Section-A

Q.1 – Q.25 : Carry ONE mark each.

1. Jahn-Teller distortion of $CuSO_4.5H_2O$ acts to
(a) Raise symmetry
(b) Remove an electronic degeneracy
(c) Cause loss of H_2O ligand
(d) Promote a d-electron to an antibonding molecular orbital.

2. Among the following, the group of molecules that undergoes rapid hydrolysis is:
(a) SF_6, Al_2Cl_6, $SiMe_4$ (b) BCl_3, SF_6, $SiCl_4$
(c) BCl_3, $SiCl_4$, PCl_5 (d) SF_6, Al_2Cl_6, $SiCl_4$

3. The reaction of solid XeF_2 with AsF_5 in 1:1 ratio affords
(a) XeF_4 and AsF_3 (b) XeF_6 and AsF_3
(c) $[XeF]^+[AsF_6]^-$ (d) $[Xe_2F_3]^+[AsF_6]^-$

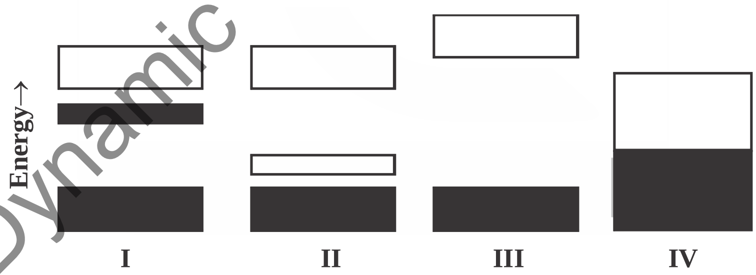
4. A well known naturally occuring organometallic compound is:
(a) vitamin B_{12} coenzyme (b) chlorophyll
(c) cytochrome P-450 (d) myoglobin

5. The complex that exists as a pair of enantiomers is
(a) trans-$[Co(H_2NCH_2CH_2NH_2)_2Cl_2]^+$ (b) cis-$[Co(NH_3)_4Cl_2]^+$
(c) $[Pt(PPh_3)(Cl)(Br)(CH_3)]^-$ (d) $[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$

6. The region of electromagnetic spectrum employed in the electron spin resonance (ESR) spectroscopy is:
(a) radiowave (b) microwave (c) infrared (d) visible

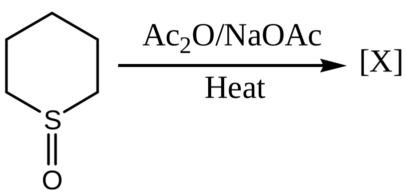
7. The red color of oxyhaemoglobin is mainly due to the
(a) d-d transition (b) metal to ligand charge transfer transition
(c) ligand to metal charge transfer transition (d) intraligand $\pi-\pi^*$ transition.

8. The band structure in an n-type semiconductor is

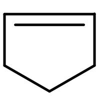
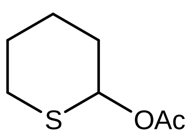


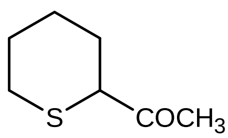
(a) I (b) II (c) III (d) IV

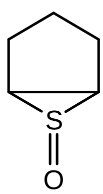
9. In the following reaction



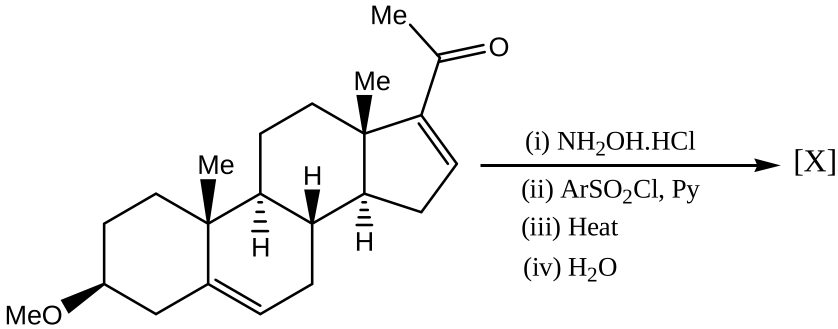
The major product [X] is:

(a) 
(b) 

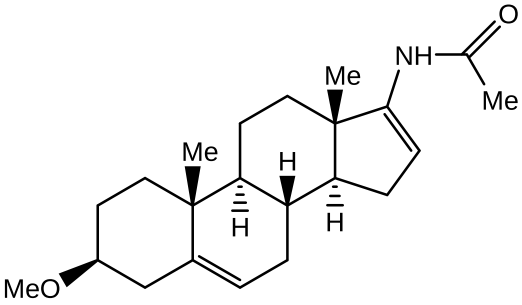
(c) 

