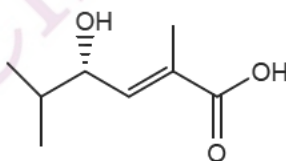


## CHEMISTRY-CY

## Q.1 – Q.20 : Carry ONE mark each.

- The  $^{31}\text{P}$  NMR spectrum of  $\text{P}_4\text{S}_3$  consists of
  - a singlet
  - a doublet and a triplet
  - a doublet and a quartet
  - two doublets.
- The geometry around the central atom in  $\text{ClF}_4^+$  is
  - square planar
  - square pyramidal
  - octahedral
  - trigonal bipyramidal
- The correct statement about the Cu-N bond distances in  $[\text{Cu}(\text{NH}_3)_6]^{2+}$  is :
  - all the bond distances are equal
  - the axial bonds are longer than the equatorial ones.
  - the equatorial bonds are longer than the axial ones.
  - all the bond distances are unequal.
- The reaction of phosgene with an excess of  $\text{NH}_3$  produces
  - $\text{HN}=\text{C}=\text{O}$
  - $\text{H}_2\text{N}-\text{C}(\text{Cl})=\text{O}$
  - $(\text{H}_2\text{N})_2\text{C}=\text{O}$
  - $(\text{H}_2\text{N})_2\text{CCl}_2$
- The number of metal-metal bonds in  $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})]_2$  is
  - zero
  - one
  - two
  - three
- The coordination number of the  $\text{Ba}^{2+}$  ions in barium fluoride is 8. The coordination number of the fluoride ion is:
  - 8
  - 4
  - 1
  - 2.
- In the transformation of oxyhaemoglobin to deoxyhaemoglobin
  - $\text{Fe}^{2+}$  in the low spin state changes to  $\text{Fe}^{2+}$  in the high spin state
  - $\text{Fe}^{2+}$  in the low spin state changes to  $\text{Fe}^{3+}$  in the low spin state.
  - $\text{Fe}^{2+}$  in the high spin state changes to  $\text{Fe}^{2+}$  in the low spin state
  - $\text{Fe}^{2+}$  in the high spin state changes to  $\text{Fe}^{3+}$  in the high spin state.

8. For the compound



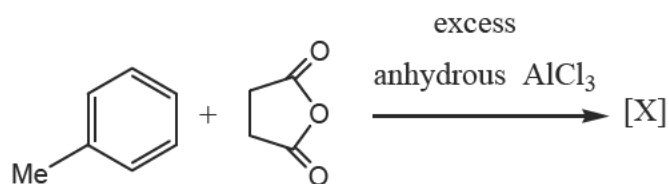
the stereochemical notations are

- 2Z, 4R
- 2Z, 4S
- 2E, 4R
- 2E, 4S

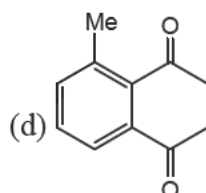
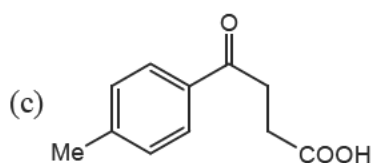
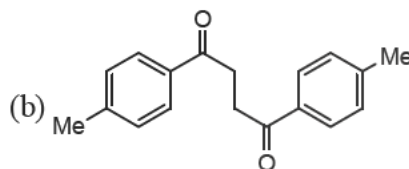
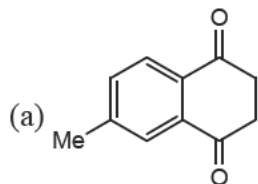
9. The compound  is

- aromatic and has high dipole moment
- aromatic and has no dipole moment
- non-aromatic and has high dipole moment
- anti-aromatic and has no dipole moment.

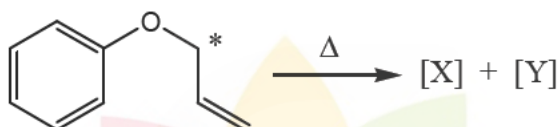
10. In the reaction,



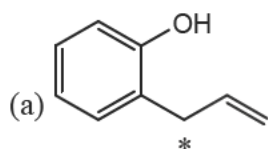
the major product X is:



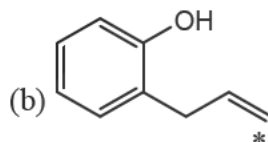
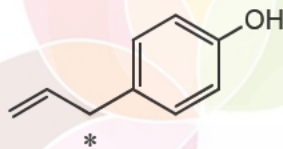
11. In the reaction



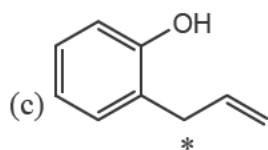
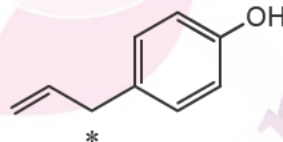
the major products X and Y are



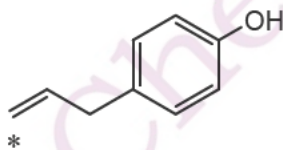
and



and



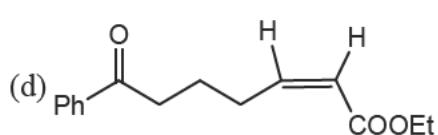
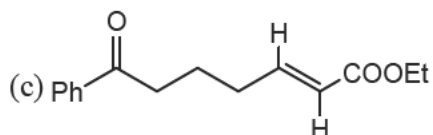
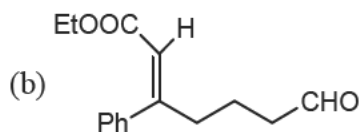
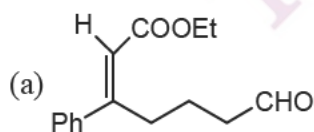
and



