (c) C and D (d) A and D



94. Fe^{2+} -porphyrins fail to exhibit reversible oxygen transport and cannot differentiate CO from O_2 . However, the hemoglobin is free from both these pit falls. Among the following
- (A) Fe^{2+} - porphyrins undergo μ -oxodimer formation and the same is prevented in case of the hemoglobin.
- (B) Fe-CO bond strength is much low in case of hemoglobin when compared to the Fe^{2+} - porphyrins.
- (C) While Fe-CO is linear, Fe-O_2 is bent and is recognized by hemoglobin
- (D) The interlinked four monomeric units in the hemoglobin are responsible to overcome the pit-falls.

The correct set of statements is

- (a) A and B (b) A and C (c) C and D (d) B and D
95. Reactions A and B are, termed as respectively.



- (a) Insertion, Metathesis (b) Metathesis, insertion
- (c) Oxidative, addition, metathesis (d) Oxidative addition, insertion
96. A metal crystallizes in fcc structure with a unit cell side of 500 pm. If the density of the crystal is 1.33 g/cc, the molar mass of the metal is close to
- (a) 23 (b) 24 (c) 25 (d) 26
97. The activation energy for the bimolecular reaction $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$ is E_0 in the gas phase. If the reaction is carried out in a confined volume of λ^3 , the activation energy is expected to
- (a) remain unchanged (b) increase with decreasing λ .
- (c) decrease with decreasing λ . (d) oscillate with decreasing λ .
98. In a many-electron atom, the total orbital angular momentum (L) and spin (S) are good quantum numbers instead of the individual orbital (l_1, l_2) and spin (s_1, s_2) angular momenta in the presence of
- (a) inter-electron repulsion (b) spin-orbit interaction
- (c) hyperfine coupling (d) external magnetic field.
99. The packing fraction of a simple cubic lattice is close to
- (a) 0.94 (b) 0.76 (c) 0.52 (d) 0.45
100. The number of IR active vibrational modes of pyridine is:

C_{2v}	E_2	C_2	σ_v	σ'_v	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	1	y, R_x

- (a) 12 (b) 20 (c) 24 (d) 33

101. One of the excited states of Ti has the electric configuration $[\text{Ar}] 4s^2 3d^1 4p^1$. The number of microstates with zero total spin (S) for this configuration is
 (a) 9 (b) 15 (c) 27 (d) 60
102. For the reaction $A_2 \rightleftharpoons 2A$ in a closed container, the relation between the degree of dissociation (α) and the equilibrium constant K_p at a fixed temperature is given by
 (a) $\alpha = \left[\frac{K_p}{K_p + 4p} \right]$ (b) $\alpha = \left[\frac{K_p}{K_p + 4p} \right]^{1/2}$
 (c) $\alpha = \left[\frac{(K_p + 4p)}{K_p} \right]$ (d) $\alpha = \left[\frac{(K_p + 4p)}{K_p} \right]^{1/2}$
103. The fugacity of a gas depends on pressure and the compressibility factor $Z (= p\bar{V}/RT)$ through the relation (\bar{V} is the molar volume)
 For most gases at temperature T and up to moderate pressure, this equation shows that
 (a) $f < p$, if $T \rightarrow 0$ (b) $f < p$, if $T \rightarrow \infty$
 (c) $f > p$, if $T \rightarrow 0$ (d) $f = p$, if $T \rightarrow 0$
104. The internal pressure $(\partial U/\partial V)_T$ of a real gas is related to the compressibility factor $Z = p\bar{V}/RT$ by [\bar{V} is the molar volume]
 (a) $(\partial U/\partial V)_T = RT(\partial Z/\partial V)_T$ (b) $(\partial U/\partial V)_T = RT/(\bar{V} Z)$
 (c) $(\partial U/\partial V)_T = (RT^2/\bar{V})(\partial Z/\partial T)_V$ (d) $(\partial U/\partial V)_T = (\bar{V}/RT^2)(\partial Z/\partial T)_V$
105. Suppose, the ground stationary state of a harmonic oscillator with force constant 'k' is given by

$$\psi_0 = \exp[-Ax^2]$$
 Then, A should depend on k as
 (a) $A \propto k^{-1/2}$ (b) $A \propto k$ (c) $A \propto k^{1/2}$ (d) $A \propto k^{1/3}$
106. Combining two real wave functions ϕ_1 and ϕ_2 , the following functions are constructed: $A = \phi_1 + \phi_2$, $B = \phi_1 + i\phi_2$, $C = \phi_1 - i\phi_2$, $D = i(\phi_1 + \phi_2)$. The correct statement will then be
 (a) A and B represent the same state (b) A and C represent the same state.
 (c) A and D represents the same state (d) B and D represent the same state.
107. Crystal A diffracts from (1 1 1) and (2 0 0) planes but not from (1 1 0) plane, while the crystal B diffracts from (1 1 0) and (2 0 0) planes but not from the (1 1 1) plane. From the above, we may conclude that
 (a) A has fcc lattice while B has bcc lattice (b) A has bcc lattice while B has fcc lattice
 (c) A and B both have fcc lattice (d) A and B both have bcc lattice.