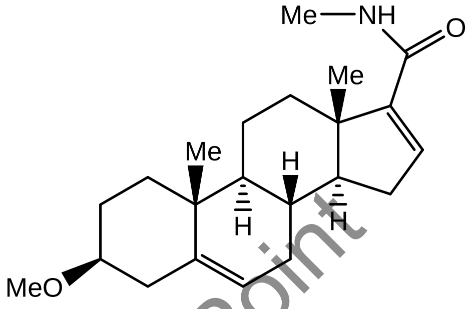
(d) 

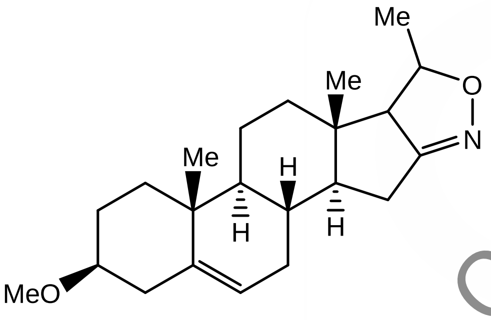
10. In the following reaction sequence

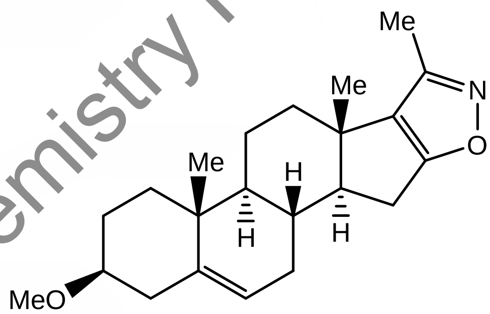


the major product [X] is:

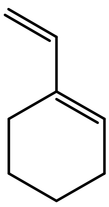
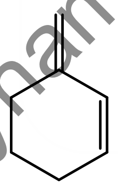
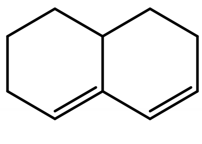
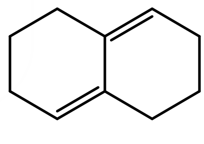
(a) 

(b) 

(c) 

(d) 

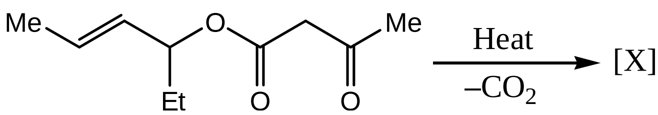
11. The diene which undergoes Diels-Alder reaction with maleic anhydride is:

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

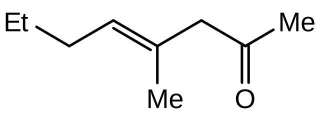
12. The sequence of an mRNA molecule produced from a DNA template strand with the composition 5'– AGCTACACT – 3' is

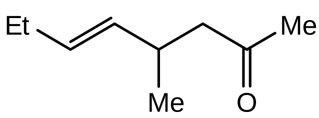
(a) 5'– AGUGUAGCU – 3'
(b) 5'– UCGAUGUGA – 3'
(c) 5'– AGTGTAGCT – 3'
(d) 5'– TCGATGTGA – 3'

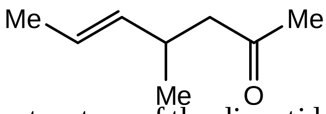
13. In the following reaction,

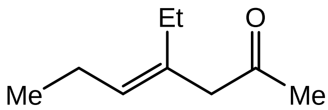


the major product [X] is:

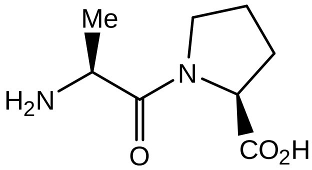
(a) 

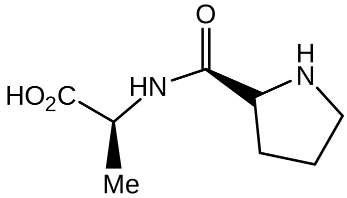
(b) 

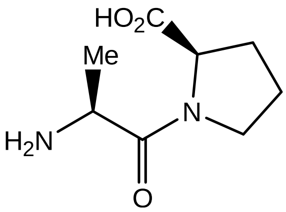
(c) 