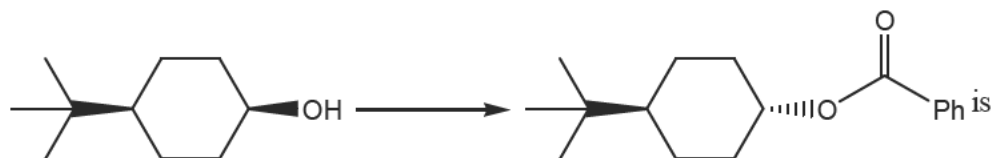
(d) None of these

12.

In the reaction,  $\text{Ph-CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CHO} \xrightarrow{\text{Ph}_3\text{P=CHCOOEt}} [\text{X}]$   
 the major product X is:

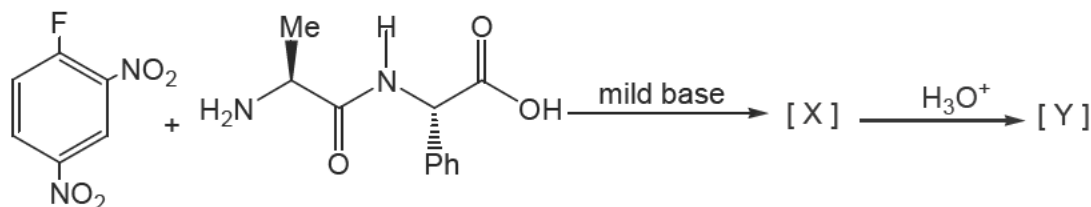


13. The most suitable reagent combination to bring out the following transformation

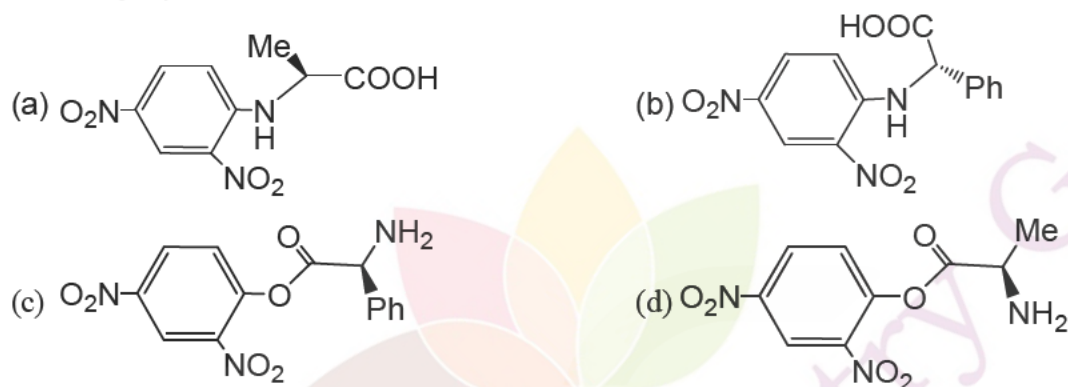


- (a)  $\text{PhCOCl}$  and pyridine  
 (b) DCC and  $\text{PhCOOH}$   
 (c)  $\text{PhBr}$ ,  $\text{CO}$  and  $\text{Pd}(\text{PPh}_3)_4$   
 (d)  $\text{EtOOC-N=N-COOEt}$ ,  $\text{PPh}_3$  and  $\text{PhCOOH}$

14. In the two steps reaction sequence :

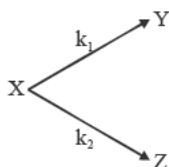


the major product Y is :



15. Among the following the system that would require the least amount of thermal energy to bring its temperature to  $80^\circ\text{C}$  is:  
 (a) 200 gm of water at  $40^\circ\text{C}$   
 (b) 100 gm of water at  $20^\circ\text{C}$   
 (c) 150 gm of water at  $50^\circ\text{C}$   
 (d) 300 gm of water at  $30^\circ\text{C}$ .
16. Among the following, the reaction that is accompanied by a decrease in the entropy is  
 (a)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$   
 (b)  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$   
 (c)  $\text{PCl}_5(\text{s}) \rightarrow \text{PCl}_3(\text{l}) + \text{Cl}_2(\text{g})$   
 (d)  $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$
17. The number of degrees of freedom of a system consisting of solid sucrose in equilibrium with an aqueous solution of sucrose is  
 (a) 0  
 (b) 1  
 (c) 2  
 (d) 3
18. The lowest allowed energy is equal to zero for  
 (a) the hydrogen atom  
 (b) a rigid rotor  
 (c) a harmonic oscillator  
 (d) a particle in a 3-dimensional box
19. According to the Debye-Hückel limiting law, if the concentration of a dilute aqueous solution of  $\text{KCl}$  is increased 4-fold, the value of  $\ln \gamma_{\pm}$  ( $\gamma_{\pm}$  is the molal mean ionic activity coefficient) will  
 (a) decrease by a factor of 2  
 (b) increase by a factor of 2  
 (c) decrease by a factor of 4  
 (d) increase by a factor of 4.

