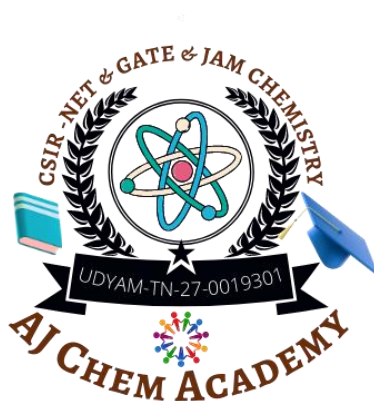


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**Q.21 – Q.70 Multiple Choice Question (MCQ), carry TWO marks each (for each wrong answer: –0.5). You are required to Answer Maximum 35 Questions.**

21. In the reactions (P) and (Q),



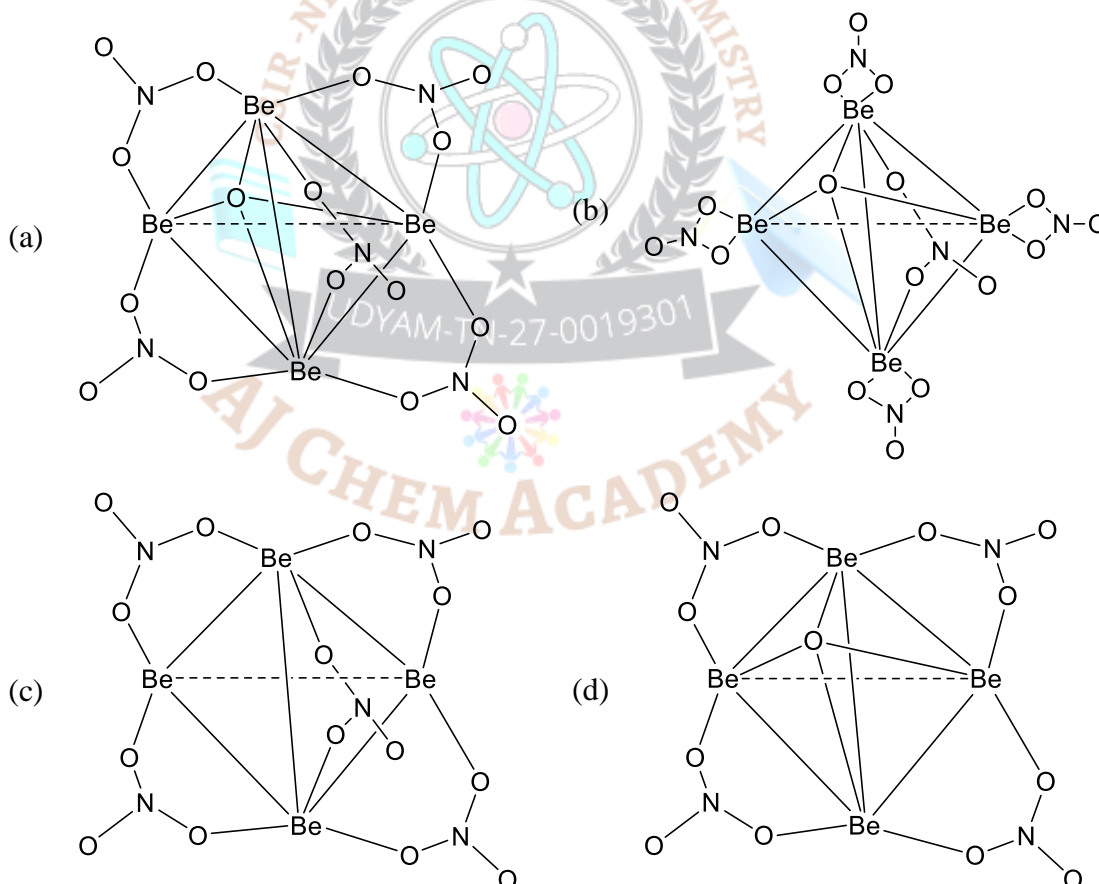
**Water behaves as:**

- (a) An acid in both (P) and (Q)                      (b) An acid in (P) and a base in (Q)  
 (c) A base in (P) and acid in (Q)                      (d) A base in both (P) and (Q)

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:



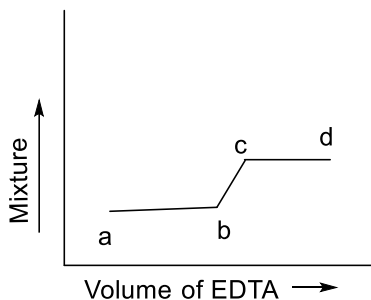
24. The total number of lone pairs of electrons in  $\text{I}_3^-$  is:

- (a) Zero                      (b) Three                      (c) Six                      (d) Nine

25. If massbauer 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  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  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  $cd \equiv$  excess EDTA  
 (d) Volume  $ab \equiv [\text{Cu}^{2+}]$  and volume  $cd \equiv$  excess EDTA
27. In 'carbon-dating' application of radioisotopes,  $^{14}\text{C}$  emits:  
 (a)  $\beta$ -particle (b)  $\alpha$ -particle (c)  $\gamma$ -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 L, yields  $\text{Ni}(\text{CO})_3\text{L}$ . The reaction is,  
 ( $\text{L} = \text{PMe}_3$  or  $\text{P(OMe)}_3$ )  
 (a) Associative (b) Dissociative (c) Interchange ( $I_a$ ) (d) Interchange ( $I_d$ )
31. As a ligand  $\text{Cl}^-$  is:  
 (a) only a  $\sigma$ -donor (b) only a  $\pi$ -donor  
 (c) both a  $\sigma$ -donor and a  $\pi$ -donor (d) a  $\sigma$ -donor and a  $\pi$ -acceptor
32. The correct d-electron configuration showing spin-orbit coupling is  
 (a)  $t_{2g}^6 e_g^2$  (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 ( $\text{RLi}$ ) 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 aprotic solvents
34. For the reaction:  $\text{trans-}[\text{IrCl}(\text{CO})(\text{PPh}_3)_2] + \text{Cl}_2 \rightarrow \text{trans-}[\text{IrCl}_3(\text{CO})(\text{PPh}_3)_2]$ ,



The correct observation is

- (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)  $0.5 a_0$

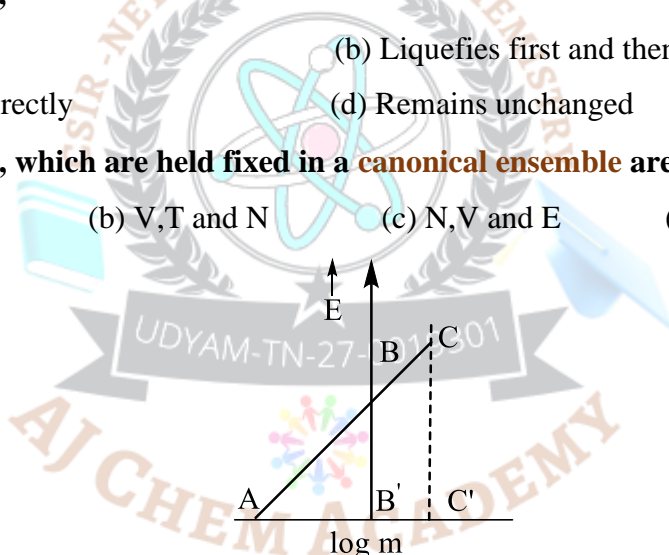
41. Among the following, the CORRECT statement is:

- (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  $3.9 \text{ cm}^{-1}$ . The energy for the rotational transition from  $J = 3$  to  $J = 4$  state would be:



- (a)  $3.9 \text{ cm}^{-1}$       (b)  $7.8 \text{ cm}^{-1}$       (c)  $11.7 \text{ cm}^{-1}$       (d)  $15.6 \text{ cm}^{-1}$
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) Liquefies      (b) Liquefies 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)  $\mu, V$  and  $P$
- 47.