108. The decomposition of NH_3 on Mo surface follows Langmuir-Hinshelwood mechanism. The decomposition was carried out at low pressures. The initial pressure of NH_3 was 10^{-2} torr. The pressure of NH_3 was reduced to 10^{-4} torr in 10 minutes. The rate constant of decomposition of NH_3 is:
- (a) $9.9 \times 10^{-4} \text{ torr min}^{-1}$ (b) 0.4606 min^{-1}
 (c) $9.9 \times 10^{-3} \text{ torr min}^{-1}$ (d) 0.693 min^{-1}
109. A polymer sample has the following composition.

Number of molecules	Molecular weight
10	1000
50	2000
40	4000

The polydispersity index (P.D.I) of the polymer is

- (a) $\frac{85000}{27}$ (b) $\frac{85}{81}$ (c) $\frac{850}{729}$ (d) $\frac{729}{850}$

110. The equilibrium constant for an electrochemical reaction,



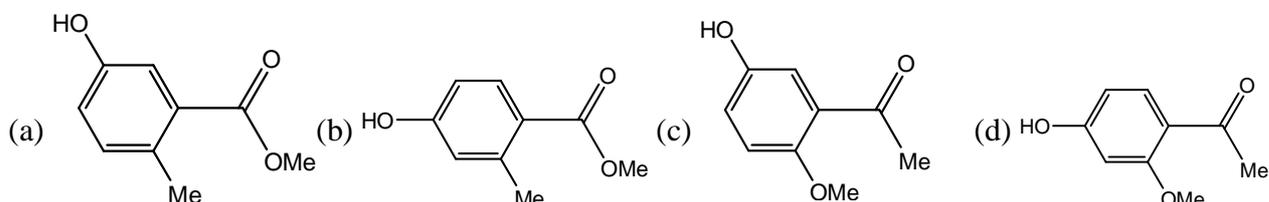
is $\left[E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.75 \text{ V}, E^0(\text{Sn}^{4+}/\text{Sn}^{2+}) = 0.15 \text{ V}, (2.303RT/F) = 0.06 \text{ V} \right]$

- (a) 10^{10} (b) 10^{20} (c) 10^{30} (d) 10^{40}
111. A bacterial colony grows most commonly by cell division. The change in the population due to cell division in an actively growing colony is $dN = \lambda_g N dt$. The population of bacterial colony at time 't' is $[N_0 = N(t=0)]$
- (a) $N_0 \lambda_g t$ (b) $N_0 \exp[-\lambda_g t]$ (c) $N_0 \exp[\lambda_g t]$ (d) $N_0 (\lambda_g t)^2$
112. The Arrhenius parameters for the thermal decomposition of NOCl , $2\text{NOCl}(g) \rightarrow 2\text{NO}(g) + \text{Cl}_2(g)$, are $A = 10^{13} \text{ M}^{-1} \text{ s}^{-1}$, $E_a = 105 \text{ kJ mol}^{-1}$ and $RT = 2.5 \text{ kJ mol}^{-1}$. The enthalpy (in kJ mol^{-1}) of the activated complex will be
- (a) 110 (b) 105 (c) 102.5 (d) 100
113. The rotational partition function of H_2 is:

- (a) $\sum_{J=0,1,2,\dots} (2J+1) e^{-\beta hc B J(J+1)}$ (b) $\sum_{J=1,3,5,\dots} (2J+1) e^{-\beta hc B J(J+1)}$
 (c) $\sum_{J=0,2,4,\dots} (2J+1) e^{-\beta hc B J(J+1)}$
 (d) $\frac{1}{4} \left[\sum_{J=0,2,4,\dots} (2J+1) e^{-\beta hc B J(J+1)} + 3 \sum_{J=1,3,5,\dots} (2J+1) e^{-\beta hc B J(J+1)} \right]$

