Section-A

Q.1 – Q.20 : Carry ONE mark each.

1. The ^{31}P NMR spectrum of P_4S_3 consists of
(a) a singlet
(b) a doublet and a triplet
(c) a doublet and a quartet
(d) two doublets.

2. The geometry around the central atom in ClF_4^+ is
(a) square planar
(b) square pyramidal
(c) octahedral
(d) trigonal bipyramidal

3. The correct statement about the Cu-N bond distances in $\left[Cu\left(NH_3\right)_6\right]^{2+}$ is :
(a) all the bond distances are equal
(b) the axial bonds are longer than the equatorial ones.
(c) the equatorial bonds are longer than the axial ones.
(d) all the bond distances are unequal.

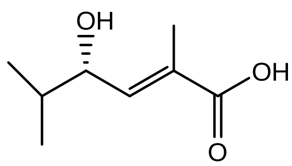
4. The reaction of phosgene with an excess of NH_3 produces
(a) $HN=C=O$
(b) $H_2N-C(Cl)=O$
(c) $(H_2N)_2C=O$
(d) $(H_2N)_2CCl_2$

5. The number of metal – metal bonds in $[(C_5H_5)Fe(CO)]_2$ is
(a) zero
(b) one
(c) two
(d) three

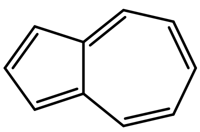
6. The coordination number of the Ba^{2+} ions in barium fluoride is 8. The coordination number of the fluoride ion is:
(a) 8
(b) 4
(c) 1
(d) 2.

7. In the transformation of oxyhaemoglobin to deoxyhaemoglobin
(a) Fe^{2+} in the low spin state changes to Fe^{2+} in the high spin state
(b) Fe^{2+} in the low spin state changes to Fe^{3+} in the low spin state.
(c) Fe^{2+} in the high spin state changes to Fe^{2+} in the low spin state
(d) Fe^{2+} in the high spin state changes to Fe^{3+} in the high spin state.

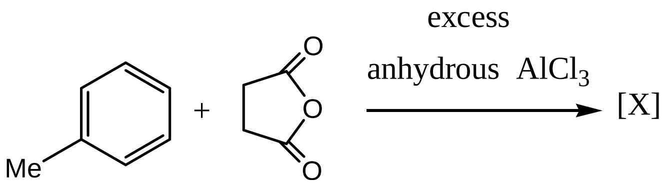
8. For the compound



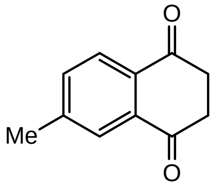
the stereochemical notations are
(a) 2Z, 4R
(b) 2Z, 4S
(c) 2E, 4R
(d) 2E, 4S

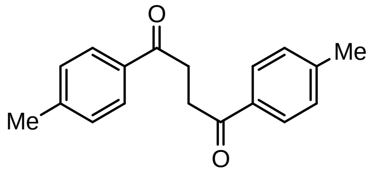
9. The compound  is
(a) aromatic and has high dipole moment
(b) aromatic and has no dipole moment
(c) non-aromatic and has high dipole moment
(d) anti-aromatic and has no dipole moment.

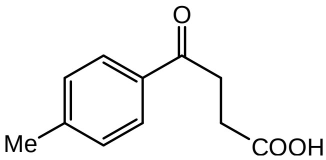
10. In the reaction,

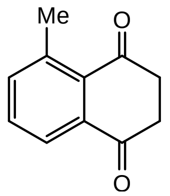


the major product X is:

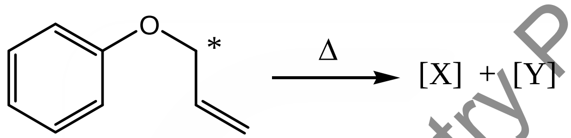
(a) 

(b) 

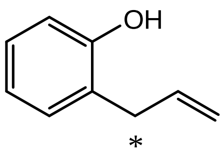
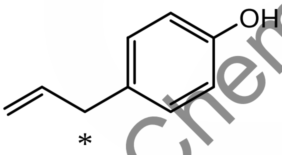
(c) 