20. For the parallel first order reaction shown below



the value of  $k_1$  is  $1 \times 10^{-4} \text{ s}^{-1}$ . If the reaction starts from X, the ratio of the concentrations of Y and Z at any given

time during the course of the reaction is found to be  $\frac{[Y]}{[Z]} = \frac{1}{4}$

The value of  $k_2$  is:

- (a)  $1 \times 10^{-4} \text{ s}^{-1}$       (b)  $2.5 \times 10^{-5} \text{ s}^{-1}$       (c)  $4 \times 10^{-4} \text{ s}^{-1}$       (d)  $4 \times 10^4 \text{ s}^{-1}$

**Q.21 – Q.60 : Carry TWO marks each.**

21. The correct order of  $\nu_{\text{CO}}$  for the compounds  $[\text{Mo}(\text{CO})_3(\text{NMe}_3)_3]$ ,  $[\text{Mo}(\text{CO})_3(\text{P}(\text{OPh})_3)_3]$ ,  $[\text{Mo}(\text{CO})_3(\text{PMe}_3)_3]$ ,  $[\text{Mo}(\text{CO})_3(\text{PCl}_3)_3]$  in the IR spectrum is:

- (a)  $[\text{Mo}(\text{CO})_3(\text{NMe}_3)_3] > [\text{Mo}(\text{CO})_3(\text{P}(\text{OPh})_3)_3] > [\text{Mo}(\text{CO})_3(\text{PMe}_3)_3] > [\text{Mo}(\text{CO})_3(\text{PCl}_3)_3]$   
 (b)  $[\text{Mo}(\text{CO})_3(\text{PCl}_3)_3] > [\text{Mo}(\text{CO})_3(\text{NMe}_3)_3] > [\text{Mo}(\text{CO})_3(\text{P}(\text{OPh})_3)_3] > [\text{Mo}(\text{CO})_3(\text{PMe}_3)_3]$   
 (c)  $[\text{Mo}(\text{CO})_3(\text{PCl}_3)_3] > [\text{Mo}(\text{CO})_3(\text{P}(\text{OPh})_3)_3] > [\text{Mo}(\text{CO})_3(\text{PMe}_3)_3] > [\text{Mo}(\text{CO})_3(\text{NMe}_3)_3]$   
 (d)  $[\text{Mo}(\text{CO})_3(\text{PMe}_3)_3] > [\text{Mo}(\text{CO})_3(\text{NMe}_3)_3] > [\text{Mo}(\text{CO})_3(\text{PCl}_3)_3] > [\text{Mo}(\text{CO})_3(\text{P}(\text{OPh})_3)_3]$

22. 2.5 g of an iron compound upon suitable treatment yielded 0.391 g of iron (III) oxide. The percentage of iron in the compound is

- (a) 10.94      (b) 12.15      (c) 11.31      (d) 9.11

23. In the reaction,  $\text{Ph}_3\text{P} \xrightarrow{\text{MeI}} [\text{X}] \xrightarrow{\text{n-BuLi}} [\text{Y}]$ , the compounds X and Y, respectively are

- (a)  $[\text{Ph}_3\text{P}(\text{Me})\text{I}]$ ;  $\text{Ph}_3\text{P} = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$   
 (b)  $[\text{Ph}_3\text{P}(\text{Me})][\text{I}]$ ;  $\text{Ph}_3\text{P} = \text{CH}_2$   
 (c)  $[\text{Ph}_3\text{P}(\text{Me})_2]$ ;  $\text{Ph}_3\text{P} = \text{CH}_2$   
 (d)  $[\text{Ph}_3\text{P}(\text{Me})][\text{I}]$ ;  $\text{Ph}_3\text{P}$

24. The  $^1\text{H}$  NMR spectrum of HD consists of a

- (a) singlet      (b) 1:1 doublet      (c) 1:1:1 triplet      (d) 1:2:1 triplet.

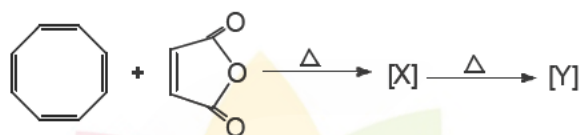
25. The X-ray powder pattern of NaCl shows an intense cone at  $\theta = 15.87^\circ$  using X-rays of wavelength  $1.54 \times 10^{-8}$  cm. The spacing between the planes (in Å) of NaCl crystal is

- (a) 1.41      (b) 2.82      (c) 4.23      (d) 5.63

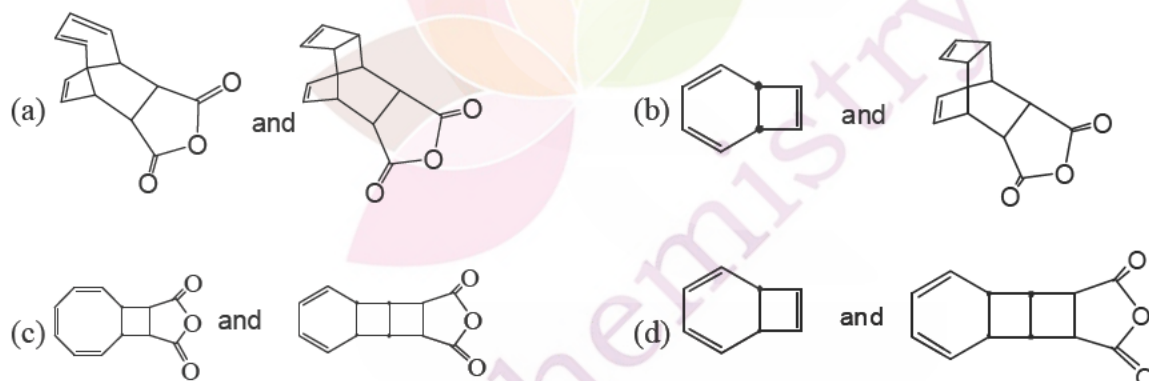
26. Among the following, the isoelectronic and isostructural pair is