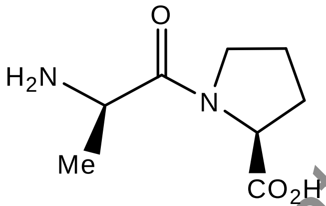
(d) 

14. The structure of the dipeptide Ala-Pro derived from the natural amino acids is:

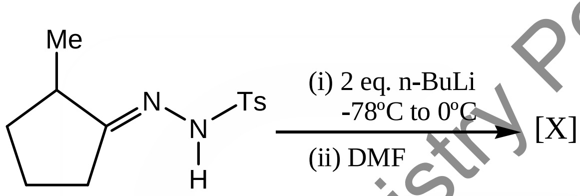
(a) 

(b) 

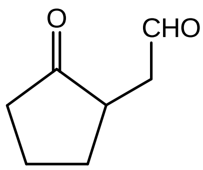
(c) 

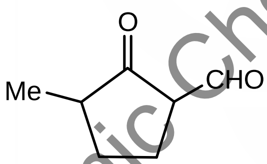
(d) 

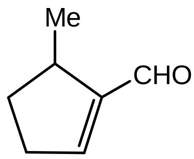
15. In the following reaction

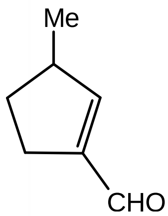


the major product [X] is:

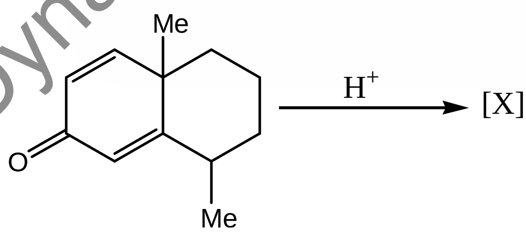
(a) 

(b) 

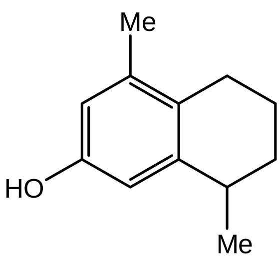
(c) 

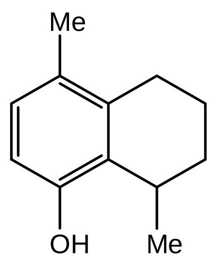
(d) 

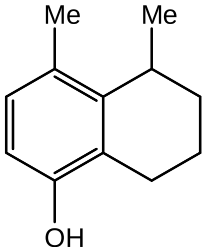
16. In the following reaction,

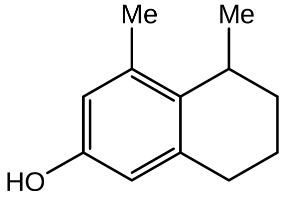


the major product [X] is:

(a) 

(b) 

(c) 

(d) 

17. For a given first order reaction, the reactant reduces to 1/4th its initial value in 10 minutes. The rate constant of the reaction is:
(a) 0.1386 min^{-1}
(b) 0.0693 min^{-1}
(c) 0.1386 mol L^{-1} min^{-1}
(d) 0.0693 mol L^{-1} min^{-1}.

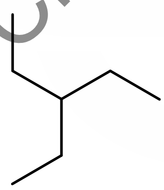
18. The freezing point constant for water is 1.86 K $(mol\ kg^{-1})^{-1}$. The change in freezing point when 0.01 mol glucose is added to 1 kg water is:
(a) 1.86 K (b) –1.86 K (c) 0.186 K (d) –0.0186 K

19. On the pressure-temperature diagram for a one-component system, the point where the solid-liquid and the liquid-gas curves intersect is:
(a) triple point (b) critical point (c) melting point (d) boiling point

20. The wave function for a harmonic oscillator described by $Nx\exp\left(-\alpha x^2/2\right)$ has
(a) One maximum only
(b) One maximum, one minimum only
(c) Two maxima, one minimum only
(d) Two maxima, two minima only

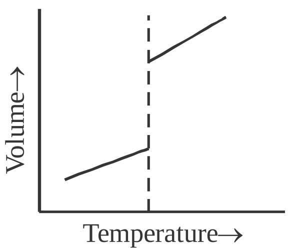
21. If an arbitrary wave function is used to calculate the energy of a quantum mechanical system, the value calculated is never less than the true energy.
The above statement relates to
(a) Perturbation theory
(b) Variation principle
(c) Heisenberg's uncertainty principle
(d) quantization of energy

22. The point group symmetry of the given planar shape is:



(a) D_{3h} (b) C_3 (c) C_{3h} (d) C_{3v}

23. $\left(\frac{\partial G}{\partial P}\right)_T =$
(a) V (b) S (c) –S (d) –V

24. 