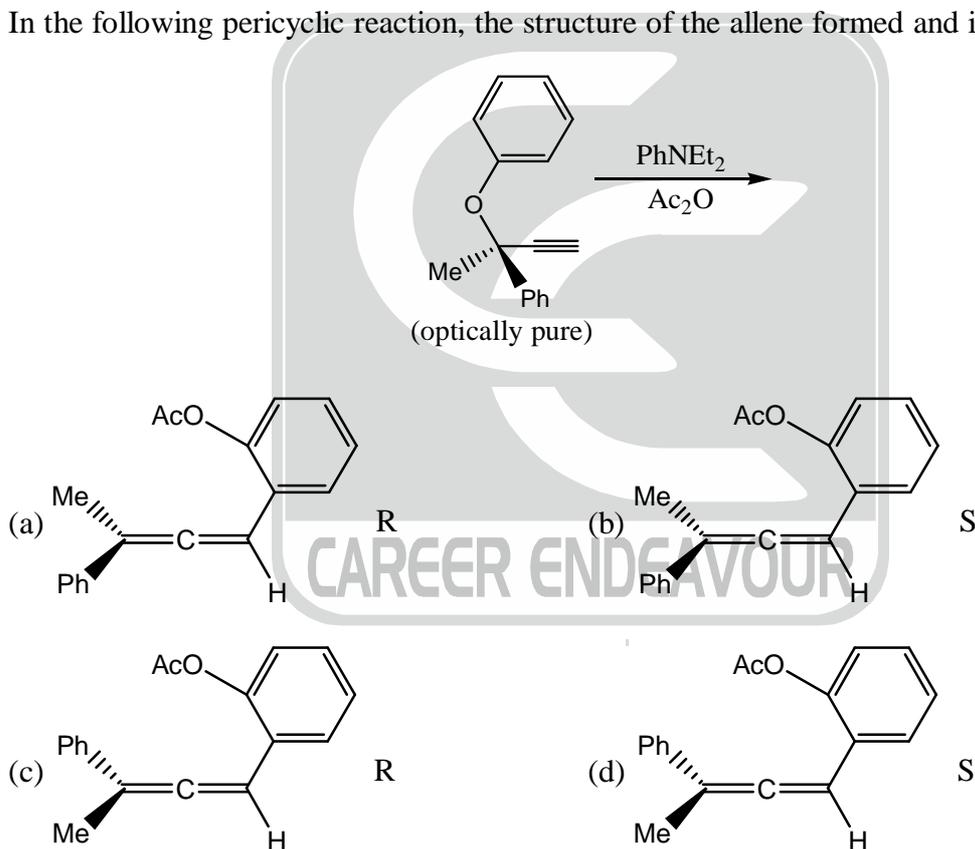
114. The potential in Debye-Hückel theory is proportional to
 (a) $1/\kappa r$ (b) $\exp[-\kappa r]$ (c) $\exp[-\kappa r]/r$ (d) κr
115. The vibrational frequency and anharmonicity constant of an alkali halide are 300 cm^{-1} and 0.0025 respectively. The positions (in cm^{-1}) of its fundamental mode and first overtone are respectively.
 (a) 300, 600 (b) 298.5, 595.5 (c) 301.5, 604.5 (d) 290, 580
116. The adsorption of a gas is described by the Langmuir isotherm with the equilibrium constant $K = 0.9\text{ kPa}^{-1}$ at 25°C . The pressure (in kPa) at which the fractional surface coverage is 0.95, is
 (a) 1/11.1 (b) 21.1 (c) 11.1 (d) 42.2
117. The energy of a harmonic oscillator in its ground state is $\frac{1}{2}\hbar\omega$. According to the virial theorem, the average kinetic (T) and potential (V) energies of the above are
 (a) $T = \frac{1}{4}\hbar\omega$; $V = \frac{1}{4}\hbar\omega$ (b) $T = \frac{1}{8}\hbar\omega$; $V = \frac{3}{8}\hbar\omega$
 (c) $T = \hbar\omega$; $V = -\frac{1}{2}\hbar\omega$ (d) $T = \frac{3}{8}\hbar\omega$; $V = \frac{1}{8}\hbar\omega$
118. The energy of a hydrogen atom in a state is $-\frac{hcR_H}{25}$ ($R_H = \text{Rydberg constant}$). The degeneracy of the state will be
 (a) 5 (b) 10 (c) 25 (d) 50
119. The trial wave function of a system is expanded as $\psi_t = c_1\phi_1 + c_2\phi_2$. The matrix elements of the Hamiltonian are $\langle\phi_1|H|\phi_1\rangle = 0$; $\langle\phi_1|H|\phi_2\rangle = 2.0 = \langle\phi_2|H|\phi_1\rangle$ and $\langle\phi_2|H|\phi_2\rangle = 3.0$. The approximate ground-state energy of the system from the linear variational principle is
 (a) -1.0 (b) -2.0 (c) +4.0 (d) +5.0
120. One molecular orbital of a polar molecule AB has the form $c_A\psi_A + c_B\psi_B$, where ψ_A and ψ_B are normalized atomic orbitals centred on A and B, respectively. The electron in this orbital is found on atom B with a probability of 90%. Neglecting the overlap between ψ_A and ψ_B , a possible set of c_A and c_B is:
 (a) $c_A = 0.95$, $c_B = 0.32$ (b) $c_A = 0.10$, $c_B = 0.90$
 (c) $c_A = -0.95$, $c_B = 0.32$ (d) $c_A = 0.32$, $c_B = 0.95$
121. 4-Hydroxybenzoic acid exhibited signals at δ 171, 162, 133, 122 and 116 ppm in its broadband decoupled ^{13}C NMR spectrum. The correct assignment of the signals is
 (a) δ 171(C-4), 162(COOH), 133(C-3 & 5), 122(C-1) and 116(C-2 & 6)
 (b) δ 171(COOH), 162(C-4), 133(C-2 & 6), 122(C-1) and 116(C-3 & 5)
 (c) δ 171(C-4), 162(COOH), 133(C-2 & 6), 122(C-1) and 116(C-3 & 5)
 (d) δ 171(COOH), 162(C-4), 133(C-3 & 5), 122(C-1) and 116(C-2 & 6)

122. An organic compound ($C_9H_{10}O_3$) exhibited the following spectral data:
 IR: $3400, 1680\text{ cm}^{-1}$;
 $^1\text{H NMR}$: δ 7.8(1H, d, $J = 8\text{ Hz}$), 7.0 (1 H, d, $J = 8\text{ Hz}$), 6.5 (1 H, s), 5.8 (1 H, s, D_2O exchangeable), 3.9(3H, s), 2.3 (3 H, s).
 The compound is