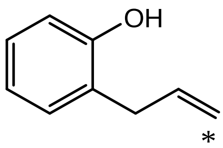
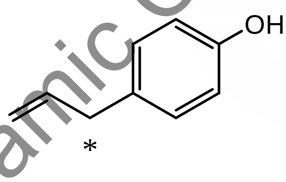
(d) 

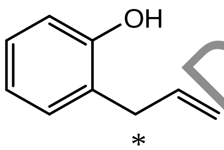
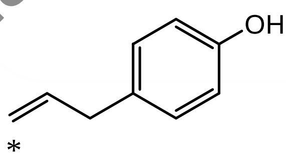
11. In the reaction



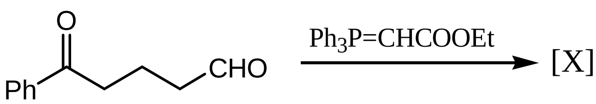
the major products X and Y are

(a)  and 

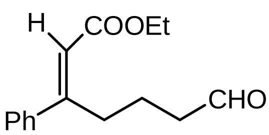
(b)  and 

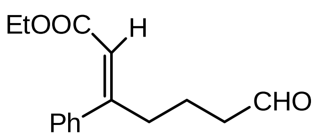
(c)  and 

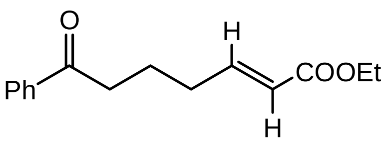
(d) None of these

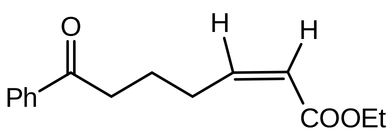
12. In the reaction, 

the major product X is:

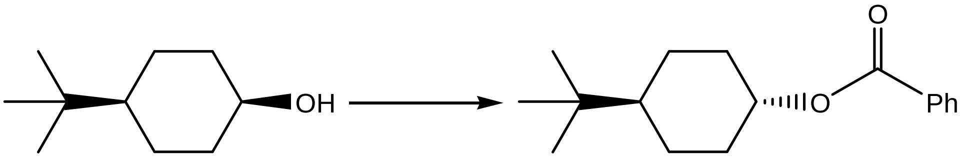
(a) 

(b) 

(c) 

(d) 

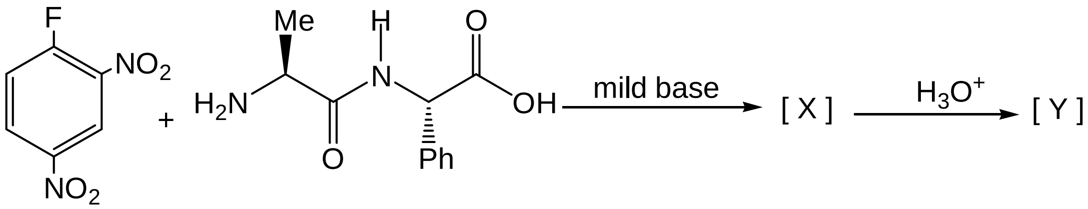
13. The most suitable reagent combination to bring out the following transformation



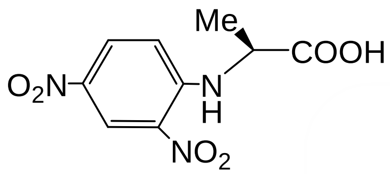
is

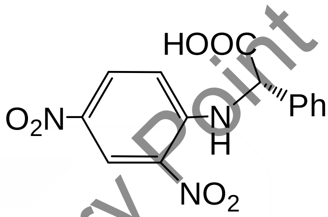
(a) PhCOCl and pyridine
(b) DCC and PhCOOH
(c) PhBr, CO and $Pd(PPh_3)_4$
(d) EtOOC–N=N–COOEt, PPh_3 and PhCOOH

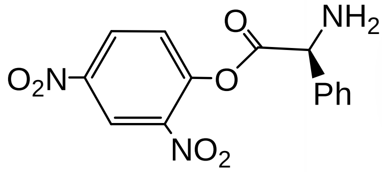
14. In the two steps reaction sequence :

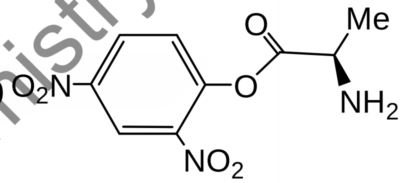


the major product Y is :

(a) 

(b) 

(c) 

(d) 

15. Among the following the system that would require the least amount of thermal energy to bring its temperature to 80ºC is:
(a) 200 gm of water at 40ºC
(b) 100 gm of water at 20ºC
(c) 150 gm of water at 50ºC
(d) 300 gm of water at 30ºC.