The correct value of  $E^\circ$ , 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 the 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  $27^\circ\text{C}$  was found to be  $k = 5.4 \times 10^{11} \text{ e}^{-50}$ . The **activation energy** of the reaction is:

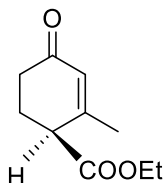


- (a)  $50 \text{ J mol}^{-1}$       (b)  $415 \text{ J mol}^{-1}$       (c)  $15,000 \text{ J mol}^{-1}$       (d)  $1,25,000 \text{ J mol}^{-1}$
50. During the **addition polymerisation**, the reaction proceeds via  
 (a) Step-growth process      (b) Free-radical chain reaction  
 (c) Cascade process      (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)  $\text{CaF}_2$       (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 **P** and **Q** have the following characteristics:

Experiment	P	Q
Mean	50 units	100 units
Standard deviation	2 units	2 units

It may be concluded that:

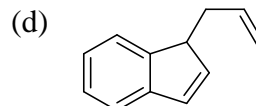
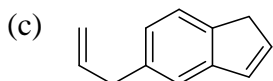
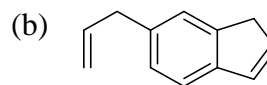
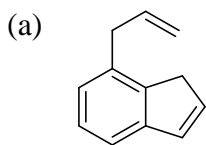
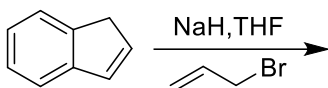
- (a) P is more precise than Q  
 (b) P is less precise than Q  
 (c) P and Q are of the same precision  
 (d) Relative precision of P and Q cannot be assessed
55. The **IUPAC name** of the compound given below is:



- (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 broad band decoupled  $^{13}\text{C}$ -NMR spectrum of **phenanthrene** and **anthracene**, respectively are:

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

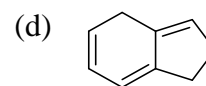
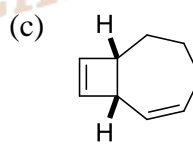
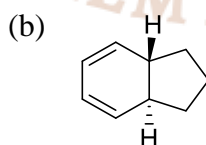
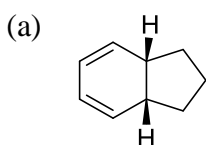
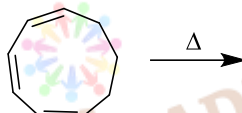
58. The co-enzyme that is involved in the reduction of a double bond in **fatty acid biosynthesis** is:

- (a) NADH      (b) Biotin      (c) Pyridoxal      (d)  $\text{FADH}_2$

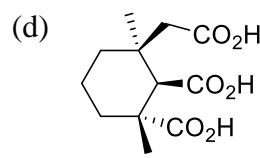
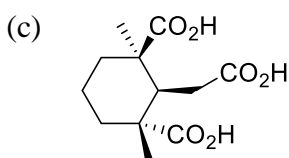
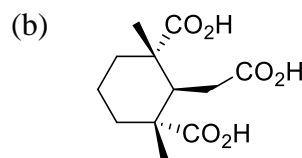
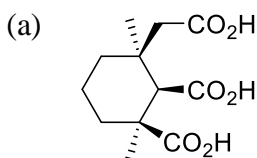
59. Epoxidation of **(R)-cyclohex-2-enol** with peracetic acid yields a **95 : 5** mixture of compounds P and Q. Compounds P and Q are:

- (a) enantiomers      (b) diastereomers      (c) constitutional isomers      (d) homomers

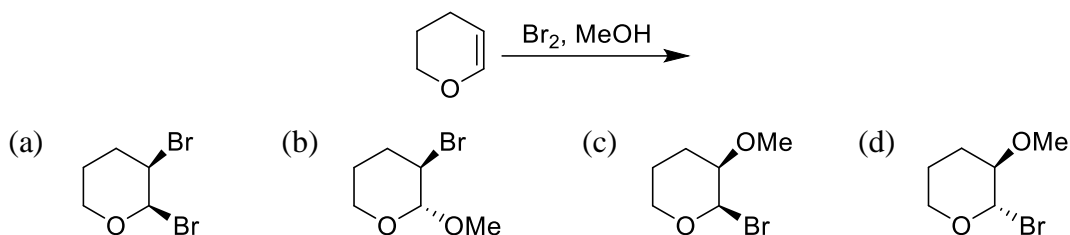
60. The **major product** formed in the following **concerted reaction** is:



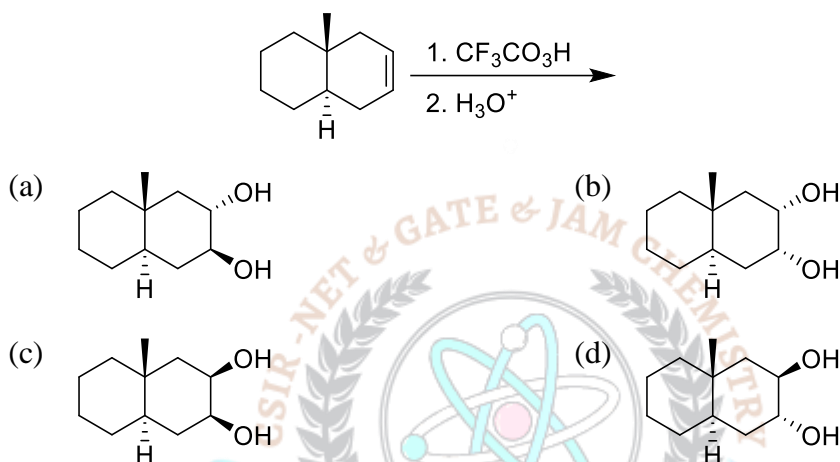
61. The structure of **meso-tricarboxylic acid** that is formed on **potassium permanganate oxidation** of **abietic acid** is:



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:

- (a) Nitroethane and base (b)  $\alpha$ -chloroacrylonitrile  
(c) Ethylmagnesium bromide (d) Acetyl chloride and triethylamine

65. Among the following, the compound that undergoes **deprotection** easily on treatment with hydrogen in the presence of **10 % Pd/C** to generate  $\text{RNH}_2$  is:



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

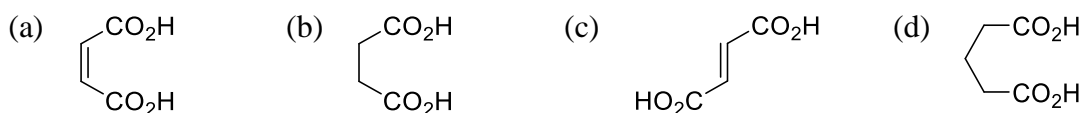
- (a) Tyrosine (b) Asparagine (c) Leucine (d) Arginine

67. "**Phosphorescence**" is represented as

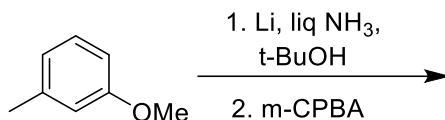
- (a)  $T_1 \rightarrow S_0 + h\nu$  (b)  $T_1 \rightarrow S_0 + \Delta$  (c)  $S_1 \rightarrow S_0 + h\nu$  (d)  $S_1 \rightarrow T_1 + \Delta$