- (a)  $\text{CO}_2$  and  $\text{SO}_2$       (b)  $\text{SO}_3$  and  $\text{SeO}_3$       (c)  $\text{NO}_2^+$  and  $\text{TeO}_2$       (d)  $\text{SiO}_4^{4-}$  and  $\text{PO}_4^{3-}$

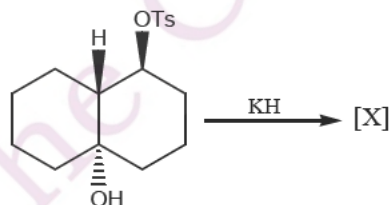
27. Two samples have been given to you :  $[\text{NiCl}_2(\text{PPh}_3)_2]$  and  $[\text{PdCl}_2(\text{PPh}_3)_2]$ . A physical method that can be used to identify these compounds unambiguously is  
 (a) HPLC (b) magnetic susceptibility  
 (c)  $^{13}\text{C}$  NMR spectroscopy (d) Mössbauer spectroscopy
28. In the reaction  $\text{HSO}_4^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{SO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\ell)$ , the conjugate acid-base pairs are  
 (a)  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$ ;  $\text{H}_2\text{O}$  and  $\text{OH}^-$  (b)  $\text{HSO}_4^-$  and  $\text{H}_3\text{O}^+$ ;  $\text{SO}_4^{2-}$  and  $\text{OH}^-$   
 (c)  $\text{HSO}_4^-$  and  $\text{OH}^-$ ;  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{O}$  (d)  $\text{HSO}_4^-$  and  $\text{OH}^-$ ;  $\text{SO}_4^{2-}$  and  $\text{H}_3\text{O}^+$
29. Designate the following complexes X, Y and Z as inert or labile:  
 $\text{X} = [\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$ ,  $\text{Y} = [\text{V}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{Z} = [\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$   
 (a) X and Y are inert; Z is labile (b) X and Z are labile; Y is inert.  
 (c) X is inert; Y and Z are labile (d) X is labile; Y and Z are inert.
30. In the reaction sequence :