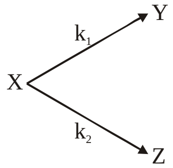
16. Among the following, the reaction that is accompanied by a decrease in the entropy is
(a) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
(b) $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$
(c) $PCl_5(s) \rightarrow PCl_3(l) + Cl_2(g)$
(d) $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

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 KCl is increased 4-fold, the value of $\ln \gamma_{\pm}$ $\left(\gamma_{\pm}\right.$ is the molal mean ionic activity coefficient$\left.\right)$ 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 $1\times10^{-4}\,s^{-1}$. 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) $1\times10^{-4}\,s^{-1}$ (b) $2.5\times10^{-5}\,s^{-1}$ (c) $4\times10^{-4}\,s^{-1}$ (d) $4\times10^{4}\,s^{-1}$

Q.21 – Q.60 : Carry TWO marks each.

21. The correct order of ν_{CO} for the compounds $[Mo(CO)_3(NMe_3)_3]$, $[Mo(CO)_3(P(OPh)_3)_3]$, $[Mo(CO)_3(PMe_3)_3]$, $[Mo(CO)_3(PCl_3)_3]$ in the IR spectrum is:

(a) $[Mo(CO)_3(NMe_3)_3] > [Mo(CO)_3(P(OPh)_3)_3] > [Mo(CO)_3(PMe_3)_3] > [Mo(CO)_3(PCl_3)_3]$

(b) $[Mo(CO)_3(PCl_3)_3] > [Mo(CO)_3(NMe_3)_3] > [Mo(CO)_3(P(OPh)_3)_3] > [Mo(CO)_3(PMe_3)_3]$

(c) $[Mo(CO)_3(PCl_3)_3] > [M0(CO)_3(P(OPh)_3)_3] > [Mo(CO)_3(PMe_3)_3] > [Mo(CO)_3(NMe_3)_3]$

(d) $[Mo(CO)_3(PMe_3)_3] > [Mo(CO)_3(NMe_3)_3] > [Mo(CO)_3(PCl_3)_3] > [Mo(CO)_3(P(OPh)_3)_3]$

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, $Ph_3P \xrightarrow{MeI} [X] \xrightarrow{n\text{-}BuLi} [Y]$, the compounds X and Y, respectively are

(a) $[Ph_3P(Me)I]$; $Ph_3P=CH-CH_2-CH_2-CH_3$

(b) $[Ph_3P(Me)][I]$; $Ph_3P=CH_2$

(c) $[Ph_3P(Me)_2]$; $Ph_3P=CH_2$

(d) $[Ph_3P(Me)][I]$; Ph_3P

24. The ^{1}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 $\theta=15.87°$ using X-rays of wavelength 1.54×10^{-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) CO_2 and SO_2 (b) SO_3 and SeO_3 (c) NO_2^+ and TeO_2 (d) SiO_4^{4-} and PO_4^{3-}

27. Two samples have been given to you : $[NiCl_2(PPh_3)_2]$ and $[PdCl_2(PPh_3)_2]$. A physical method that can be used to identify these compounds unambiguously is

(a) HPLC
(b) magnetic susceptibility
(c) ^{13}C NMR spectroscopy
(d) Mössbauer spectroscopy

28. In the reaction $HSO_4^-(aq) + OH^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2O(\ell)$, the conjugate acid-base pairs are

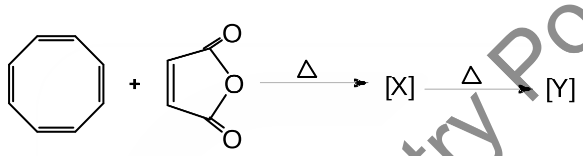
(a) HSO_4^- and SO_4^{2-}; H_2O and OH^-
(b) HSO_4^- and H_3O^+; SO_4^{2-} and OH^-
(c) HSO_4^- and OH^-; SO_4^{2-} and H_2O
(d) HSO_4^- and OH^-; SO_4^{2-} and H_3O^+