According to Ehrenfest classification of phase transitions, the above diagram refers to
(a) Zeroth order phase transition
(b) First order phase transition
(c) Second order phase transition
(d) λ transition.

25. According to conventional transition state theory, for elementary bimolecular reactions, the molar entropy of activation $\Delta S^{0\ddagger}$ is :

(a) Positive (b) Zero (c) Negative

(d) Positive for endothermic and negative for exothermic reactions.

Q.26 – Q.55 : Carry TWO marks each.

26. The crystal field stabilization energy (CFSE) value for $[Ti(H_2O)_6]^{3+}$ that has an absorption maximum at 492 nm is:
(a) 20, 325 cm^{-1} (b) 12, 195 cm^{-1} (c) 10, 162 cm^{-1} (d) 8, 130 cm^{-1}

27. For Et_2AlX ($X = PPh_2^-, Ph^-, Cl^-$ and H^-), the tendency towards dimeric structure follows the order

(a) $PPh_2^- > Cl^- > H^- > Ph^-$ (b) $Cl^- > PPh_2^- > H^- > Ph^-$

(c) $Ph^- > H^- > Cl^- > PPh_2^-$ (d) $H^- > Ph^- > PPh_2^- > Cl^-$

28. In the isoelectronic series, VO_4^{3-}, CrO_4^{2-} and MnO_4^-, all members have intense charge transfer (CT) transitions. The **INCORRECT** statement is

(a) CT transitions are attributed to excitations of electrons from ligand (σ) to metal (e)

(b) MnO_4^- exhibits charge transfer at shortest wavelength among the three

(c) The wavelength of transitions increase in the order $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$

(d) The charge on metal nucleus increases in the order $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$

29. The increasing order of wavelength of absorption for the complex ions

(i) $\left[Cr(NH_3)_6\right]^{3+}$ (ii) $\left[CrCl_6\right]^{3-}$ (iii) $\left[Cr(OH_2)_6\right]^{3+}$ (iv) $\left[Cr(CN)_6\right]^{3-}$, is

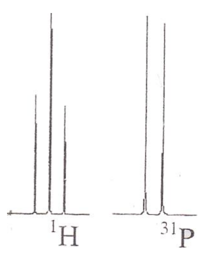
(a) iv < ii < i < iii (b) iv < iii < ii < i (c) iv < i < iii < ii (d) ii < iii < i < iv

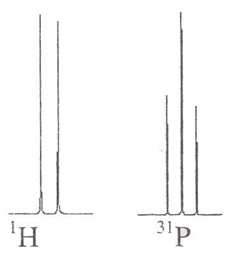
30. The total number of metal-metal bonds in $Ru_3(CO)_{12}$ and $Co_4(CO)_{12}$, respectively, is
(a) 3 and 6 (b) 4 and 5 (c) zero and 4 (d) 3 and 4

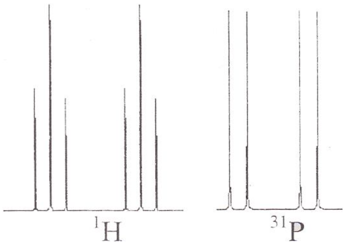
31. According to VSEPR theory the shapes of $[SF_2Cl]^+$ and $[S_2O_4]^{2-}$ should be
(a) trigonal planar for $[S_2O_4]^{2-}$ and trigonal pyramidal for $[SF_2Cl]^+$
(b) both trigonal planar
(c) trigonal pyramidal for $[S_2O_4]^{2-}$ and trigonal planar for $[SF_2Cl]^+$
(d) both trigonal pyramidal

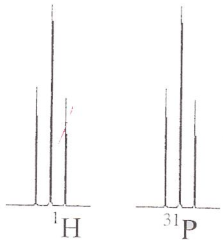
32. The product of the reaction between $CH_3Mn(CO)_5$ and ^{13}CO is:
(a) $(CH_3\,^{13}CO)Mn(CO)_5$ (b) $(CH_3CO)Mn(CO)_4(^{13}CO)$
(c) $(^{13}CH_3CO)Mn(CO)_5$ (d) $CH_3Mn(CO)_4$