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 G MHz  $^1\text{H-NMR}$**  spectrum, of organic compound exhibited a **doublet**. The two lines of the doublet are at  **$\delta$  2.35 and 2.38 ppm**. The **coupling constant (J) value** is

- (a) 3 Hz (b) 6 Hz (c) 9 Hz (d) 12 Hz

**Q.71 – Q.145 Multiple Choice Question (MCQ), carry FOUR marks each (for each wrong answer: -1). You are required to Answer Maximum 25 Questions.**

71. The strength of  $\text{p}_\pi - \text{d}_\pi$  bonding in  $\text{E}-\text{O}$  ( $\text{E} = \text{Si, P, S and Cl}$ ) follows the order:

- (a)  $\text{Si}-\text{O} > \text{P}-\text{O} > \text{S}-\text{O} > \text{Cl}-\text{O}$  (b)  $\text{P}-\text{O} > \text{Si}-\text{O} > \text{S}-\text{O} > \text{Cl}-\text{O}$   
 (c)  $\text{S}-\text{O} > \text{Cl}-\text{O} > \text{P}-\text{O} > \text{Si}-\text{O}$  (d)  $\text{Cl}-\text{O} > \text{S}-\text{O} > \text{P}-\text{O} > \text{Si}-\text{O}$

72. In the following reactions carried out in liquid  $\text{NH}_3$ .



$\text{KNH}_2$  and  $\text{NH}_4\text{NO}_3$  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-butyl phosphate** and concentrated  $\text{HNO}_3$  is:

- (a) La(III) (b) Eu(III) (c) Nd(III) (d) Lu(III)

75. The quantitative determination of  $\text{N}_2\text{H}_4$  with  $\text{KIO}_3$  proceeds in a mixture of  $\text{H}_2\text{O}/\text{CCl}_4$  as follows,  $\text{N}_2\text{H}_4 + \text{KIO}_3 + 2\text{HCl} \rightarrow \text{N}_2 + \text{KCl} + \text{ICl} + 3\text{H}_2\text{O}$

The end point for the titrimetric reaction is:

- (a) Consumption of  $\text{N}_2\text{H}_4$   
 (b)  $\text{ICl}$  formation  
 (c) Disappearance of the yellow colour due to  $\text{Cl}_2$  in  $\text{CCl}_4$  layer  
 (d) Displacement of the red colour due to  $\text{I}_2$  in  $\text{CCl}_4$  layer
76. Among the given halides, those which produce two different acids,
- |                                  |                                  |                                   |
|----------------------------------|----------------------------------|-----------------------------------|
| <b>P</b>                         | <b>Q</b>                         | <b>R</b>                          |
| <b><math>\text{NCl}_3</math></b> | <b><math>\text{PCl}_3</math></b> | <b><math>\text{AsCl}_3</math></b> |
- (a) P and Q                      (b) P and R                      (c) Q and R                      (d) P, Q and R

77. The decreasing order of dipole moment of molecules is

- (a)  $\text{NF}_3 > \text{NH}_3 > \text{H}_2\text{O}$                       (b)  $\text{NH}_3 > \text{NF}_3 > \text{H}_2\text{O}$   
 (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  $^{13}\text{C}$ -NMR spectrum of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_3$  shows a triplet at  $-65^\circ\text{C}$  owing to the presence of ( $^{103}\text{Rh}$ , nuclear spin,  $I = \frac{1}{2}$ , 100 %) )

- (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  $\pi$ -acceptors  
 (d) Complexes with low oxidation states will easily lose electrons to  $\text{O}_2$  but will not bind to a  $\pi$ -donor molecule like  $\text{H}_2\text{O}$

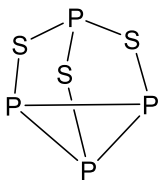
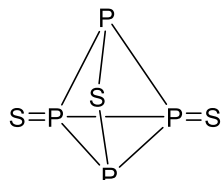
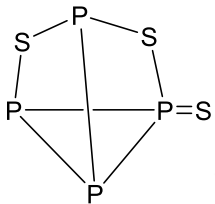
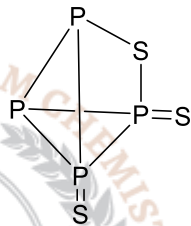
81. The metal complex that exhibits a triplet as well as a doublet in its  $^{31}\text{P}$ -NMR spectrum is

- (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)  $[\text{W}(\text{CO})_3(\text{SiMe}_3)(\text{Cl})(\text{NCMe})_2]$

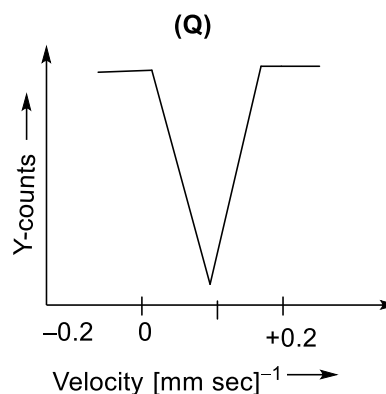
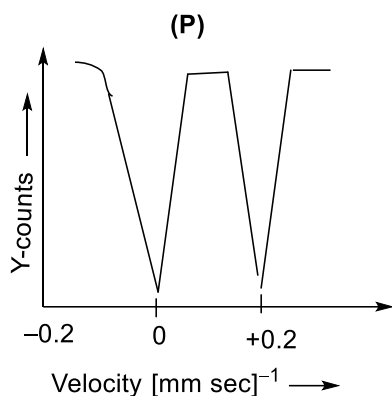


- (c)  $[\text{IrCl}_3(\text{PPh}_3)_2(\text{AsPh}_2)]^-$  (d)  $[\text{Os}(\text{N})\text{Br}_2(\text{PMe}_3)(\text{NMe}_2)]^-$
83. The number of spin-allowed ligand field transitions for octahedral Ni(II) complexes with  $^3\text{A}_{2g}$  ground state is:
- (a) Two (b) Three (c) One (d) Four
84. The correct structure of  $\text{P}_4\text{S}_3$  is:
- (a) 
- (b) 
- (c) 
- (d) 
85. Final product of reaction:  $[\text{Mn}(\text{CO})_6]^+ + \text{MeLi} \rightarrow$  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)  $\text{HCl (excess)} + \text{AlCl}_3 + \text{Li} \rightarrow$  (b)  $\text{H}_2 + \text{Al} + \text{Li} \rightarrow$   
 (c)  $\text{LiH (excess)} + \text{AlCl}_3 \rightarrow$  (d)  $\text{LiH (excess)} + \text{Al} \rightarrow$
87. The number of microstates for  $d^5$  electron configuration is:
- (a)  $21 \times 6^3$  (b)  $14 \times 6^3$  (c)  $7 \times 6^2$  (d)  $28 \times 6^3$
88. The carbon-14 activity of an old wood sample is found to be 14.2 disintegrations  $\text{min}^{-1} \text{g}^{-1}$ . Calculate age of old wood sample, if for a fresh wood sample carbon-14 activity is 15.3 disintegrations  $\text{min}^{-1} \text{g}^{-1}$ , is:
- ( $t_{1/2}$  of carbon-14 is 5730 years)
- (a) 5,000 years (b) 4,000 years (c) 877 years (d) 617 years
89. The reaction:  $3[\text{Rh}_4(\text{CO})_{12}] \rightarrow 2[\text{Rh}_6(\text{CO})_{16}] + 4 \text{CO}$  [ $25^\circ\text{C}$ , 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) Entropically favorable but enthalpically unfavorable such that  $\Delta G = 0$   
 (d) Thermodynamically unfavorable ( $\Delta G > 0$ )