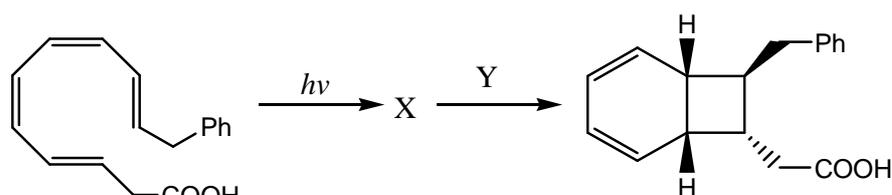


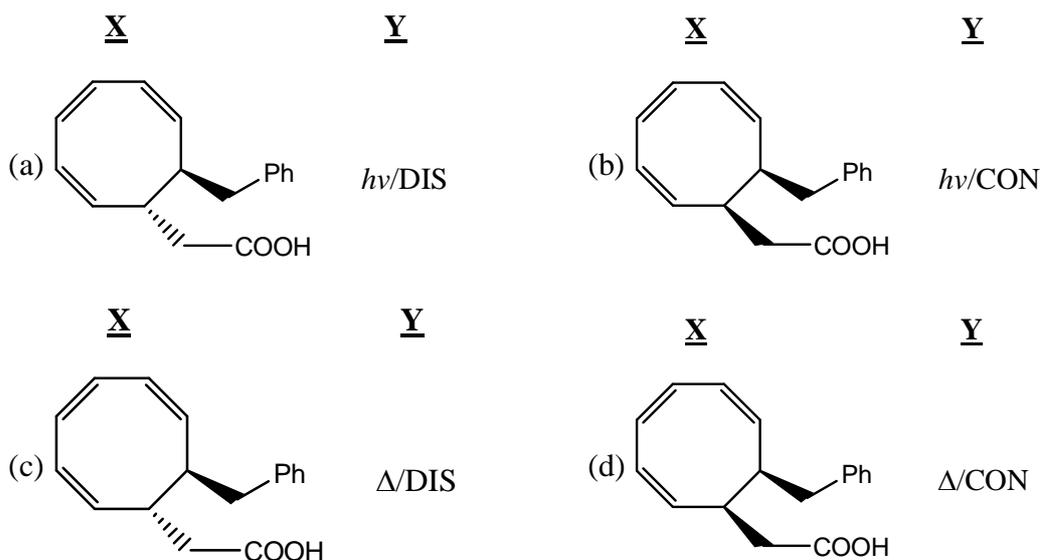
123. The $[\alpha]_D$ of a 90% optically pure 2-arylpropanoic acid solution is $+135^\circ$. On treatment with a base at RT for one hour, $[\alpha]_D$ changed to $+120^\circ$. The optical purity is reduced to 40% after 3 hours. If so, the optical purity of the solution after 1 hour, and its $[\alpha]_D$ after 3 hours, respectively, would be
 (a) 80% and 60° (b) 70% and 40° (c) 80% and 90° (d) 70% and 60°