29. Designate the following complexes X, Y and Z as inert or labile:

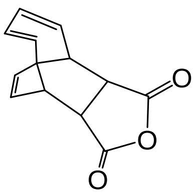
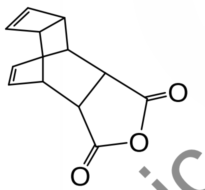
$X = [Al(C_2O_4)_3]^{3-}$, $Y = [V(H_2O)_6]^{2+}$, $Z = [Cr(C_2O_4)_3]^{3-}$

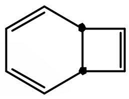
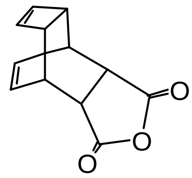
(a) X and Y are inert; Z is labile
(b) X and Z are labile; Y is inert.
(c) X is inert; Y and Z are labile
(d) X is labile; Y and Z are inert.

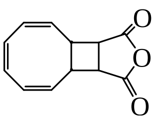
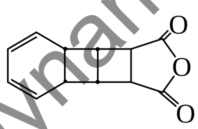
30. In the reaction sequence :

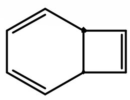
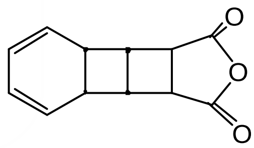


X and Y, respectively, are

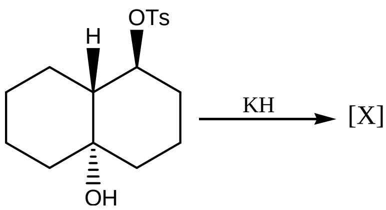
(a)  and 

(b)  and 

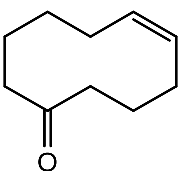
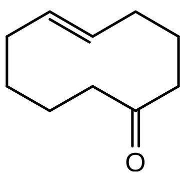
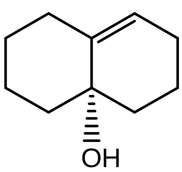
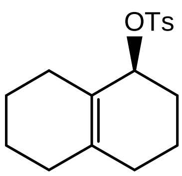
(c)  and 

(d)  and 

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



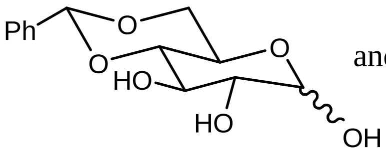
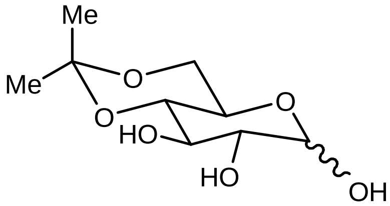
is

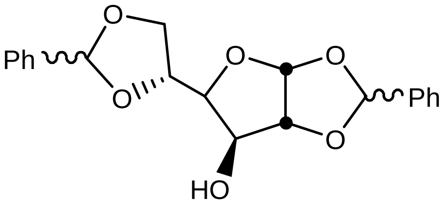
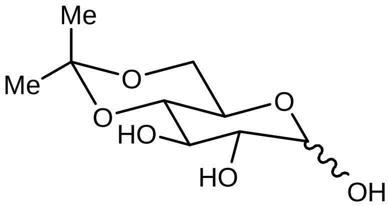
(a) 
(b) 
(c) 
(d) 

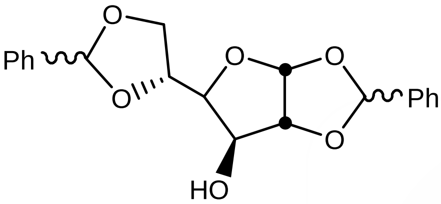
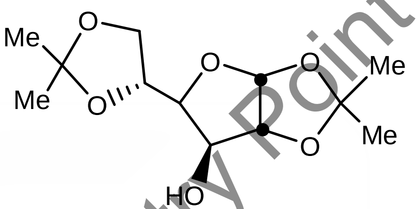
32. In the reactions,

