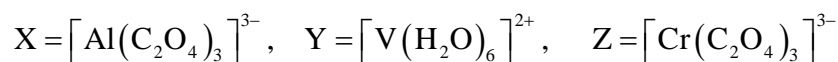


27. Two samples have been given to you : $[\text{NiCl}_2(\text{PPh}_3)_2]$ and $[\text{PdCl}_2(\text{PPh}_3)_2]$. A physical method that can be used to identify these compounds unambiguously is
- (a) HPLC (b) magnetic susceptibility
(c) ^{13}C NMR spectroscopy (d) Mössbauer spectroscopy

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

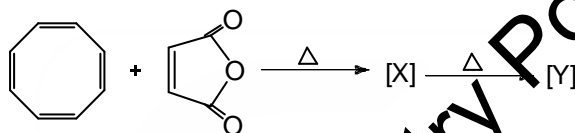
- (a) HSO_4^- and SO_4^{2-} ; H_2O and OH^- (b) HSO_4^- and H_3O^+ ; SO_4^{2-} and OH^-
(c) HSO_4^- and OH^- ; SO_4^{2-} and H_2O (d) HSO_4^- and OH^- ; SO_4^{2-} and H_3O^+

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

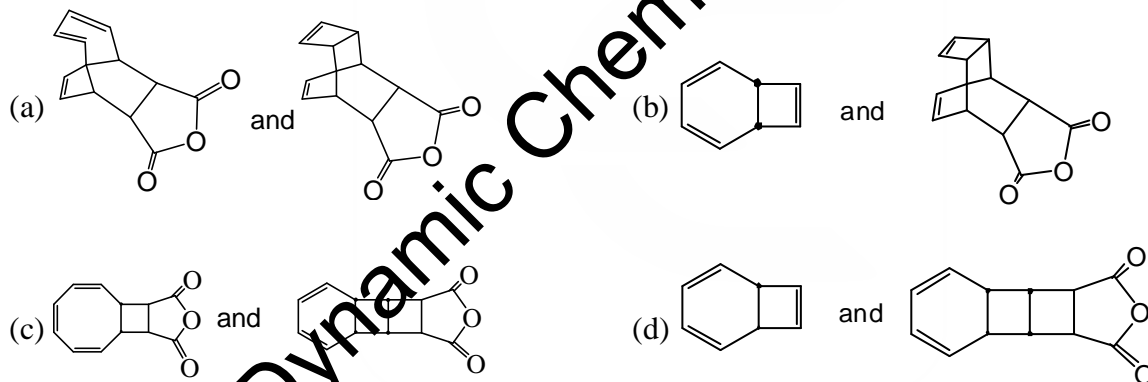


- (a) X and Y are inert; Z is labile (b) X and Z are labile; Y is inert.
(c) X is inert; Y and Z are labile (d) X is labile; Y and Z are inert.

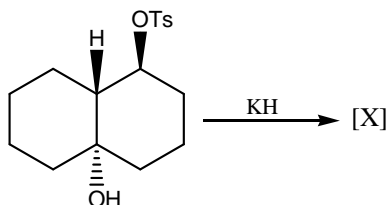
30. In the reaction sequence :



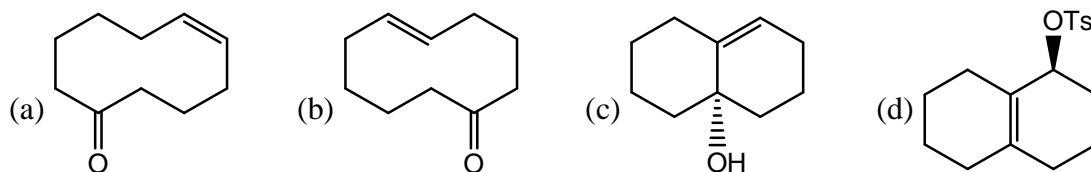
X and Y, respectively, are



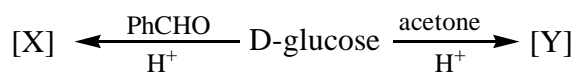
31. The major product X (based on the preferred conformation) in the reaction