124. In the following pericyclic reaction, the structure of the allene formed and its configuration are

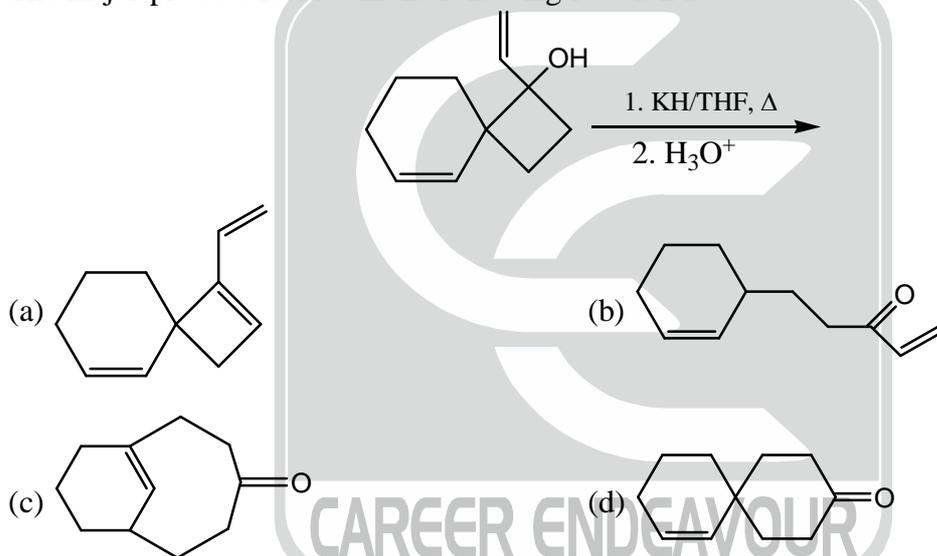


125. In the following sequence of pericyclic reactions X and Y are

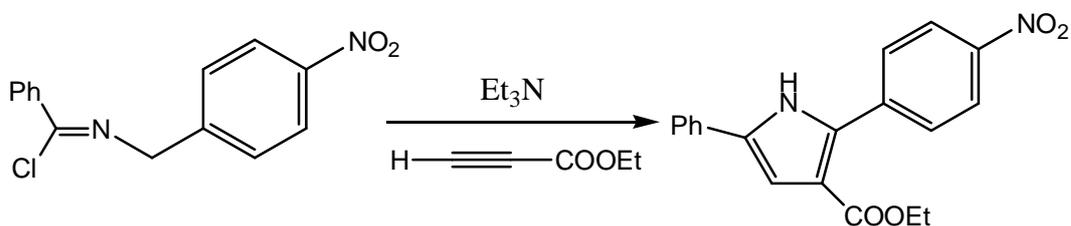




126. The major product formed in the following reaction is

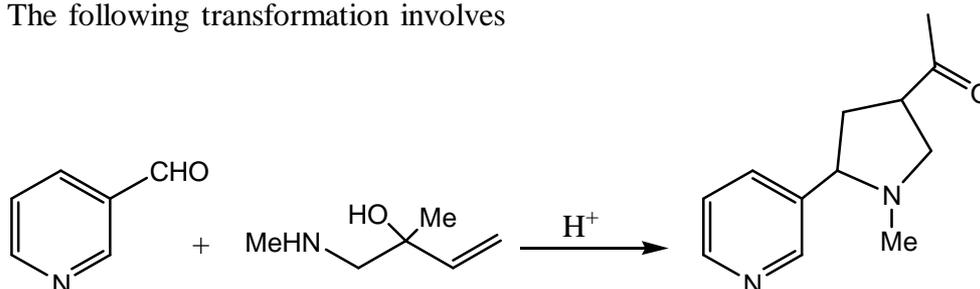


127. The following conversion involves



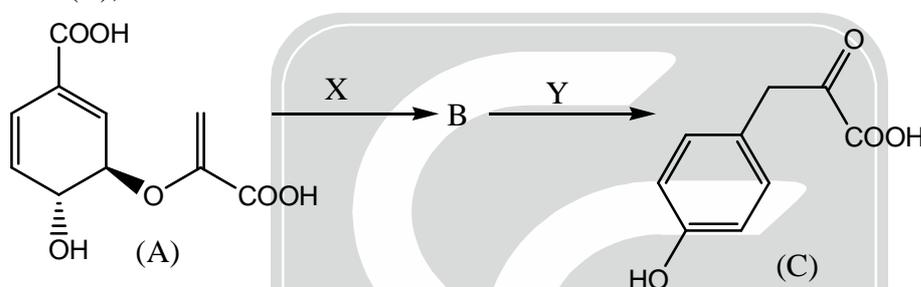
- (a) a 1, 3-dipolar species as reactive intermediate, and a cycloaddition.
 (b) a carbenium ion as reactive intermediate, and a cycloaddition.
 (c) a 1, 3-dipolar species as reactive intermediate, and an aza Wittig reaction.
 (d) a carbanion as reactive intermediate, and an aza Cope rearrangement.

128. The following transformation involves



- (a) an iminium ion, [3, 3]-sigmatropic shift and Mannich reaction.
 (b) a nitrenium ion, [3, 3]-sigmatropic shift and Michael reaction.
 (c) an iminium ion, [1, 3]-sigmatropic shift and Mannich reaction.
 (d) a nitrenium ion, [1, 3]-sigmatropic shift and Michael reaction.

129. With respect to the following biogenetic conversion of chorismic acid (A) to 4-hydroxyphenylpyruvic acid (C), the correct statement is

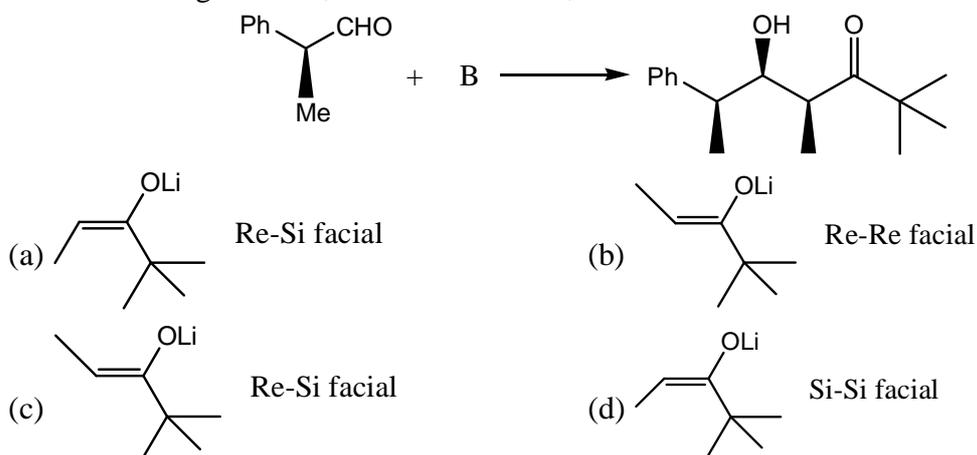


- (a) X is Claisen rearrangement; Y is oxidative decarboxylation.
 (b) X is Fries rearrangement; Y is oxidative decarboxylation.
 (c) X is Fries rearrangement; Y is dehydration.
 (d) X is Claisen rearrangement; Y is dehydration.