33. The correct pair of ^1H and ^{31}P NMR spectral patterns for $C(H)(F)(PCl_2)_2$ is:

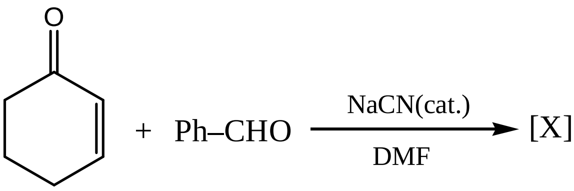
(a)


(b)


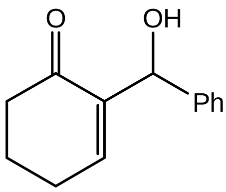
(c) 

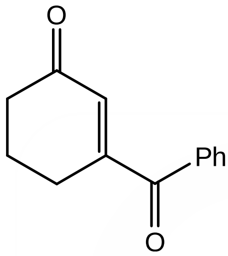
(d) 

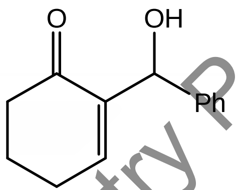
34. In the following reaction

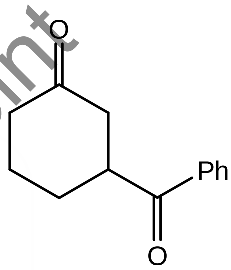


the major product [X] is:

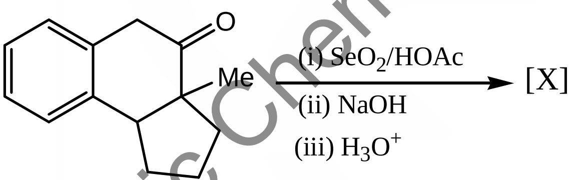
(a) 

(b) 

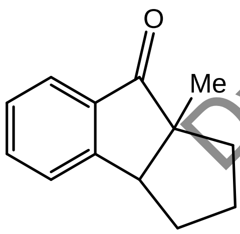
(c) 

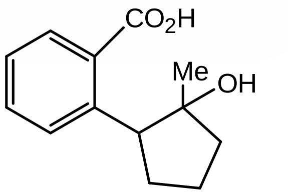
(d) 

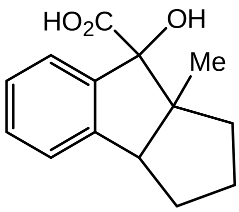
35. In the following reaction,

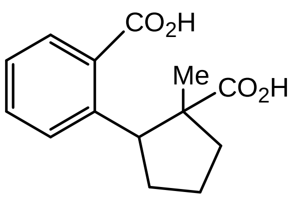


the major product [X] is:

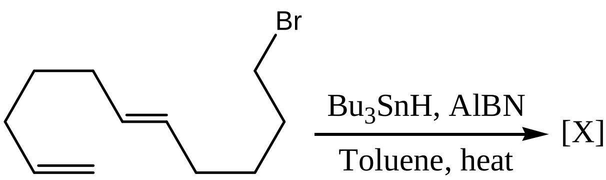
(a) 

(b) 

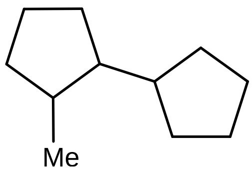
(c) 

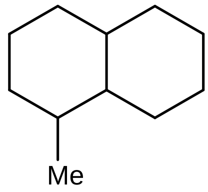
(d) 

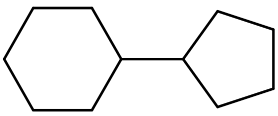
36. In the following reaction,

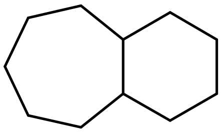


the major product [X] is:

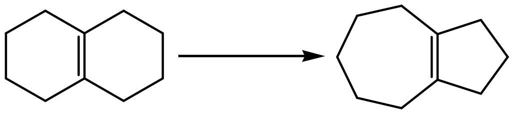
(a) 

(b) 

(c) 

(d) 

37. The most appropriate sequence of reactions for carrying out the following conversion



is

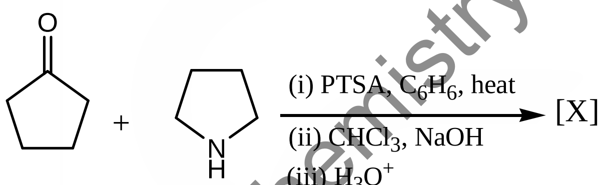
(a) (i) Peracid; (ii) H^+; (iii) Zn/dil. HCl