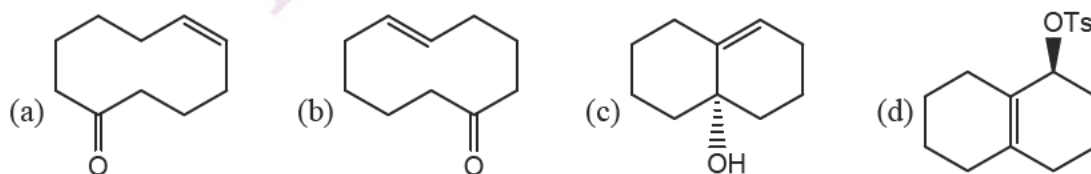
X and Y, respectively, are



31. The major product X (based on the preferred conformation) in the reaction

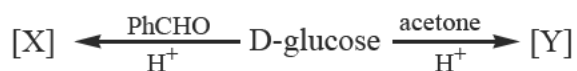


is

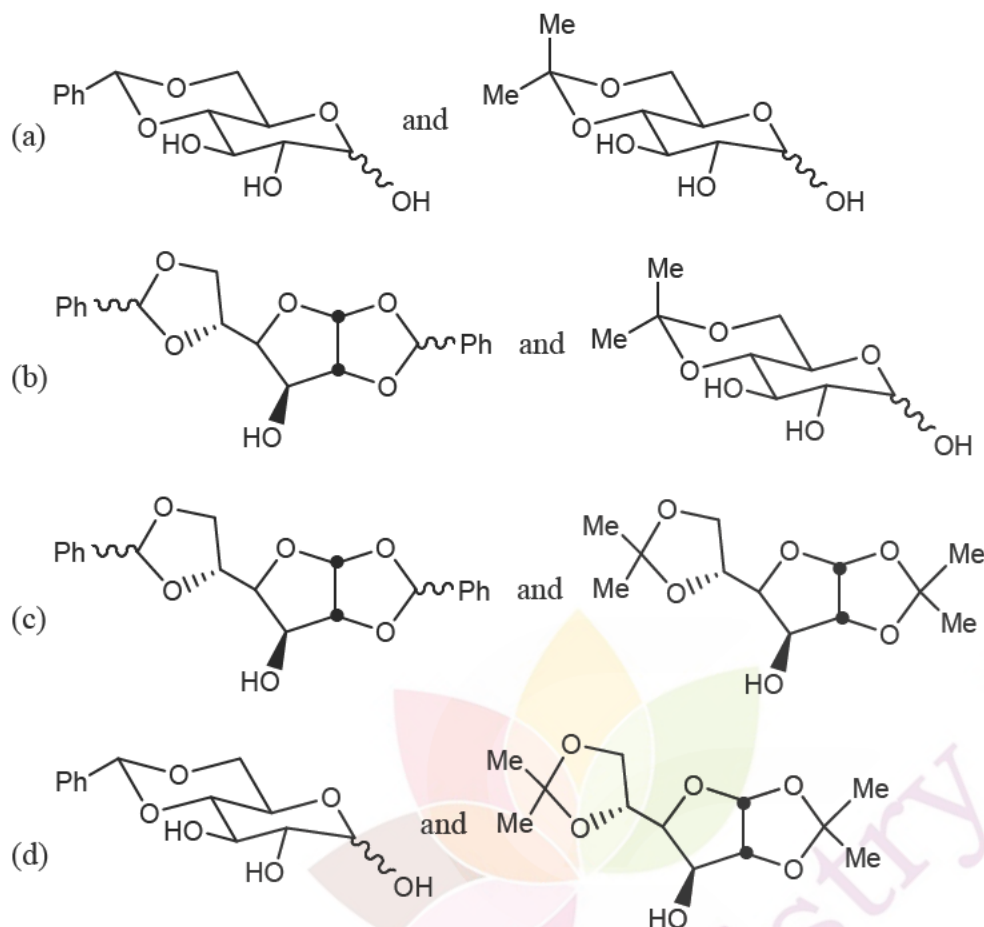




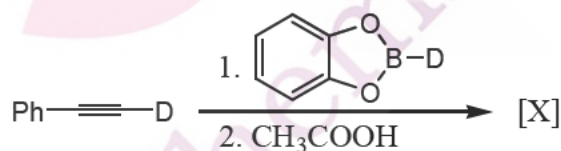
32. In the reactions,



The major products X and Y, respectively are



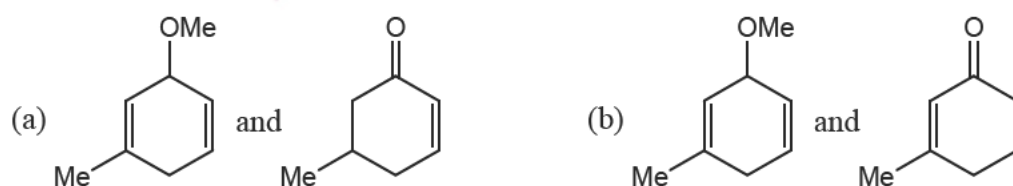
33. In the reaction

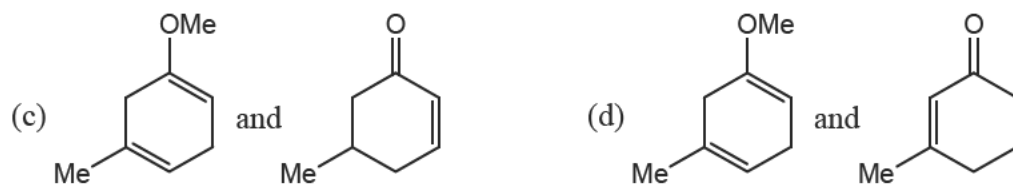


the major product X is



34. Reaction of m-methylanisole with lithium in liquid ammonia and t-butyl alcohol at  $-33^\circ\text{C}$  generates compound X as the major product. Treatment of the compound X with dilute sulphuric acid produces compound Y as the major product. The compounds X and Y, respectively, are



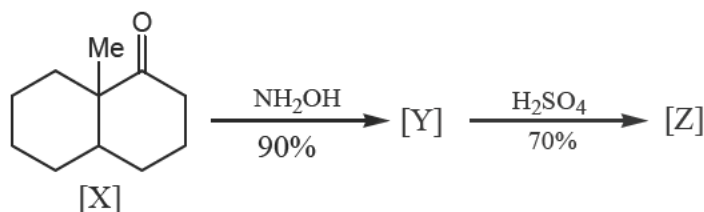


35. The number of signals that appear in the broad-band decoupled  $^{13}\text{C}$  NMR spectrum of ortho-, meta- and para-dichlorobenzenes, respectively, are

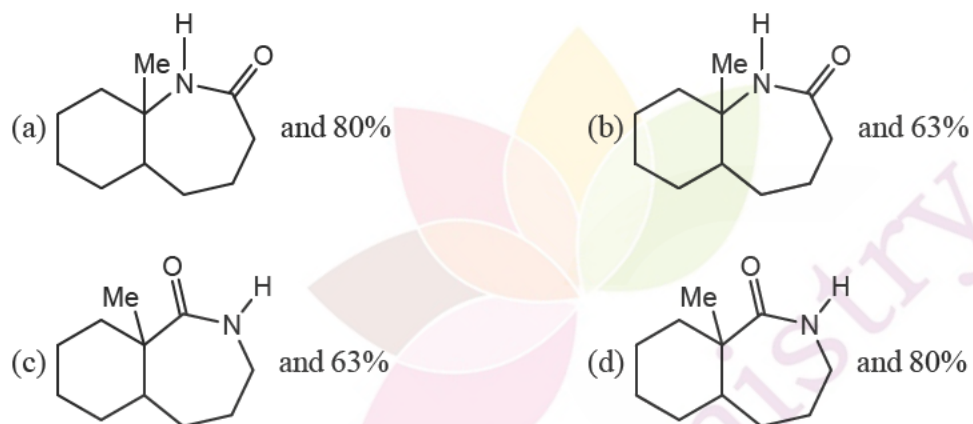
- (a) 3, 4 and 2      (b) 3, 3 and 2      (c) 4, 4 and 2      (d) 3, 4 and 4

36. In the reaction sequence,

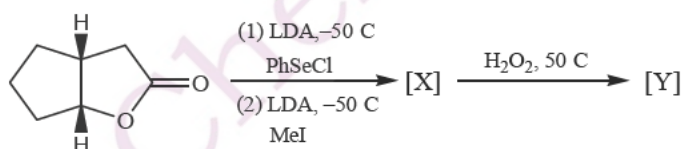
[GATE 2009]