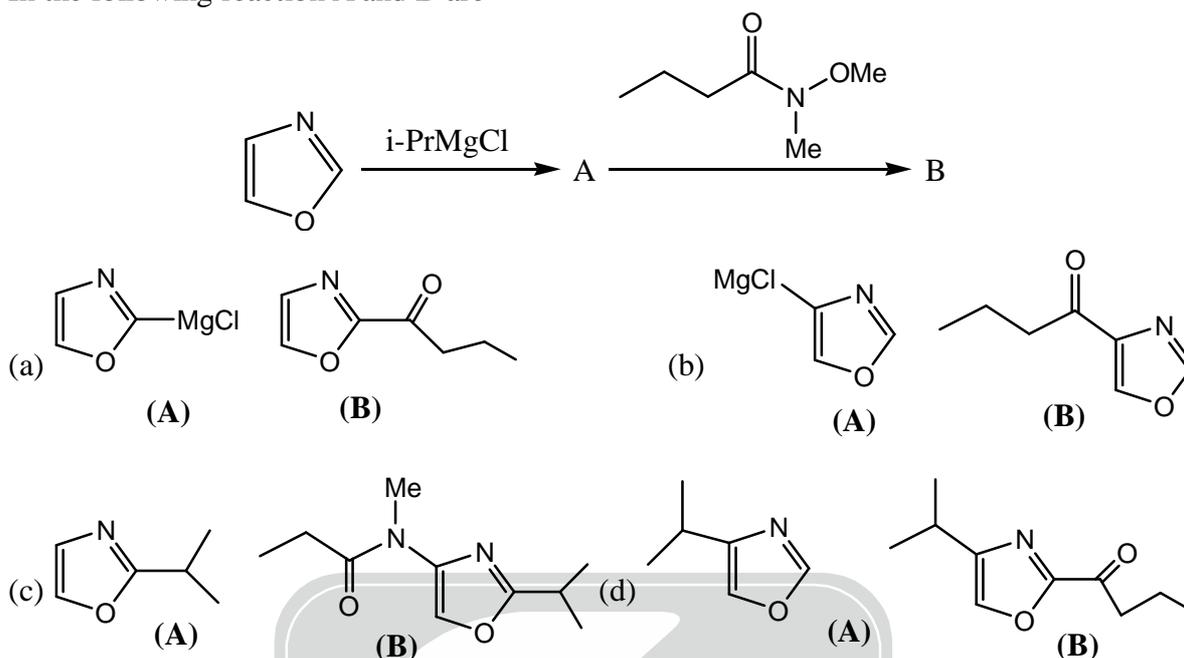
130. Match the following

- | | |
|---------------------|-----------------------------------|
| (i) β -amyrin | (A) alkaloid; secondary alcohol |
| (ii) squalene | (B) alkaloid, phenol |
| (iii) morphine | (C) triterpene, secondary alcohol |
| (iv) ephedrine | (D) acyclic triterpene, polyene |
- (a) (i)-(C), (ii)-(D), (iii)-(B), (iv)-(A) (b) (i)-(B), (ii)-(A), (iii)-(C), (iv)-(D)
 (c) (i)-(C), (ii)-(B), (iii)-(D), (iv)-(A) (d) (i)-(A), (ii)-(D), (iii)-(B), (iv)-(C)

131. In the following reaction, the structure of B, and the mode of addition are



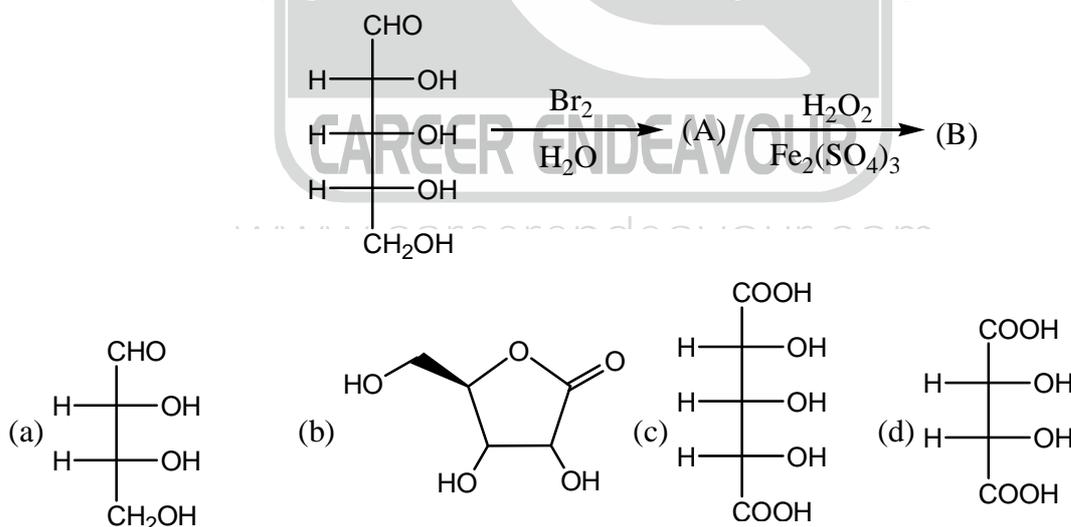
132. In the following reaction A and B are



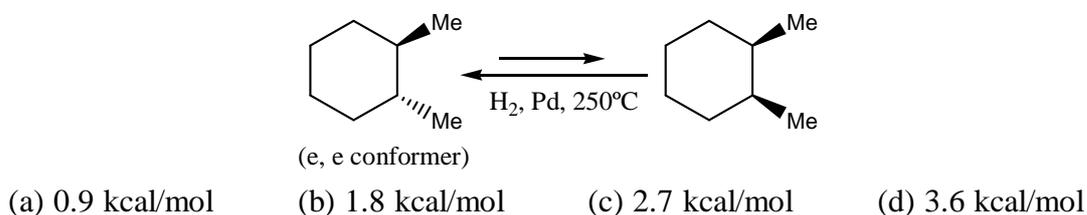
133. Match the following biochemical transformations with coenzymes involved