(b) (i) Alkaline $KMnO_4$; (ii) $NaIO_4$; (iii) N_2H_4/KOH

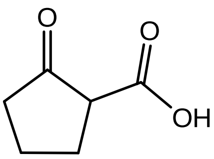
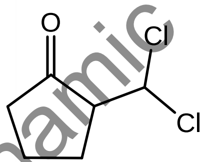
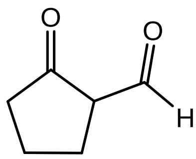
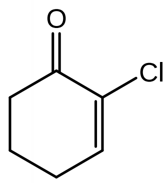
(c) (i) Alkaline $KMnO_4$; (ii) H^+; (iii) Zn/dil. HCl

(d) (i) O_3/Me_2S; (ii) NaOEt; (iii) N_2H_4/KOH

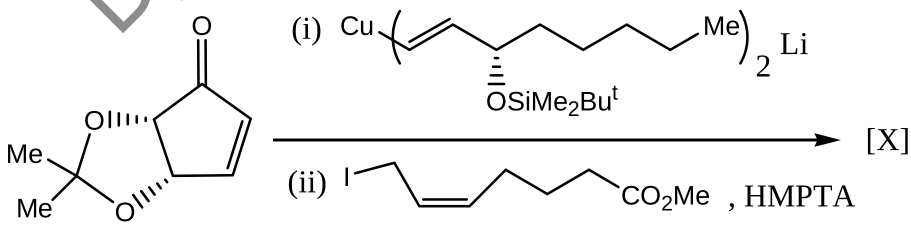
38. In the following reaction sequence



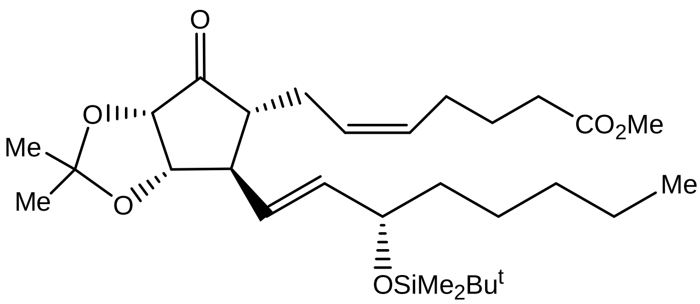
the major product [X] is:

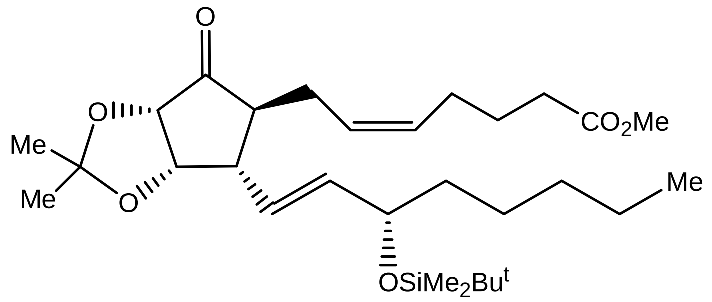
(a)  (b)  (c)  (d) 

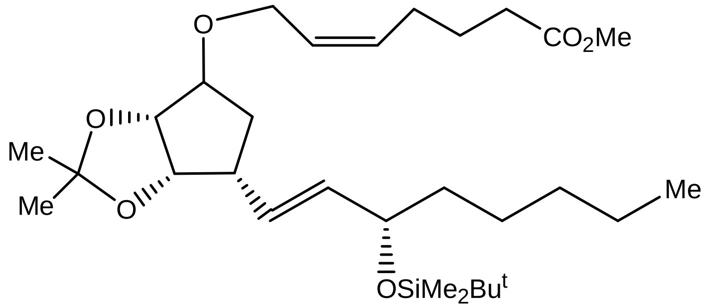
39. In the following conversion

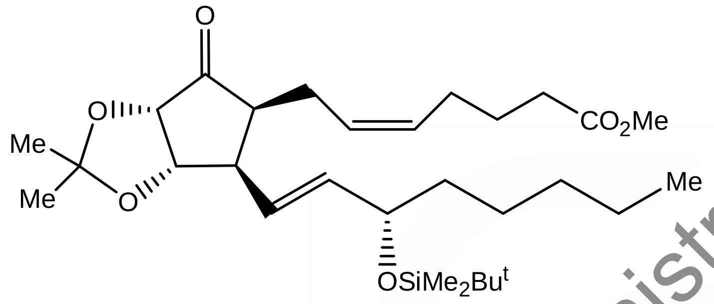


the major product [X] is:

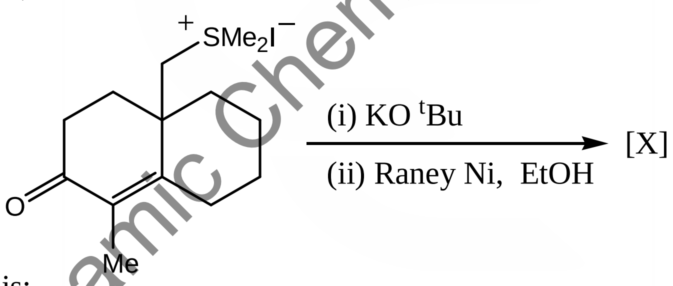
(a) 

(b) 

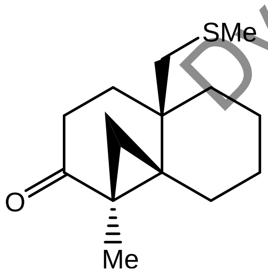
(c) 

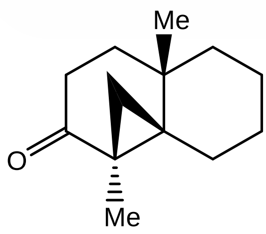
(d) 

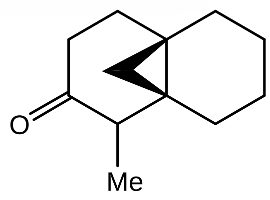
40. In the following reaction,

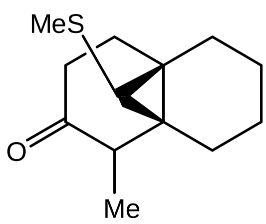


the major product [X] is:

(a) 

(b) 

(c) 

(d) 

41. In the reaction,

Optically pure (+)-trans-2-acetoxycyclohexyl tosylate $\xrightarrow[\Delta]{\text{HOAc.KOAc}}$ [X]

the major product [X] is:

(a) racemic trans-1, 2-cyclohexanediol diacetate
(b) optically active trans-1, 2-cyclohexanediol diacetate
(c) racemic cis-1, 2-cyclohexanediol diacetate
(d) optically active cis-1, 2-cyclohexanediol diacetate.

42. The activity of water at 11 bar and 298K is:

(a) 1.101 (b) 1.007 (c) 0.998 (d) 0.898

43. For the process

$$1\,\text{Ar}\left(300\text{K}, 1\,\text{bar}\right) \longrightarrow 1\,\text{Ar}\left(200\text{K}, 10\,\text{bar}\right)$$

assuming ideal gas behavior, the change in molar entropy is:

(a) -27.57 J K^{-1} mol^{-1} (b) $+27.57$ J K^{-1} mol^{-1}
(c) -24.20 J K^{-1} mol^{-1} (d) $+24.20$ J K^{-1} mol^{-1}

44. The wave function for a quantum mechanical particle in a 1-dimensional box of length 'a' is given by

$\psi = A \sin \frac{\pi x}{a}$

The value of 'A' for a box of length 200 nm is

(a) $4\times10^4\,(\text{nm})^2$ (b) $10\sqrt{2}\,(\text{nm})^{1/2}$ (c) $\sqrt{2}/10\,(\text{nm})^{-1/2}$ (d) $0.1\,(\text{nm})^{-1/2}$

45. For 1 mole of a monoatomic ideal gas, the relation between pressure (p), volume (V) and average molecular kinetic energy $(\bar{\varepsilon})$ is

(a) $p = \frac{N_A \bar{\varepsilon}}{V}$ (b) $p = \frac{N_A \bar{\varepsilon}}{3V}$ (c) $p = \frac{2N_A \bar{\varepsilon}}{3V}$ (d) $p = \frac{2N_A}{3V\bar{\varepsilon}}$

46. For a 1 molal aqueous NaCl solution, the mean ionic activity coefficient $(\gamma_\pm)$ and the Deby-Huckel Limiting Law constant (A) are related as

(a) $\log \gamma_\pm = \sqrt{2}\,A$ (b) $\log \gamma_\pm = -\sqrt{2}\,A$ (c) $\gamma_\pm = 10^{A}$ (d) $\gamma_\pm = 10^{-A}$

47. For the concentration cell
M | M^+(aq, 0.01 mol dm^{-3}) || M^+(aq, 0.1 mol dm^{-3}) | M
the EMF (E) of the cell at a temperature (T) equals