90. A column is packed with **0.5 g** of a **strongly acidic ion exchange resin** in **H<sup>+</sup>** 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 **P-S** given below) which occur when **O<sub>2</sub>** binds to **hemerythrin** are
- [P]** One iron atoms is oxidized  
**[Q]** Both the iron atoms are oxidized  
**[R]** O<sub>2</sub> binds to one iron atom and is also hydrogen bonded  
**[S]** O<sub>2</sub> binds to both the iron atoms and is also hydrogen bonded
- (a) Q and R      (b) Q and S      (c) P and S      (d) P and R
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) PC → cyt b → cyt bf      (b) cyt bf → cyt b → PC  
 (c) cyt b → cyt bf → PC      (d) PC → cyt bf → cyt b
94. The **total numbers of fine and hyperfine EPR lines** expected for **octahedral high-spin Mn(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)	(ii)	(iii)
high-spin iron (III)	high-spin iron (II)	low-spin iron (III)





The correct matches of spectra (P) and (Q) with the iron complexes are:

- (a) P with (i) and Q with (ii)                      (b) P with (ii) and Q with (i)  
 (c) P with (iii) and Q with (ii)                      (d) P with (ii) and Q with (iii)
96. The probability of finding the particle in a one dimensional box 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  $\frac{14 h^2}{8mL^2}$ . The degeneracy of the state is  
 (a) 2                      (b) 3                      (c) 6                      (d) 9
98. The following are the three statements about perturbation theory
- [P] Second order perturbation correction to the ground state energy is ALWAYS negative
- [Q] Sum of the zeroth order and first order corrections to the ground state energy is ALWAYS greater than the exact ground state energy
- [R] 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 P is true                      (b) Both P and Q are true  
 (c) Only R is true                      (d) Both Q and R are true
99. Using Huckel 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  $\sigma_g^1 \sigma_u^1$ , the spin part of the triplet state with  $m_s = 0$  is proportional to

- (a)  $\alpha(1) \beta(2)$  (b)  $[\alpha(1) \beta(2) - \beta(1) \alpha(2)]$   
 (c)  $\alpha(1) \alpha(2)$  (d)  $[\alpha(1)\beta(2) + \beta(1) \alpha(2)]$
101. A square pyramidal,  $\text{MX}_4$ , molecule belongs to  $\text{C}_{4v}$  point group. The symmetry operations are:  $\text{E}$ ,  $2\text{C}_4$ ,  $\text{C}_2$ ,  $2\sigma_v$  and  $2\sigma_d$ . The trace for the reducible representation, when symmetry operations of  $\text{C}_{4v}$  applied to  $\text{MX}_4$ , is:
- (a) 51113 (b) 11111 (c) 51111 (d) 41113
102. Character table of  $\text{C}_{2v}$  point group is:

$\text{C}_{2v}$	$\text{E}$	$\text{C}_2$	$\sigma_v$	$\sigma_{v'}$	
$\text{A}_1$	1	1	1	1	z
$\text{A}_2$	1	1	-1	-1	-
$\text{B}_1$	1	-1	1	-1	x
$\text{B}_2$	1	-1	-1	1	y

- If the initial and final states belong to  $\text{A}_1$  and  $\text{B}_1$  irreducible representations respectively, the allowed electronic transition from  $\text{A}_1$  to  $\text{B}_1$  is
- (a) z-polarized (b) y-polarized (c) x-polarized (d) x, z-polarized
103. Using cuvettes of 0.5 cm path length, a  $10^{-4} \text{ M}$  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:

P	Q	R	S	T
$^4\Sigma \rightarrow ^2\Pi$	$^3\Sigma \rightarrow ^3\Pi$	$^1\Delta \rightarrow ^1\Delta$	$^2\Pi \rightarrow ^2\Pi$	$^3\Sigma \rightarrow ^3\Delta$

- (a) P, Q, T (b) P, R, T (c) Q, R, S (d) R, S, T
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  $\omega_e$  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)  $4096 \text{ cm}^{-1}$  (b)  $6144 \text{ cm}^{-1}$  (c)  $8192 \text{ cm}^{-1}$  (d)  $16384 \text{ cm}^{-1}$
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:  $2\text{NO}_{2(g)} \rightarrow \text{N}_2\text{O}_{4(g)}$  is an exothermic process. In an equilibrium mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ , the decomposition of  $\text{N}_2\text{O}_4$  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  $\epsilon_v = nh\nu$  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:
- $$\text{Pt} | \text{H}_2(\text{p}) | \text{HCl}(\text{a}_{\pm})_1 | \text{AgCl}(\text{s}) | \text{Ag} \quad \text{Ag} | \text{AgCl}(\text{s}) | \text{HCl}(\text{a}_{\pm})_2 | \text{H}_2(\text{p}) | \text{Pt}$$
- 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-Huckel equation is (are) the validity of
- (a) Only Poisson equation  
(b) Poisson equation and Boltzmann distribution  
(c) Poisson equation, Boltzmann distribution and  $|\pm Ze\phi| \gg k_B T$   
(d) Poisson equation Boltzmann distribution and  $|\pm Ze\phi| \ll k_B T$
113. In the base ( $\text{OH}^-$ ) hydrolysis of a transition metal complex  $[\text{ML}_6]^{2+}$ , 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  $\text{CH}_3\text{CHO}$  at  $520^\circ\text{C}$  and  $0.2 \text{ bar}$  is



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

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:

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

The values of  $k_3$  ( $k_{\text{exp}}$ ,  $\text{mol L}^{-1}\text{s}^{-1}$ ) and  $K$  (Michaelis constant,  $\text{mol L}^{-1}$ ), 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 ( $E_g = 1.98 \times 10^{-19}$ ) are

$$[h = 6.626 \times 10^{-34} \text{Js}, c = 3 \times 10^8 \text{ms}^{-1}]$$

- (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  $4.04 \text{ \AA}$ . The atomic radius of the element is:

- (a)  $2.86 \text{ \AA}$  (b)  $1.43 \text{ \AA}$  (c)  $4.29 \text{ \AA}$  (d)  $5.72 \text{ \AA}$

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

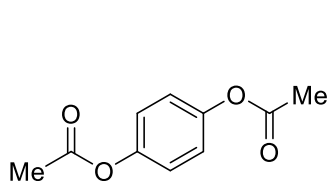
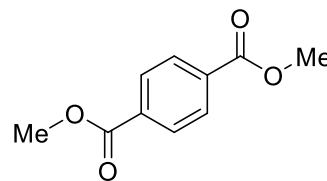


**Y(set B)** | 10.2 10.6 11.1 11.3 11.8 12.2

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

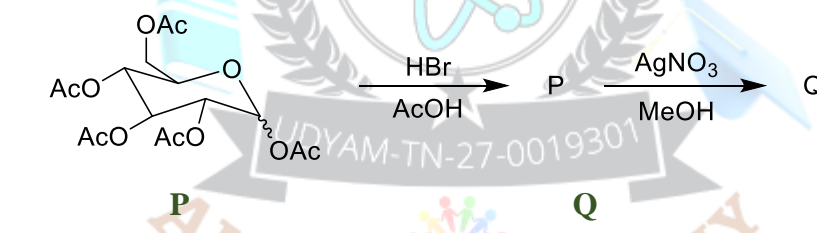
- (a)  $m_A > m_B, C_A > C_B$  (b)  $m_A < m_B, C_A > C_B$   
 (c)  $m_A > m_B, C_A < C_B$  (d)  $m_A < m_B, C_A < C_B$