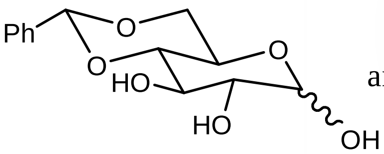
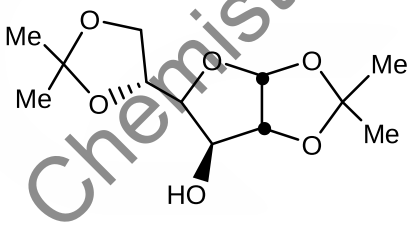
$$[X] \xleftarrow[H^+]{PhCHO} \text{D-glucose} \xrightarrow[H^+]{acetone} [Y]$$

The major products X and Y, respectively are

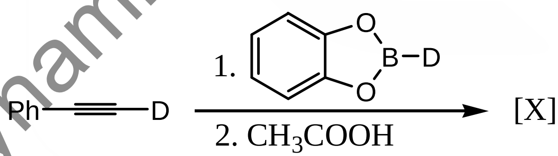
(a)  and 

(b)  and 

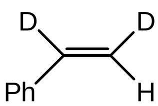
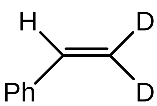
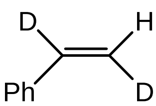
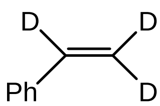
(c)  and 

(d)  and 

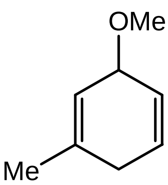
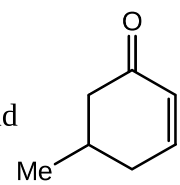
33. In the reaction

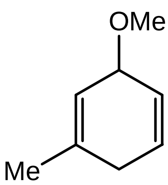
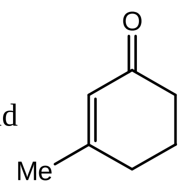


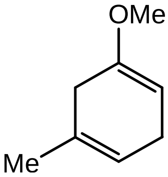
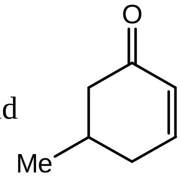
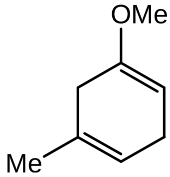
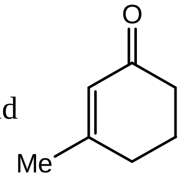
the major product X is

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

34. Reaction of m-methylanisole with lithium in liquid ammonia and t-butyl alcohol at –33ºC 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

(a)  and 

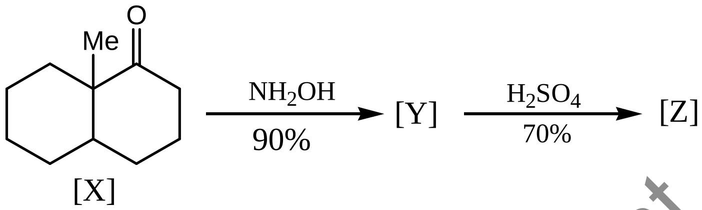
(b)  and 

(c)  and    (d)  and 

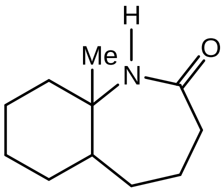
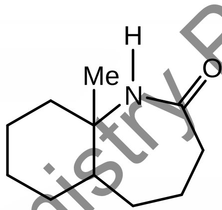
35. The number of signals that appear in the broad-band decoupled ^{13}C NMR spectrum of ortho-, meta- and para-dichlorobenzenes, respectively, are

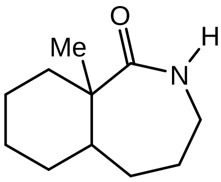
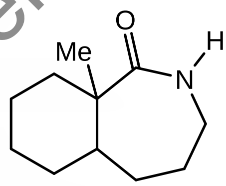
(a) 3, 4 and 2   (b) 3, 3 and 2   (c) 4, 4 and 2   (d) 3, 4 and 4

36. In the reaction seqeunce, **[GATE 2009]**

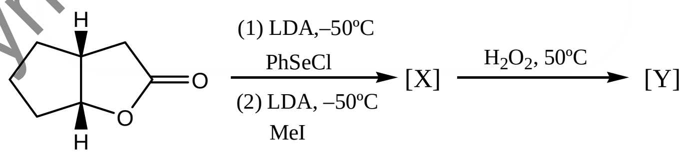


the structure of the major product Z and the overall yield for its formation from the ketone X, are