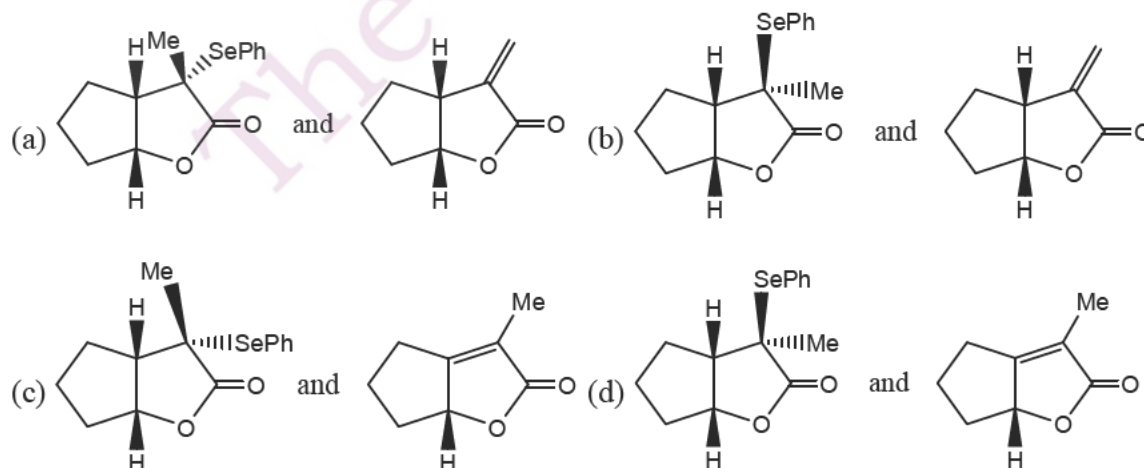
the structure of the major product Z and the overall yield for its formation from the ketone X, are



37. In the reaction sequence

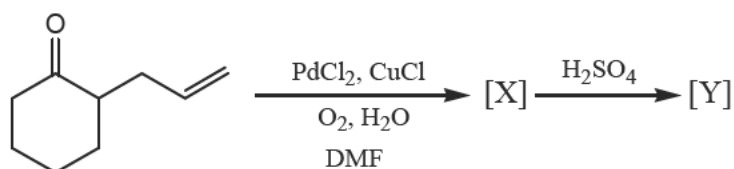


the major product respectively, are:



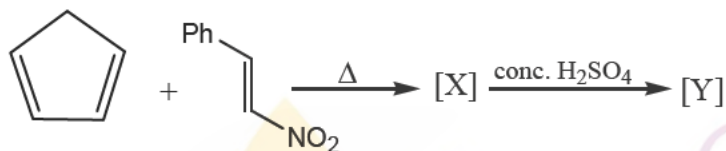
38. In the reaction sequence the major products X and Y, respectively are

[GATE 2009]



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

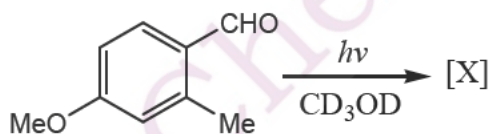
39. In the reaction sequence



The major products X and Y, respectively are

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

40. In the photochemical reaction



formation of the compound X can be inferred by the disappearance of the  $^1\text{H}$  NMR signal at  $^1\text{H}$  NMR spectrum of the starting material:

$\delta$  9.7 (1H, s), 7.8 (1H, d,  $J = 8.0$  Hz), 7.1–6.8 (2H, m), 3.9 (3H, s), 2.5 (3H, s) ppm ]

- (a)  $\delta$  9.7 ppm (b)  $\delta$  7.8 ppm (c)  $\delta$  3.9 ppm (d)  $\delta$  2.5 ppm

41. The half-life ( $t_{1/2}$ ) for the hydrolysis of an ester varies with the initial concentration of the reactant ( $[E]_0$ ) as follows:

$[E]_0 / 10^{-2} \text{ mol L}^{-1}$     5.0    4.0    3.0

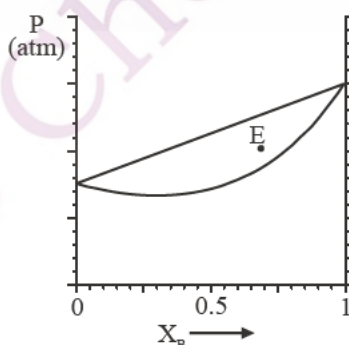
$t_{1/2} / \text{s}$                     240    300    400

The order of the reaction is:

- (a) 0 (b) 1 (c) 2 (d) 3



42. The fluorescence lifetime of a molecule in solution is 10 ns. If the fluorescence quantum yield is 0.1, the rate constant of fluorescence decay is:  
 (a)  $1 \times 10^9 \text{ s}^{-1}$  (b)  $1 \times 10^8 \text{ s}^{-1}$  (c)  $1 \times 10^7 \text{ s}^{-1}$  (d)  $9 \times 10^7 \text{ s}^{-1}$
43. The fundamental vibrational wavenumbers for  $\text{H}_2$  and  $\text{I}_2$  are  $4403.2 \text{ cm}^{-1}$  and  $214.5 \text{ cm}^{-1}$ , respectively. The relative population of the first excited vibrational states of these two molecules compared to their respective ground states at 300 K are respectively:  
 (a)  $6.75 \times 10^{-1}$  and  $3.57 \times 10^{-1}$  (b)  $6.75 \times 10^{-10}$  and  $3.57 \times 10^{-1}$   
 (c)  $3.57 \times 10^{-6}$  and  $6.75 \times 10^{-1}$  (d)  $3.57 \times 10^{-1}$  and  $6.75 \times 10^{-1}$
44. The degeneracy of a quantum particle in a cubic box having energy four times that of the lowest energy is  
 (a) 3 (b) 6 (c) 1 (d) 4
45. The rotational Raman spectrum of  $^{19}\text{F}_2$  shows a series of Stokes lines at  $19230.769 \text{ cm}^{-1}$ ,  $19227.238 \text{ cm}^{-1}$  and  $19223.707 \text{ cm}^{-1}$ . The rotational constant for  $^{19}\text{F}_2$  in GHz is:  
 (a) 26.484 (b) 52.968 (c) 105.936 (d) 3.531
46. The de-Broglie wavelength for a He atom travelling at  $1000 \text{ ms}^{-1}$  (typical speed at room temperature) is  
 (a)  $99.7 \times 10^{-12} \text{ m}$  (b)  $199.4 \times 10^{-12} \text{ m}$  (c)  $199.4 \times 10^{-18} \text{ m}$  (d)  $99 \times 10^{-6} \text{ m}$
47. Given that the standard molar enthalpies of formation of  $\text{NO}(\text{g})$  and  $\text{NO}_2(\text{g})$  are, respectively,  $90.3 \text{ kJ mol}^{-1}$  and  $33.2 \text{ kJ mol}^{-1}$ , the enthalpy change for the reaction  $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$  is  
 (a) 16.6 kJ (b) -57.1 kJ (c) -114.2 kJ (d) 57.1 kJ
48. Among the following, the equilibrium which is NOT affected by an increase in pressure is  
 (a)  $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$  (b)  $\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightleftharpoons 2\text{HI}(\text{g})$   
 (c)  $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$  (d)  $3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g})$
49. The free energy change ( $\Delta G$ ) of 1 mole of an ideal gas that is compressed isothermally from 1 atm to 2 atm is:  
 (a)  $RT \ln 2$  (b)  $-2RT$  (c)  $-RT \ln 2$  (d)  $2RT$
50. Two liquids B and C form an ideal solution. In the figure below, the vapour pressure P of this solution is shown as a function of the mole fraction,  $X_B$ , of component B.



Given a state of this vapour-liquid mixture whose overall composition corresponds to point E in the figure, the mole fraction of B in the vapour phase is approximately

- (a) 0.25 (b) 0.53 (c) 0.65 (d) 0.80

**Common data for Q. 51 and Q. 52:**

Treatment of  $W(CO)_6$  with 1 equivalent of  $Na(C_5H_5)$  in THF solution gives the ionic compound M. Reaction of M with glacial acetic acid results in product N. The  $^1H$  NMR spectrum of N displays two singlets of relative intensity 5:1. When N is heated, hydrogen gas is evolved and O is produced; O may also be prepared by refluxing  $W(CO)_6$  with cyclopentadiene and  $H_2$  is also produced. Treatment of O with an equivalent of  $Br_2$  produces P. (Use the 18 electron rule as your guide).

51. The compounds M and N, respectively, are

- (a)  $[(C_5H_5)W(CO)_3]Na$  and  $[(C_5H_5)W(CO)_3H]$   
 (b)  $[(C_5H_5)W(CO)_4]Na$  and  $[(C_5H_5)W(CO)_4H]$   
 (c)  $[(C_5H_5)W(CO)_3]Na$  and  $[(C_5H_5)W(CO)_4H]$   
 (d)  $[(C_5H_5)W(CO)_4]Na$  and  $[(C_5H_5)W(CO)_3H]$

52. The compounds O and P, respectively, are

- (a)  $[(C_5H_5)W(CO)_3]_2$  and  $[(C_5H_5)W(CO)_3Br]$   
 (b)  $[(C_5H_5)W(CO)_4]$  and  $[(C_5H_5)W(CO)_2Br(THF)]$   
 (c)  $[(C_5H_5)W(CO)_2(THF)_2]$  and  $[(C_5H_5)W(CO)_3Br]$   
 (d)  $[(C_5H_5)W(CO)_3]_2$  and  $[(C_5H_5)W(CO)_2Br(THF)]$

**Common data for Q. 53 and Q. 54:**

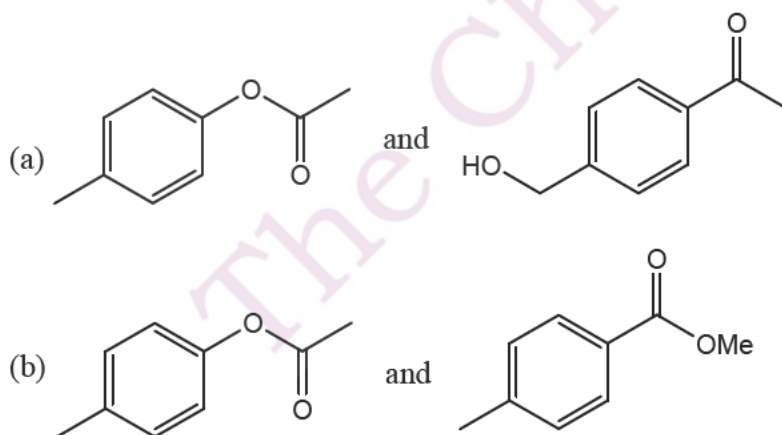
An organic compound X ( $C_9H_{10}O$ ) exhibited the following spectral data.