(a) $2.303\frac{RT}{F}$ (b) $-2.303\frac{RT}{F}$

(c) $E^0_{M^+/M} + 2.303\frac{RT}{F}$ (d) $E^0_{M^+/M} - 2.303\frac{RT}{F}$

Commond Data Questions:
Commond data for Q.48 and Q.49:
A hypothetical molecule XY has the following properties
Reduced mass: 2×10^{-26} kg
X–Y bond length: 100 pm
Force constant of the bond: 8×10^2 $N.m^{-1}$

48. The frequency of radiation (in cm^{-1} units) required to vibrationally excite the molecule from v = 0 to v = 1 state is

(a) 3184.8 (b) 2123.2 (c) 061.6 (d) 840.0

49. The frequency of radiation (in cm^{-1} units) required to rotationally excite the molecule from J = 0 to J = 1 state is

(a) 1.4 (b) 2.8 (c) 3.2 (d) 3.6

Common data for Q.50 and Q.51:
Na_2HPO_4 and NaH_2PO_4 on heating at high temperature produce a chain sodium pentaphosphate quantitatively.

50. The ideal molar ratio of Na_2HPO_4 to NaH_2PO_4 is:

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

51. The total charge on pentaphosphate anion is:

(a) –5 (b) –3 (c) –7 (d) –9

Linked Answer Q.52 and Q.53:

The decomposition of ozone to oxygen $2O_3(g) \rightarrow 3O_2(g)$ occurs by mechanism

(i) $M(g) + O_3(g) \xrightarrow{k_1} O_2(g) + O(g) + M(g)$, $\quad E_{a,1}$

(ii) $O_2(g) + O(g) + M(g) \xrightarrow{k_2} M(g) + O_3(g)$, $\quad E_{a,2}$

(iii) $O(g) + O_3(g) \xrightarrow{k_3} 2O_2(g)$, $\quad E_{a,3}$

where, M is the catalyst molecule.

k_i ' are rate constants and $k_{a,i}$'s the activation energies for the elementary steps,

52. Under the steady state approximation for the intermediates, the rate of decomposition of ozone, $-\frac{d[O_3]}{dt}$, is

(a) $\frac{2k_1k_3[O_3]^2[M]}{k_2[O_2][M]+k_3[O_3]}$ (b) $\frac{2k_1k_3[O_3]^2[M]}{k_2[O_2][M]-k_3[O_3]}$

(c) $\frac{2k_2k_3[O_3][M]}{k_2[O_2][M]+k_3[O_3]}$ (d) $\frac{2k_1k_2[O_3]^2[M]}{k_2[O_2][M]-k_3[O_3]}$

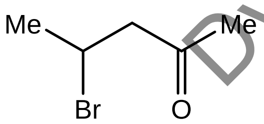
53. Assuming $k_3[O_3] >> k_2[O_2][M]$, the activation of the overall reaction is

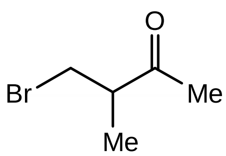
(a) $\frac{E_{a,1}E_{a,3}}{E_{a,2}}$ (b) $E_{a,3}+E_{a,1}-E_{a,2}$ (c) $E_{a,2}$ (d) $E_{a,1}$

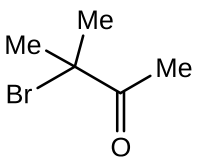
Statement for Linked Answer Q.54 and Q.55:

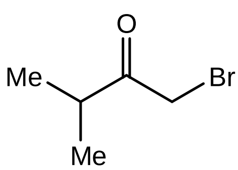
A ketone on treatment with bromine in methanol gives the corresponding monobromo compound[X] having molecular formula C_5H_9BrO. The compound [X] when treated with NaOMe in MeOH produces [Y] as the major product. The spectral data for compound [X] are: ^{1}H NMR: δ 1.17(d, 6H), 3.02 (m, 1H), 4.10(s, 2H); ^{13}C NMR: δ 17, 37, 39, 210.

54. The compound [X] is:

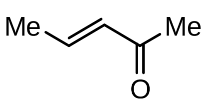
(a) 

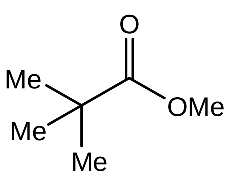
(b) 

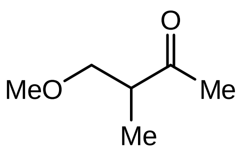
(c) 

(d) 

55. The major product [Y] is:

(a) 

(b) 

(c) 

(d)