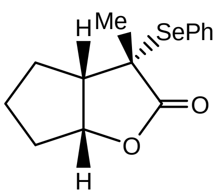
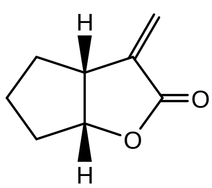
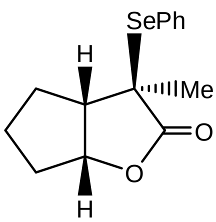
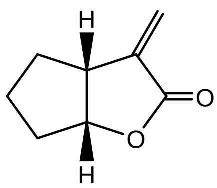
(a)  and 80%   (b)  and 63%

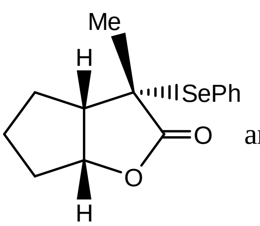
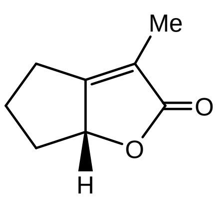
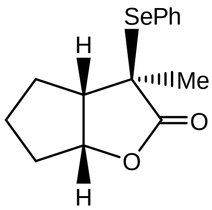
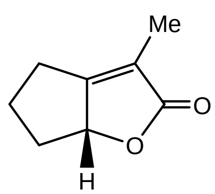
(c)  and 63%   (d)  and 80%

37. In the reaction sequence

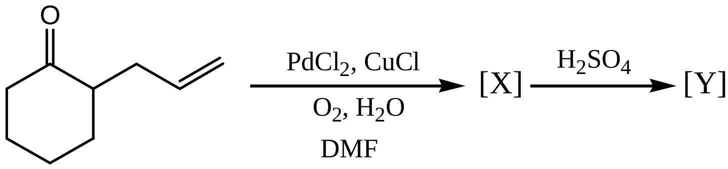


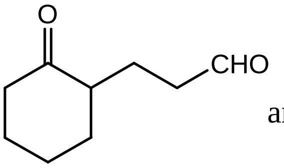
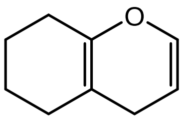
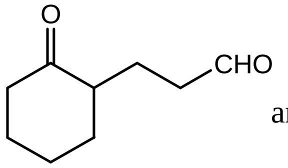
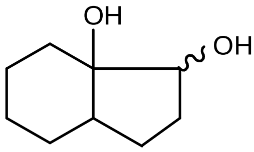
the major product respectively, are:

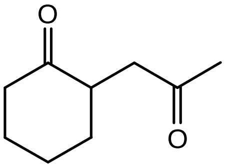
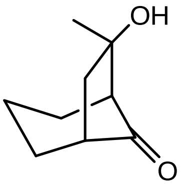
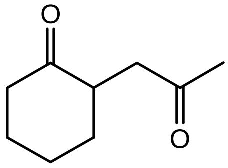
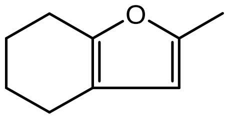
(a)  and    (b)  and 

(c)  and    (d)  and 

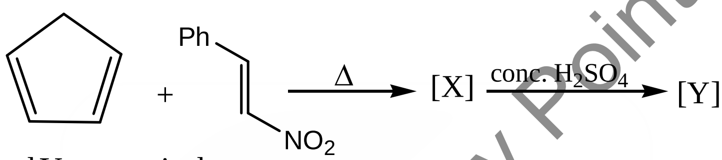
38. In the reaction sequence the major products X and Y, respectively are



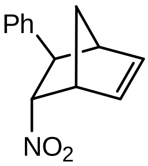
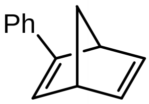
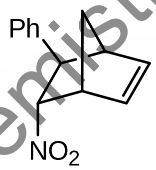
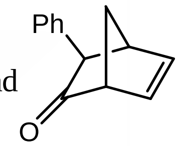
(a)  and  (b)  and 