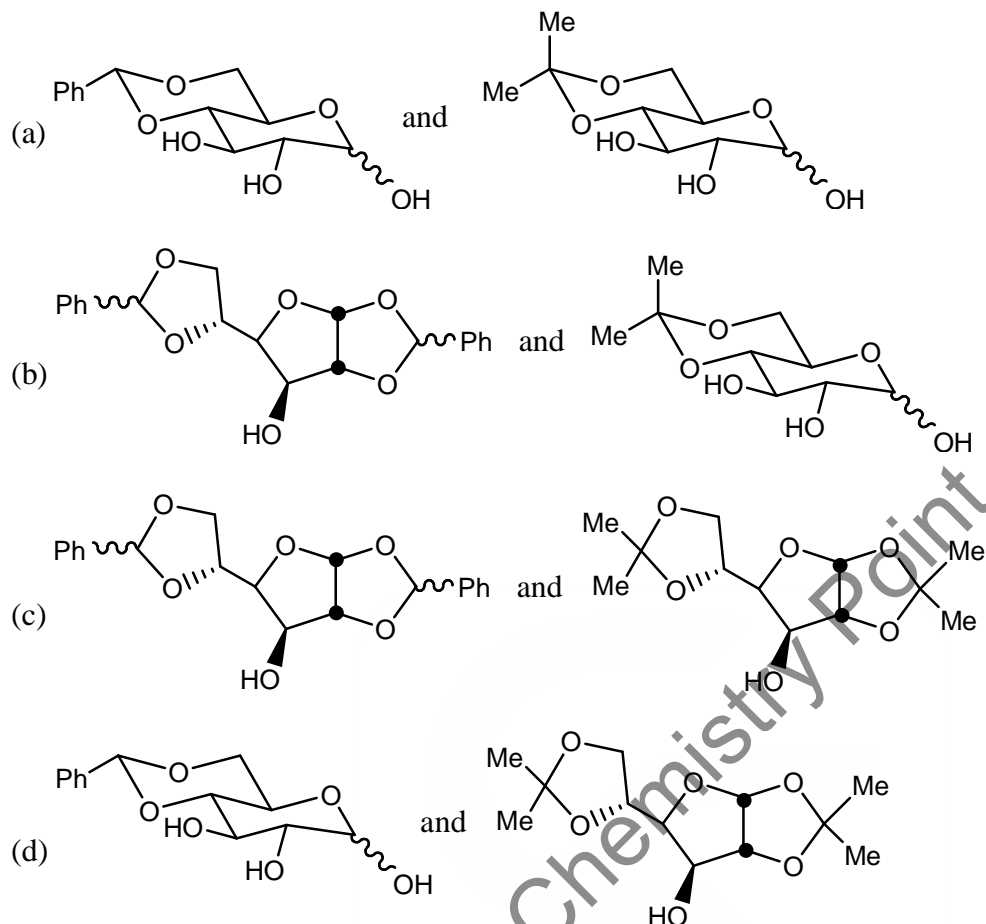
is



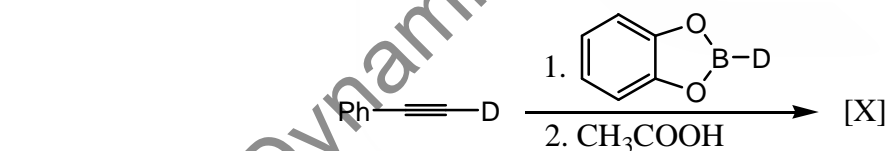
32. In the reactions,



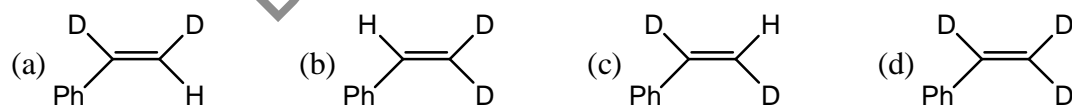
The major products X and Y, respectively are



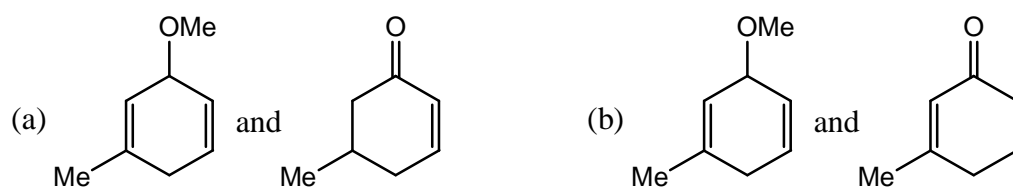
33. In the reaction

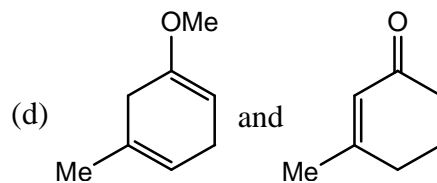
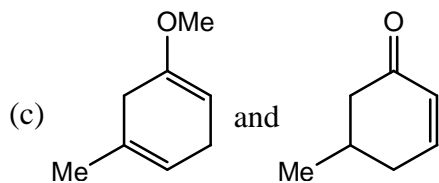