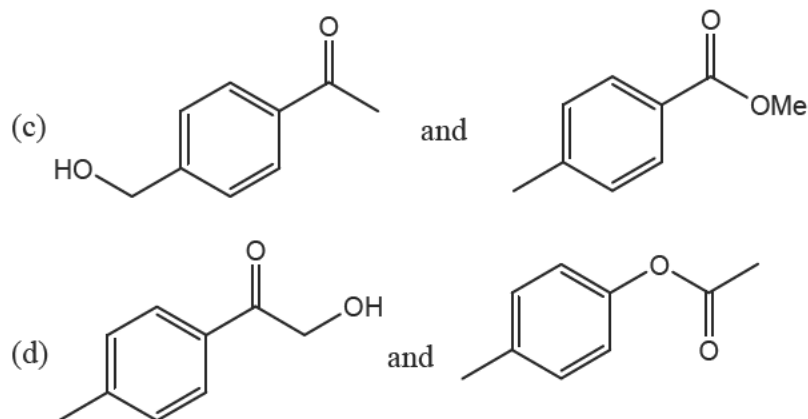
IR :  $1680\text{ cm}^{-1}$ .

$^1H$  NMR :  $\delta 7.8$  (2H, d, J 7.5 Hz),  $7.2$  (2H, d, J = 7.5 Hz),  $2.7$  (3H, s) and  $2.4$  (3H, s)

Compound X on treatment with m-chloroperbenzoic acid produced two isomeric compounds Y (major) and Z (minor).

53. Compounds Y and Z, respectively, are





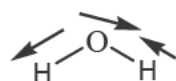
54. Compounds Y and Z can be differentiated by carrying out basic hydrolysis, because [GATE 2009]  
 (a) Y produces 4-methylphenol and Z is unaffected.  
 (b) Y produces 4-methylphenol and Z produces 4-methylbenzoic acid.  
 (c) Y is unaffected and Z produces 4-methylbenzoic acid.  
 (d) Y is unaffected and Z produces 4-methylphenol.

**Common data for Q. 55 and Q. 56.**

Character table for the point group  $C_{2v}$  is given below:

$C_{2v}$	E	$C_2$	$\sigma_y(xz)$	$\sigma_y(yz)$		
$A_1$	1	1	1	1	z	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	xy
$B_1$	1	-1	1	-1	x, $R_y$	xz
$B_2$	1	-1	-1	1	y, $R_x$	yz

55. The reducible representation corresponding to the three translational degrees of freedom,  $\Gamma_u$ , is:  
 (a) 3, 1, 1, 1      (b) 3, -1, 1, 1      (c) 3, -1, -1, -1      (d) 3, 1, -1, -1.
56. The asymmetric stretching mode of the  $H_2O$  is shown below. The molecular plane is yz and the symmetry axis of  $H_2O$  is z.



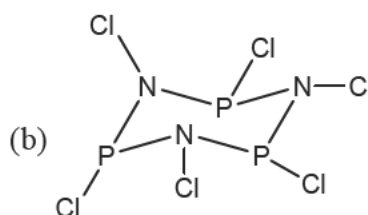
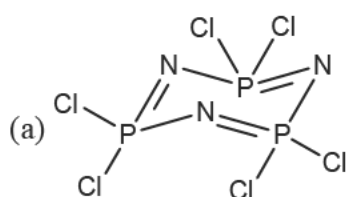
This vibration transforms as the irreducible representation

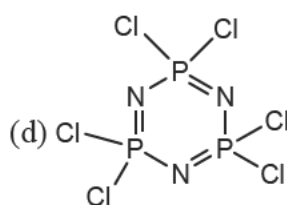
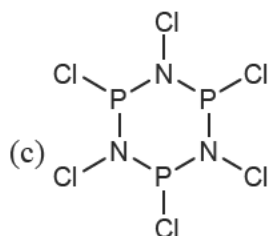
- (a)  $A_1$       (b)  $B_1$       (c)  $A_2$       (d)  $B_2$

**Linked Answer type Q.57 and Q.58.**

Triphosphazene is prepared by reacting X and Y in equimolar ratio at 120–150°C using appropriate solvents [GATE 2009]

57. The reaction X and Y, respectively, are  
 (a)  $PCl_3; NH_3$       (b)  $PCl_5; NH_3$       (c)  $PCl_5; NH_4Cl$       (d)  $PCl_3; NH_4Cl$
58. The structure of triphosphazene is





**Statement for Linked Q.59 and Q.60:**

In the reaction mechanism given,  $X + Y \xrightleftharpoons[k_2, E_{A,2}]{k_1, E_{A,1}} Z \xrightarrow{k_3, E_{A,3}} P$

'k's represent rate constants, 'E<sub>A</sub>'s represent activation energies, and  $k_2 \gg k_3$

59. The overall rate constant ( $k_{\text{overall}}$ ) for the formation of P can be expressed as

- (a)  $k_1 k_3 / k_2$       (b)  $k_1$       (c)  $k_1 / (k_2 + k_3)$       (d)  $k_1 / (k_2 - k_3)$

60. The overall activation energy ( $E_{A, \text{overall}}$ ) for the formation of P can be expressed as

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

\*\*\*\*\* END OF THE QUESTION PAPER \*\*\*\*\*