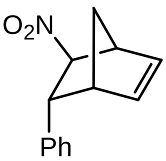
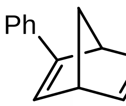
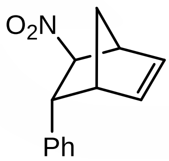
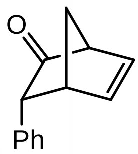
(c)  and  (d)  and 

39. In the reaction sequence

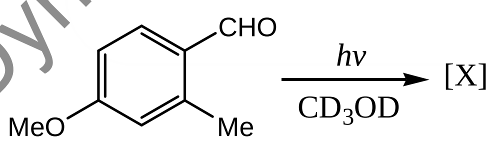


The major products X and Y, respectively are

(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}H NMR signal at ^{1}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) δ 9.7 ppm (b) δ 7.8 ppm (c) δ 3.9 ppm (d) δ 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:

$[E]_0 / 10^{-2}$ mol L^{-1}	5.0	4.0	3.0
$t_{1/2}$ / s	240	300	400

The order of the reaction is:

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

42. The fluorescene 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) $1\times10^{9}\,s^{-1}$ (b) $1\times10^{8}\,s^{-1}$ (c) $1\times10^{7}\,s^{-1}$ (d) $9\times10^{7}\,s^{-1}$

43. The fundamental vibrational wavenumbers for H_2 and I_2 are 4403.2 cm^{-1} and 214.5 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) 6.75×10^{-1} and 3.57×10^{-1} (b) 6.75×10^{-10} and 3.57×10^{-1}

(c) 3.57×10^{-6} and 6.75×10^{-1} (d) 3.57×10^{-1} and 6.75×10^{-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 $^{19}F_2$ shows a series of Stokes lines at 19230.769 cm^{-1}, 19227.238 cm^{-1} and 19223.707 cm^{-1}. The rotational constant for $^{19}F_2$ in GHz is:

(a) 26.484 (bv) 52.968 (c) 105.936 (d) 3.531

46. The de-Broglie wavelength for a He atom travelling at 1000 ms^{-1} (typical speed at room temperature) is

(a) $99.7\times10^{-12}\,m$ (b) $199.4\times10^{-12}\,m$ (c) $199.4\times10^{-18}\,m$ (d) $99\times10^{-6}\,m$

47. Given that the standard molar enthalpies of formation of NO(g) and NO_2(g) are, respectively, 90.3 kJ mol^{-1} and 33.2 kJ mol^{-1}, the enthalpy change for the reaction $2NO(g)+O_2(g)\rightarrow 2NO_2(g)$ 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

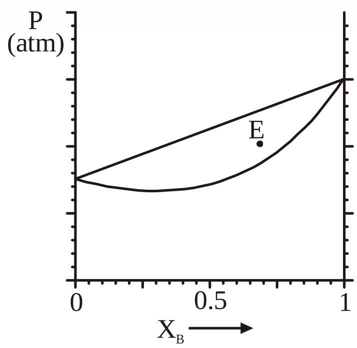
(a) $2SO_3(g) \rightleftharpoons 2SO_2(g)+O_2(g)$ (b) $H_2(g)+I_2(s) \rightleftharpoons 2HI(g)$

(c) $C(s)+H_2O(g) \rightleftharpoons CO(g)+H_2(g)$ (d) $3Fe(s)+4H_2O(g) \rightleftharpoons Fe_3O_4(s)+4H_2(g)$

49. The free energy change (ΔG) of 1 mole of an ideal gas that is compressed isothermally from 1 atm to 2 atm is:

(a) RTln2 (b) –2RT (c) –RTln2 (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 ^{1}H 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) $\left[(C_5H_5)W(CO)_3\right]Na$ and $\left[(C_5H_5)W(CO)_3H\right]$