121. Compounds **P** and **Q** exhibit **two singlets**, each in their  $^1\text{H-NMR}$  spectra. The **expected chemical shifts** are at  $\delta$

**(P)****(Q)**

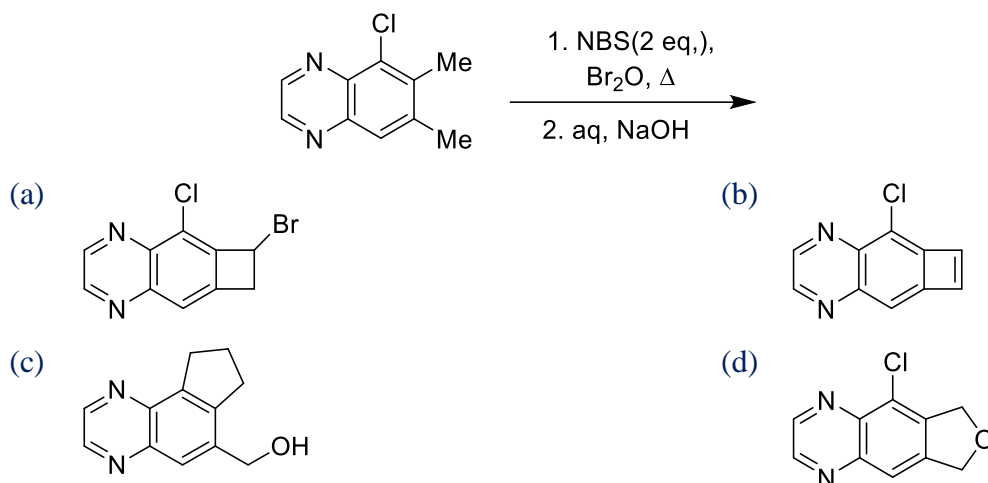
- (a) 6.9 and 2.1 for P; 7.7 and 3.9 for Q (b) 7.7 and 3.9 for P; 6.9 and 2.1 for Q  
 (c) 6.9 and 3.9 for P; 7.7 and 2.1 for Q (d) 7.7 and 2.1 for P; 6.9 and 3.9 for Q

122. In the following reaction sequence, the **major products P** and **Q** are:

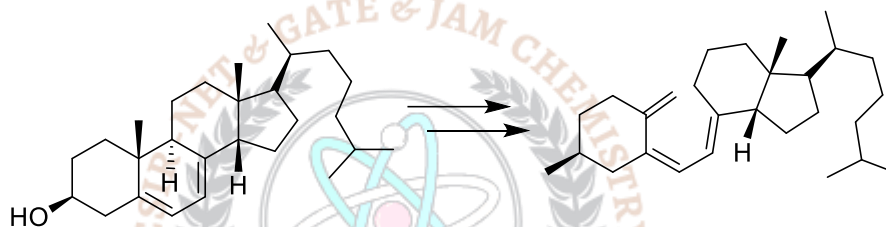


- (a) ;   
 (b) ;   
 (c) ;   
 (d) ;

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

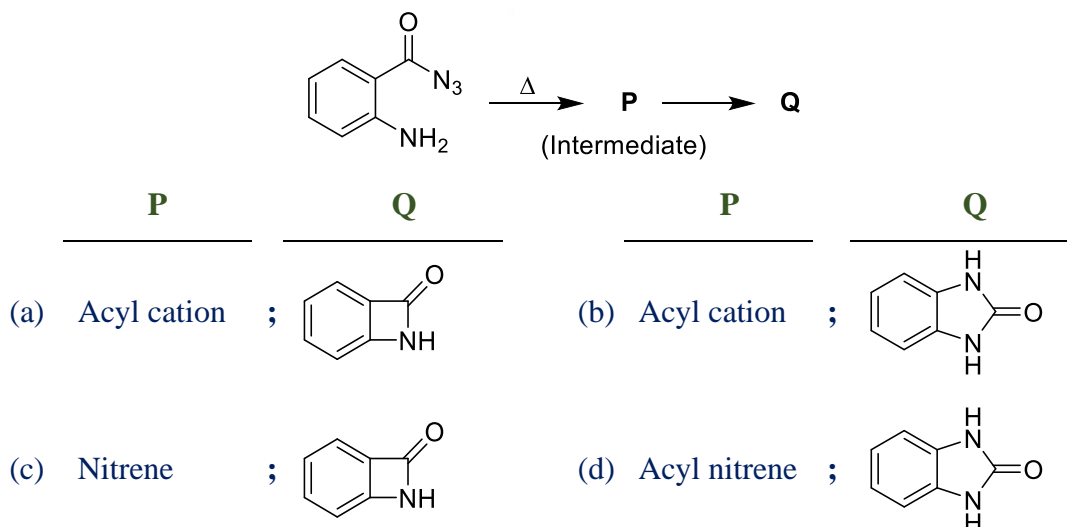


124. The two step conversion of 7-dehydrocholesterol to vitamin D<sub>3</sub> proceeds through

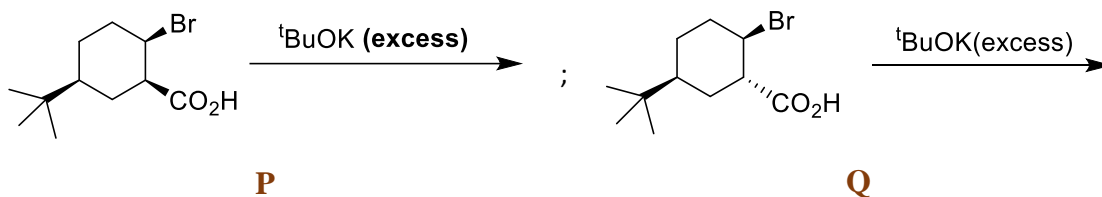


- (a) Photochemical electrocyclic disrotatory ring opening; and thermal antarafacial [1,7]-H shift
- (b) Photochemical electrocyclic conrotatory ring opening; and thermal antarafacial [1,7]-H shift
- (c) Thermal electrocyclic conrotatory ring opening; and photochemical suprafacial [1,7]-H shift
- (d)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

125. The intermediate-P and the major product-Q in the following reaction are:

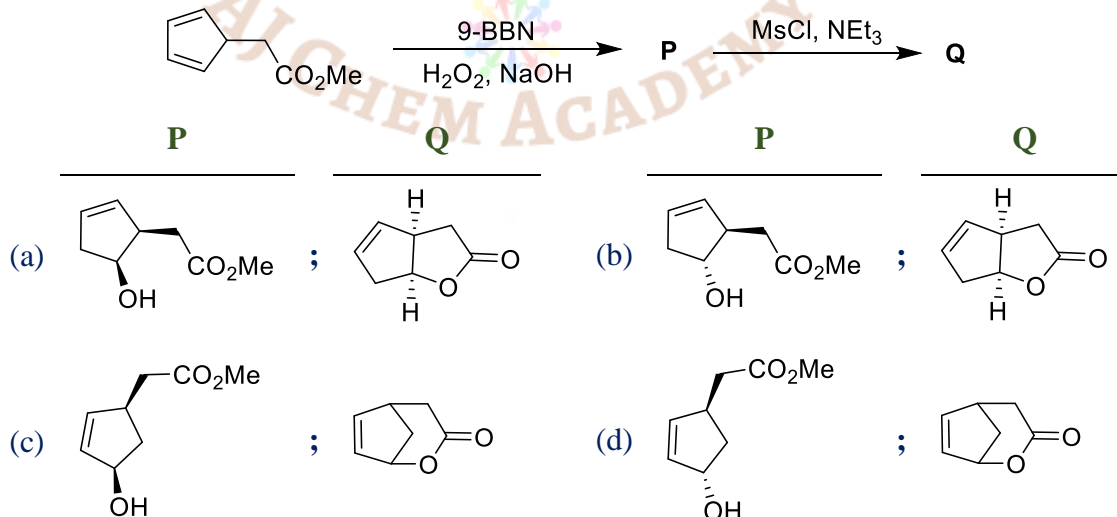


126. For the following two reactions P and Q, the correct statement is:

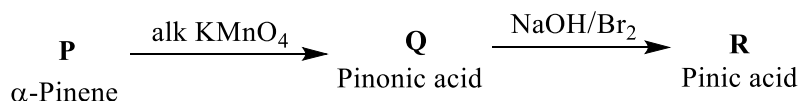


- (a) **P** gives ; **Q** gives
- (b) **P** gives ; **B** gives
- (c) Both **P** and **Q** give
- (d) Both **P** and **Q** give