- | | |
|--|-----------------------------|
| (i) α -ketoglutarate to glutamic acid | (A) tetrahydrofolate |
| (ii) uridine to thymidine | (B) NADH |
| (iii) pyruvic acid to acetyl coenzyme A | (C) thiamine pyrophosphate. |
| | (D) pyridoxamine |
- (a) (i)-(D), (ii)-(A), (iii)-(C) (b) (i)-(A), (ii)-(B), (iii)-(D)
- (c) (i)-(B), (ii)-(A), (iii)-(C) (d) (i)-(D), (ii)-(B), (iii)-(C)

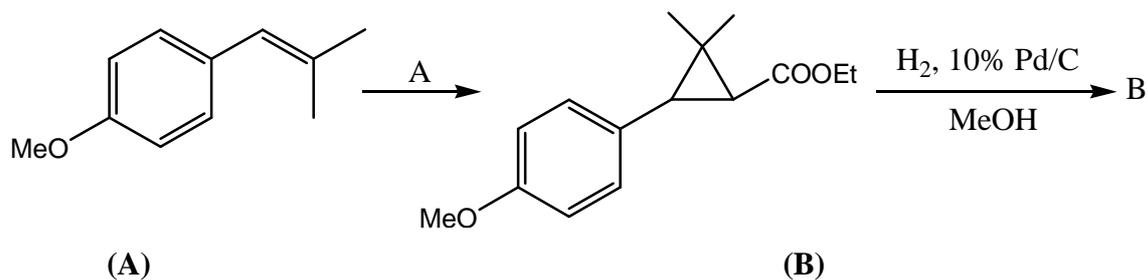
134. The structure of major product B formed in the following reaction sequence is



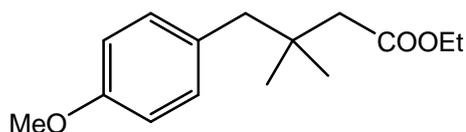
135. Given the energy of each gauche butane interaction is 0.9 kcal/mol, ΔG value of the following reaction is



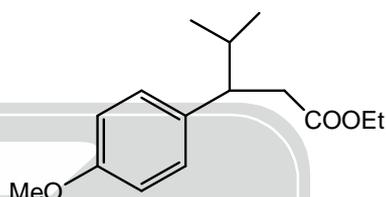
136. In the following reaction, the reagent A and the major product B are

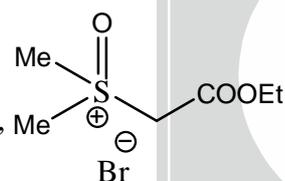


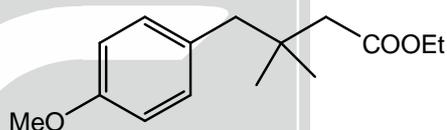
(a) $\text{N}_2\text{CHCOOEt}$, $\text{Cu}(\text{acac})_2$

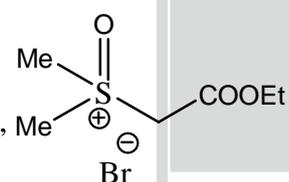


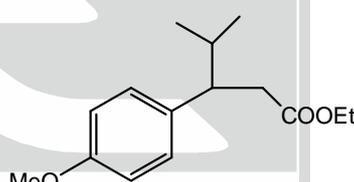
(b) $\text{N}_2\text{CHCOOEt}$, $\text{Cu}(\text{acac})_2$



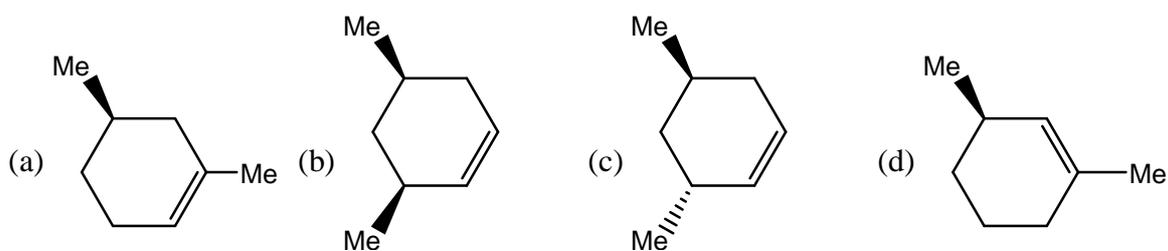
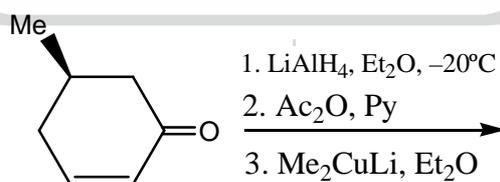
(c) NaH , Me  COOEt



(d) NaH , Me  COOEt



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



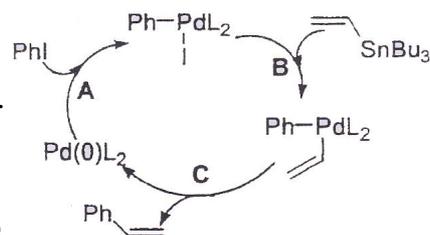
138. 12.0 g of acetophenone on reaction with 76.2 g of iodine in the presence of aq. NaOH gave solid A in 75% yield. Approximate amount of A obtained in the reaction and its structure are

(a) 80 g, Cl_4 (b) 40 g, Cl_4 (c) 60 g, CHI_3 (d) 30 g, CHI_3 .