(b) $\left[(C_5H_5)W(CO)_4\right]Na$ and $\left[(C_5H_5)W(CO)_4H\right]$

(c) $\left[(C_5H_5)W(CO)_3\right]Na$ and $\left[(C_5H_5)W(CO)_4H\right]$

(d) $\left[(C_5H_5)W(CO)_4\right]Na$ and $\left[(C_5H_5)W(CO)_3H\right]$

52. The compounds O and P, respectively, are

(a) $\left[(C_5H_5)W(CO)_3\right]_2$ and $\left[(C_5H_5)W(CO)_3Br\right]$

(b) $\left[(C_5H_5)W(CO)_4\right]$ and $\left[(C_5H_5)W(CO)_2Br(THF)\right]$

(c) $\left[(C_5H_5)W(CO)_2(THF)_2\right]$ and $\left[(C_5H_5)W(CO)_3Br\right]$

(d) $\left[(C_5H_5)W(CO)_3\right]_2$ and $\left[(C_5H_5)W(CO)_2Br(THF)\right]$

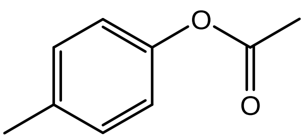
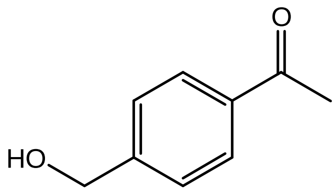
Common data for Q. 53 and Q. 54:

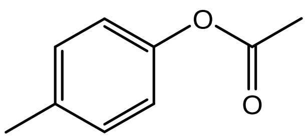
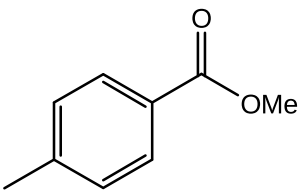
An organic compound $X(C_9H_{10}O)$ exhibited the following spectral data.
IR : 1680 cm^{-1}.

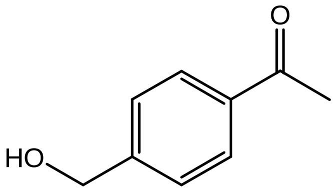
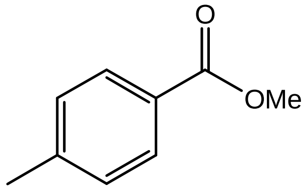
^1H NMR : $\delta 7.8(2H, d, J\ 7.5\ Hz), 7.2(2H, d, J = 75\ Hz), 2.7\ (3H, s)$ and $2.4(3H, s)$

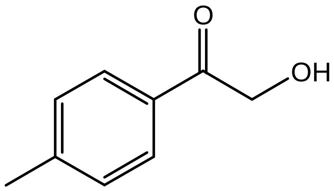
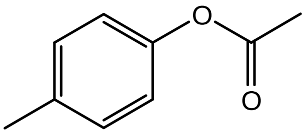
Compound X on treatment with m-chloroperbenzoic acid produced two isomeric compounds Y (major) and Z (minor).

53. Compounds Y and Z, respectively, are

(a)  and 

(b)  and 

(c)  and 

(d)  and 

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.

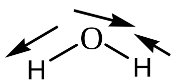
Common data for Q. 55 and Q. 56.

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, Γ_{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.



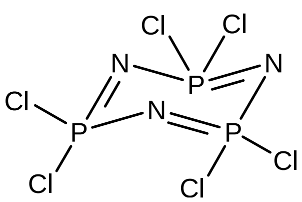
This vibration transforms as the irreducible representation
(a) A_1 (b) B_1 (c) A_2 (d) B_2

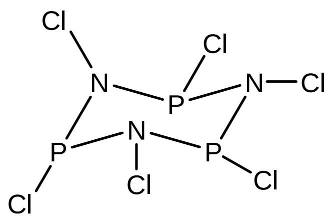
Linked Answer type Q.57 and Q.58.

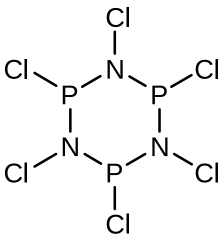
Triphosphazene is prepared by reacting X and Y in equimolar ratio at 120–150ºC using appropriate solvents

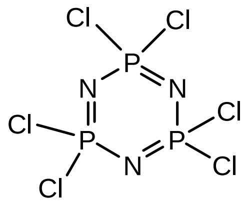
57. The reaction X and Y, respectively, are
(a) PCl_3; NH_3 (b) PCl_5; NH_3 (c) PCl_5; NH_4Cl (d) PCl_3; NH_4Cl

58. The structure of triphosphazene is

(a) 

(b) 

(c) 

(d) 

Statement for Linked Q.59 and Q.60:

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

'k's represent rate constants, 'E_A's represent activation energies, and $k_2 >> k_3$

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

(a) k_1k_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 $(E_{A,\,overall})$ for the formation of P can expressed as

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