127. The major compound **Q** formed in the reaction sequence given below exhibited a carbonyl absorption band at  $1770\text{ cm}^{-1}$  in the IR spectrum. The structure **P** and **Q** are:



128. Consider the following reaction sequence starting with monoterpene  $\alpha$ -pinene. Identify the correct statement:

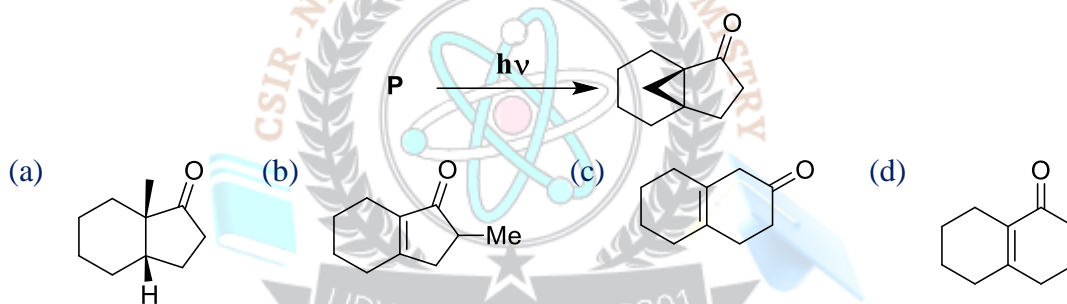


- (a) P has a disubstituted double bond; Q and R are dicarboxylic acids
- (b) P has a trisubstituted double bond; Q is a methyl ketone; and R is a dicarboxylic acid
- (c) P has a disubstituted double bond; Q is a methyl ketone; and R is a dicarboxylic acid
- (d) P has an exocyclic double bond; Q and R are monocarboxylic acids

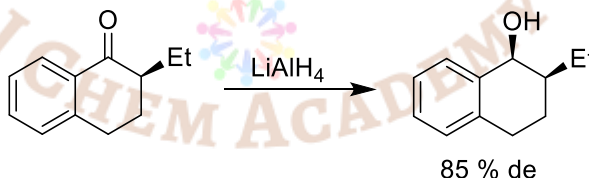
129. The major product formed when (3R, 4S)-3, 4-dimethylhexa-1, 5-diene is heated at 240 °C is:

- (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-P in the following photochemical Norrish reaction, is:



131. Considering the following reaction, among P-R, the correct statements are



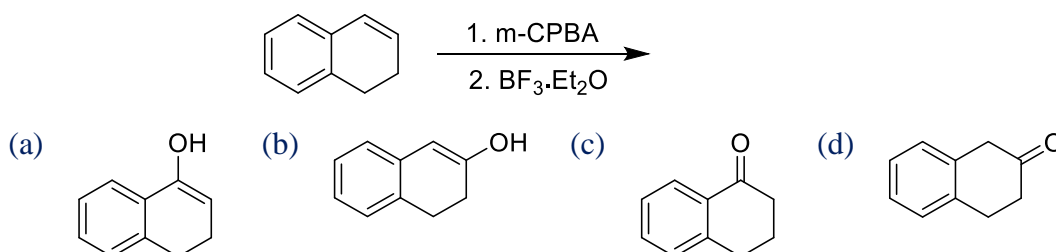
(P) The carbonyl group has enantiotopic faces

(Q) The hydride attack is re-facial

(R) It is a diastereoselective reduction

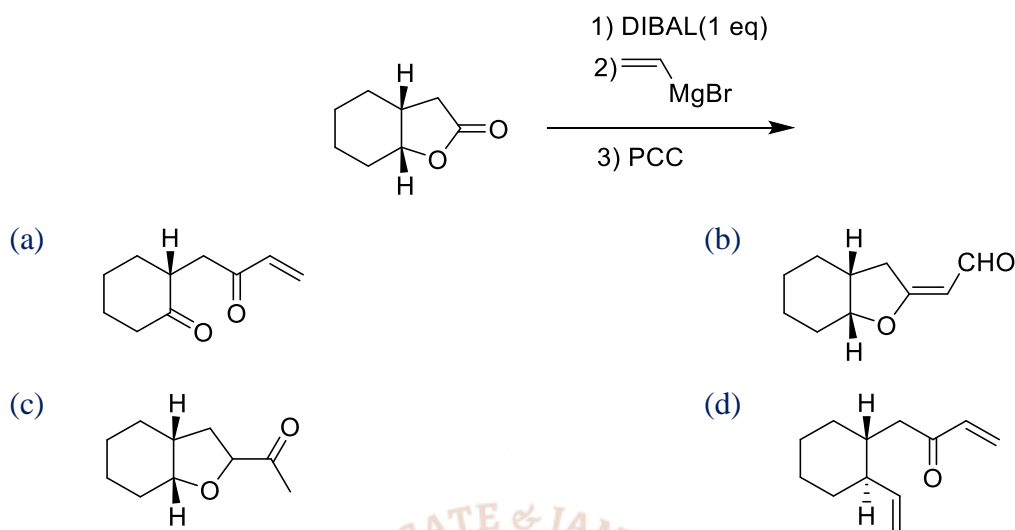
- (a) (P) and (Q) only
- (b) (P) and (R) only
- (c) (Q) and (R) only
- (d) (P), (Q) and (R)

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





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



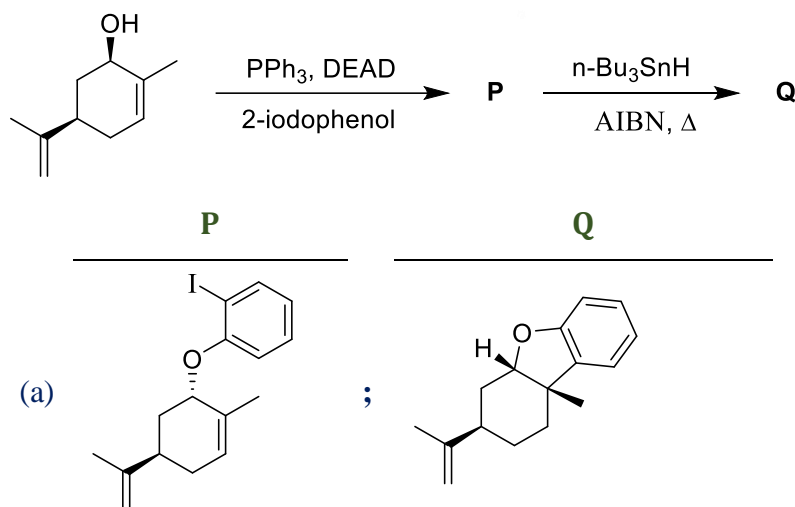
134. Match the following:

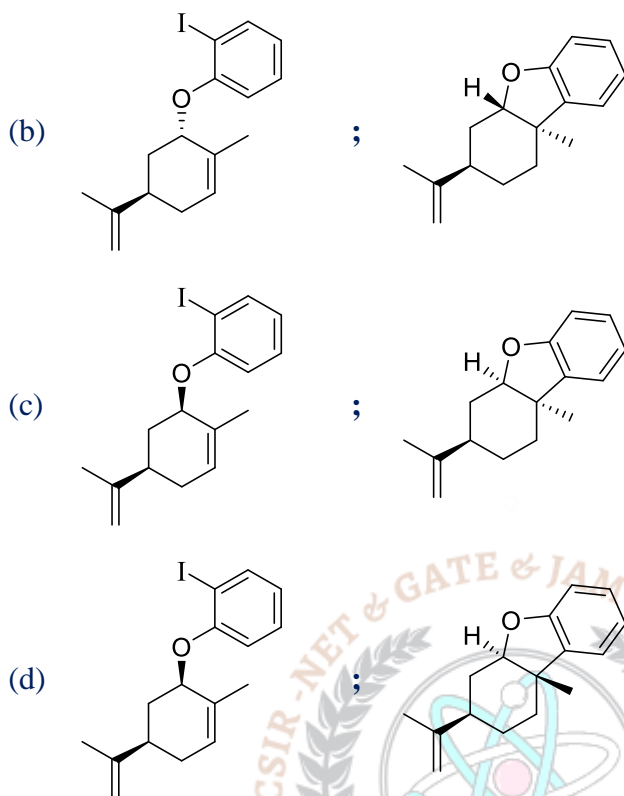
	Compound		$^{13}\text{C-NMR}$ chemical shift ( $\delta$ ppm)
(P)	Acetic acid	(i)	95
(Q)	Acetonitrile	(ii)	115
(R)	Acetone	(iii)	175
(S)	Carbon tetrachloride	(iv)	205

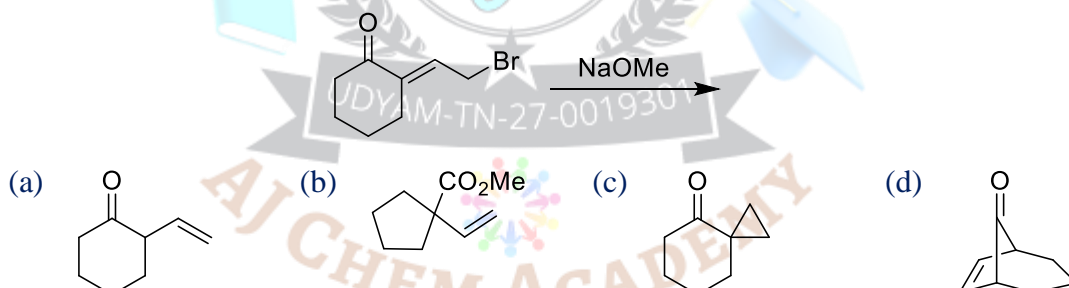
P	Q	R	S
(a) iii ; ii ; iv ; i	(b) iii ; iv ; i ; ii		
(c) i ; ii ; iv ; ii	(d) iii ; i ; ii ; iv		

135. The major products **P** and **Q** in the following reaction sequence are:

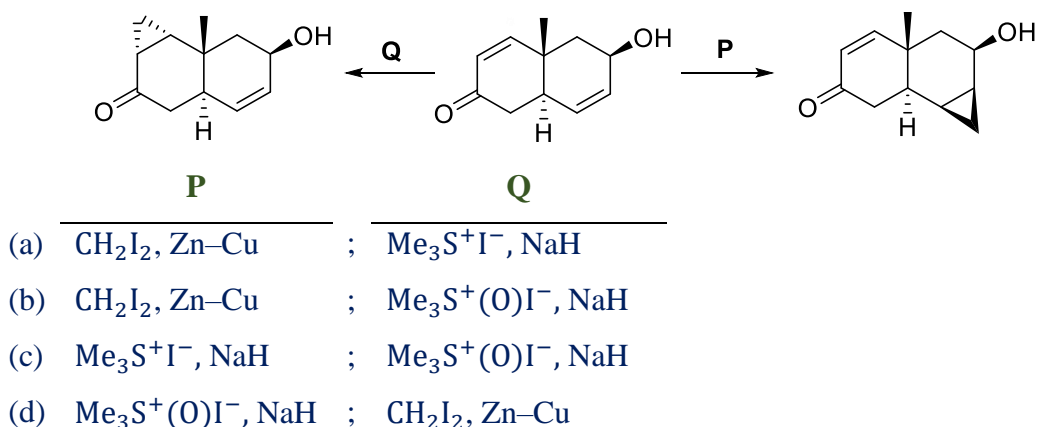




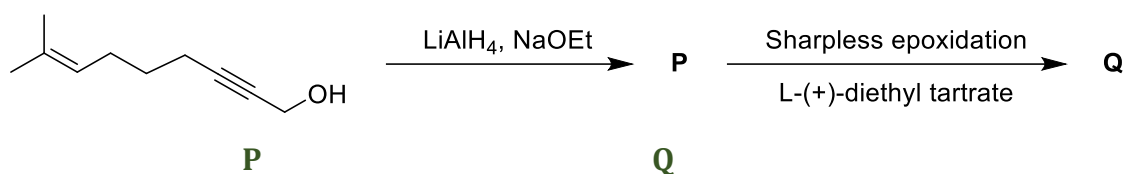
136. The major product formed in the following reaction is:



137. The reagents P and Q in the following reactions are

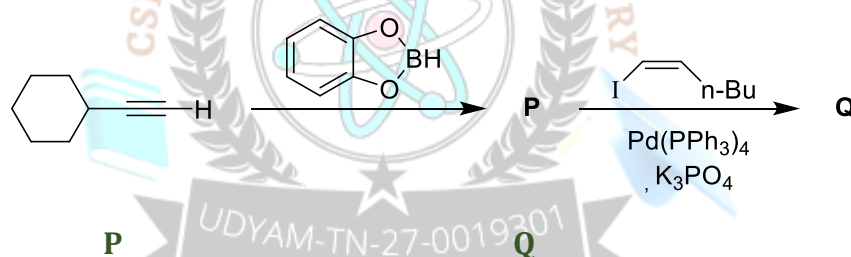


138. The major products P and Q formed in the following reaction sequence are



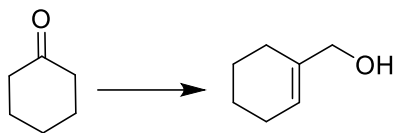
- (a) CC(C)=CCCC=CCO ; CC(C)[C@H](O)CCCC[C@H](O)C1OC1
- (b) CC(C)=CCCC=CCO ; CC(C)C=CCCC[C@H](O)C1OC1
- (c) CC(C)=CCCC=CCO ; CC(C)[C@H](O)CCCC[C@H](O)C1OC1
- (d) CC(C)=CCCC=CCO ; CC(C)C=CCCC[C@H](O)C1OC1