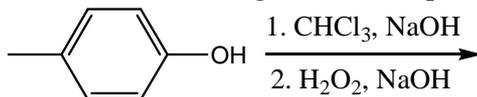
139. Consider the following reaction mechanism

The steps A, B and C, respectively, are

- (a) Oxidative addition; transmetalation; reductive elimination.
 (b) Oxidative addition; carbopalladation; β -hydride elimination.
 (c) Carbopalladation; transmetalation; reductive elimination.
 (d) Metal halogen exchange; transmetalation; metal extrusion.

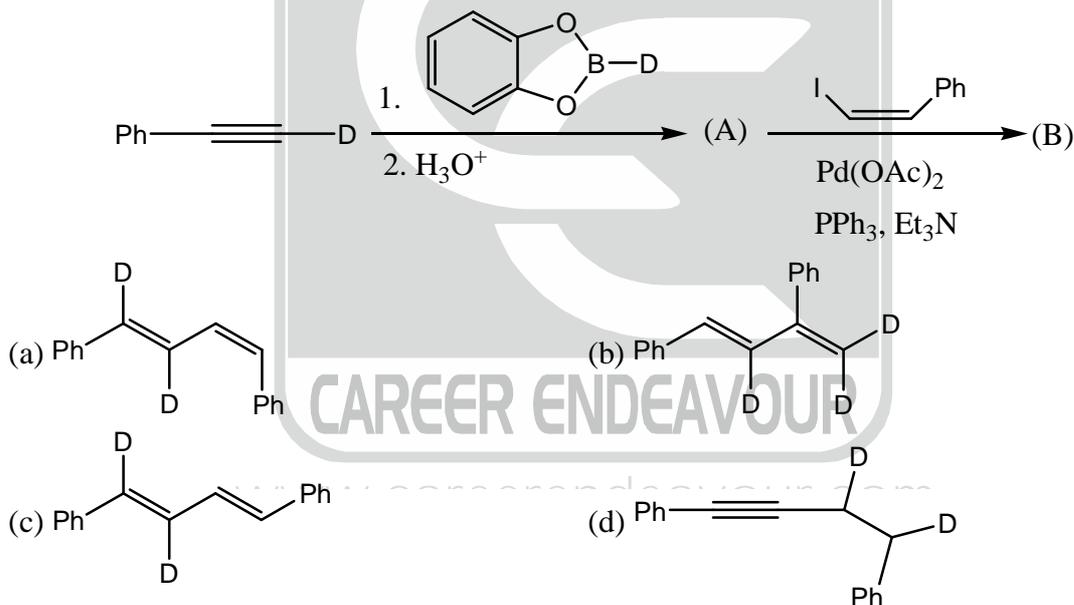


140. The major product formed in the following reaction sequence is

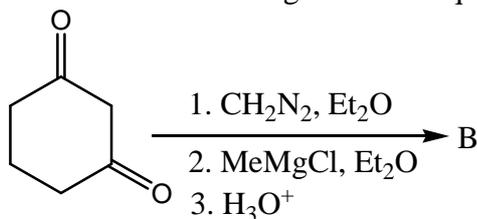


- (a)
- (b)
- (c)
- (d)

141. The major product B formed in the following reaction sequence is

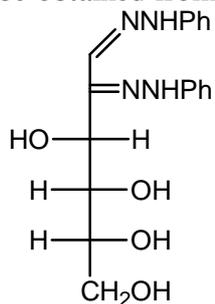


142. The major product B formed in the following reaction sequence is



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

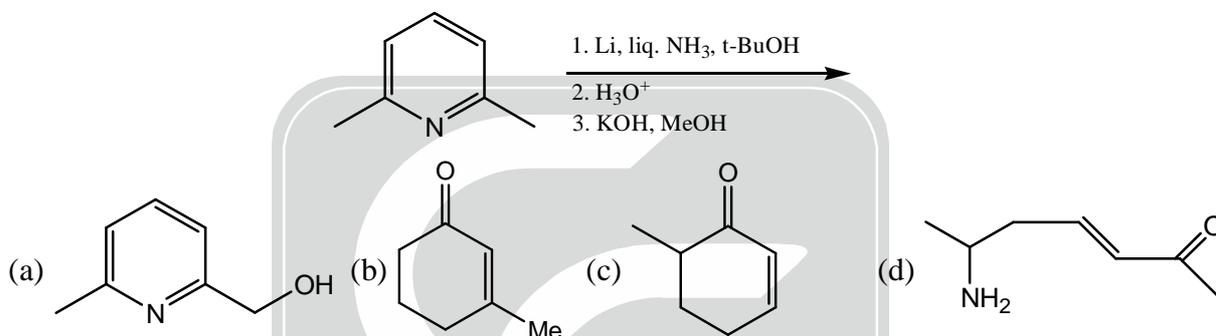
143. The osazone A could be obtained from



(A)

- (a) glucose and mannose
(b) mannose and galactose
(c) gulcose and fructose
(d) galactose and fructose

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



145. In the following enantioselective reaction, the major product formed is