139. The major products **P** and **Q** formed in the following reaction sequence are:



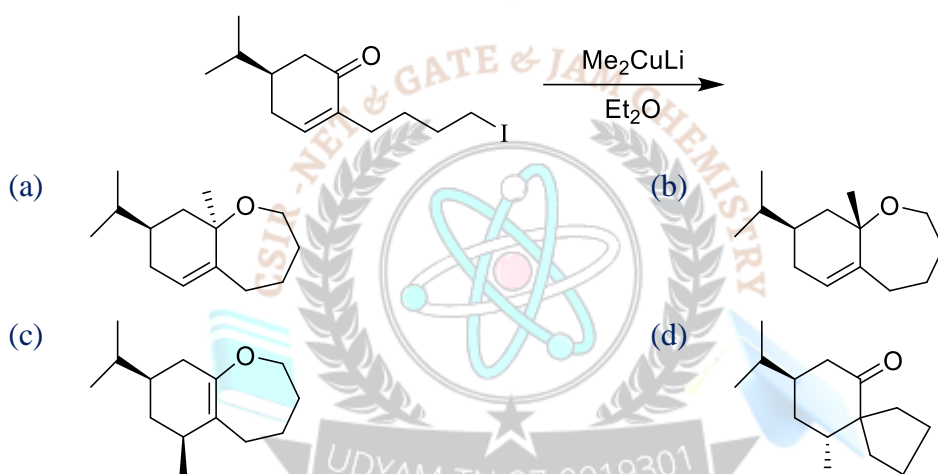
- (a) C1CCCCC1C#C ; C1CCCCC1C#C
- (b) C1CCCCC1C#C ; C1CCCCC1C#C
- (c) C1CCCCC1C#C ; C1CCCCC1C#C
- (d) C1CCCCC1C#C ; C1CCCCC1C#C

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

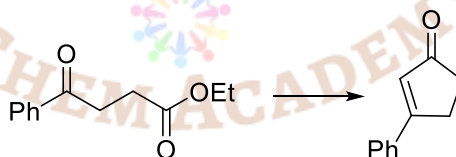


- |     | (i)   | (ii)                       | (iii)                        |
|-----|---|----------------------------|------------------------------|
| (a) | $\text{Me}_3\text{SiCH}_2\text{OMe}, ^n\text{BuLi}$             | $\text{H}_3\text{O}^+$     | $\text{NaBH}_4, \text{MeOH}$ |
| (b) | $\text{Ph}_3\text{P}^+\text{CH}_2\text{OMeCl}^-, ^n\text{BuLi}$ | $\text{H}_3\text{O}^+$     | $\text{NaBH}_4, \text{MeOH}$ |
| (c) | $\text{NH}_2\text{NHTs}$  | $\text{NaOEt}$             | $\text{ClCOOEt}$             |
| (d) | $\text{NH}_2\text{NHTs}$  | $2\text{eq.}^n\text{BuLi}$ | $\text{HCHO}$                |

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

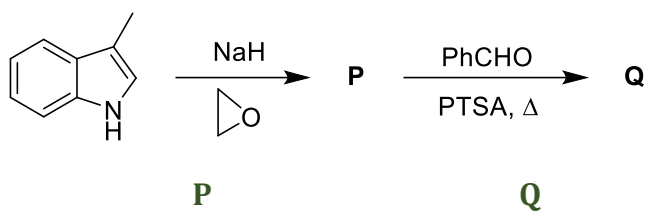


142. The correct sequence of reagents for effecting the following conversion is:



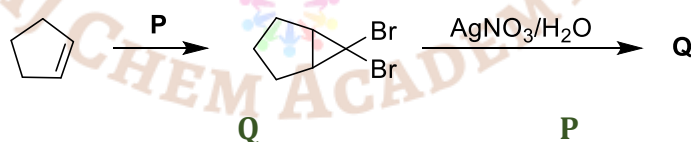
- |     | (i)  | (ii)   | (iii)                  | (iv)         |
|-----|--|--|------------------------|--------------|
| (a) | $(\text{CH}_2\text{OH})_2, \text{PTSA}$  | $\text{CP}_2\text{Ti} \begin{array}{c} \diagup \text{AlMe}_2 \\ \diagdown \text{Cl} \end{array}$ | $\text{H}_3\text{O}^+$ | $\text{KOH}$ |
|     |  | (Tebbe's reagent)  |                        |              |
| (b) | $(\text{CH}_2\text{OH})_2, \text{PTSA}$  | $\text{Ph}_3\text{P}=\text{CH}_2$  | $\text{H}_3\text{O}^+$ | $\text{KOH}$ |
| (c) | $\text{CP}_2\text{Ti} \begin{array}{c} \diagup \text{AlMe}_2 \\ \diagdown \text{Cl} \end{array}$ | $\text{H}_3\text{O}^+$   | $\text{KOH}$           |              |
|     | (Tebbe's reagent)  |  |                        |              |
| (d) | $\text{Ph}_3\text{P}=\text{CH}_2$  | $\text{H}_3\text{O}^+$   | $\text{KOH}$           |              |

143. The major products P and Q formed in the following reaction sequence are:



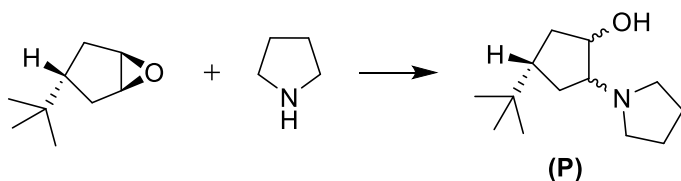
- (a) ;
- (b) ;
- (c) ;
- (d) ;

144. The reagent-**P** required, and the major product **Q** formed in the following reaction sequence are



- (a)  $\text{CH}_2\text{Br}_2$  and  $^t\text{BuOK}$  ; (b)  $\text{CH}_2\text{Br}_2$  and  $^t\text{BuOK}$  ;
- (c)  $\text{CHBr}_3$  and  $^t\text{BuOK}$  ; (d)  $\text{CHBr}_3$  and  $^t\text{BuOK}$  ;

145. Among the choices, the correct statements for **P** formed in the following reaction:



# CSIR-UGC-NET (Chemical Science) June – 2012

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

## Answer Key

### PART - B

Q.No	Ans
21.	b
22.	d
23.	a
24.	d
25.	d
26.	c
27.	a
28.	d
29.	a
30.	b
31.	c
32.	c
33.	b
34.	a
35.	d

Q.No	Ans
36.	b
37.	a
38.	d
39.	d
40.	b
41.	a
42.	d
43.	b
44.	c
45.	c
46.	b
47.	c
48.	a
49.	d
50.	b

Q.No	Ans
51.	c
52.	c
53.	b
54.	b
55.	b
56.	d
57.	c
58.	d
59.	b
60.	a

Q.No	Ans
61.	b
62.	b
63.	d
64.	a
65.	b
66.	d
67.	a
68.	a
69.	c
70.	d

### PART - C

Q.No	Ans
71.	d
72.	a
73.	b
74.	d
75.	d
76.	c

Q.No	Ans
91.	b
92.	a
93.	c
94.	c
95.	b
96.	b

Q.No	Ans
111.	c
112.	d
113.	b
114.	c
115.	c
116.	b

Q.No	Ans
131.	c
132.	d
133.	a
134.	a
135.	a
136.	b





# CSIR-UGC-NET (Chemical Science) June – 2012

77.	c
78.	b
79.	b
80.	d
81.	a
82.	d
83.	b
84.	a
85.	d
86.	c
87.	c
88.	d
89.	b
90.	d

97.	c
98.	b
99.	c
100.	d
101.	a
102.	c
103.	d
104.	c
105.	c
106.	c
107.	d
108.	b
109.	d
110.	c

117.	b
118.	b
119.	a
120.	c
121.	a
122.	b
123.	d
124.	b
125.	d
126.	b
127.	b
128.	b
129.	c
130.	c

137.	b
138.	c
139.	b
140.	d
141.	d
142.	a
143.	d
144.	c
145.	b

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