the major product X is



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



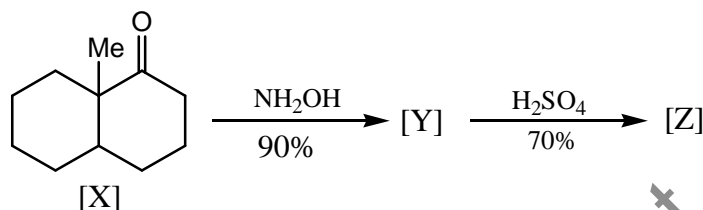


35. The number of signals that appear in the broad-band decoupled ^{13}C NMR spectrum of ortho-, meta- and para-dichlorobenzenes, respectively, are

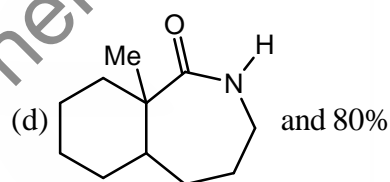
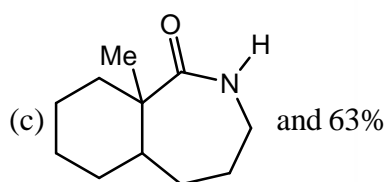
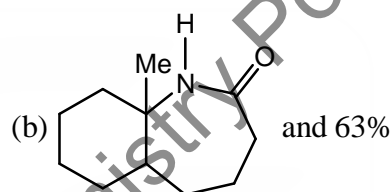
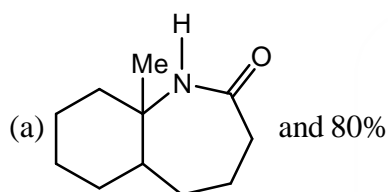
- (a) 3, 4 and 2 (b) 3, 3 and 2 (c) 4, 4 and 2 (d) 3, 4 and 4

36. In the reaction sequence,

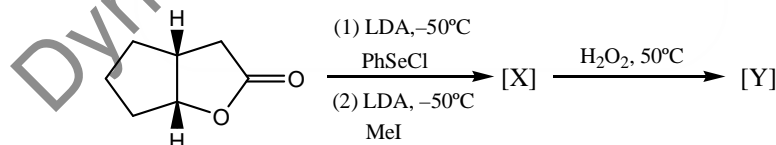
[GATE 2009]



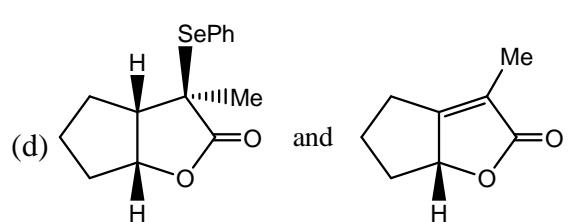
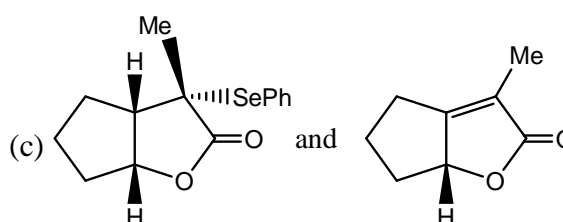
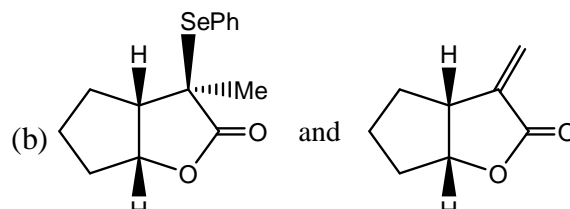
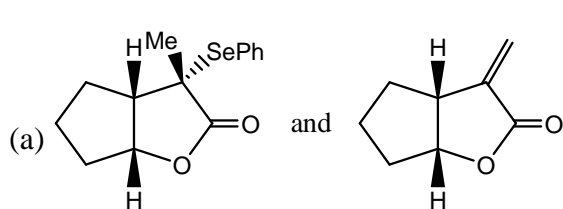
the structure of the major product Z and the overall yield for its formation from the ketone X, are



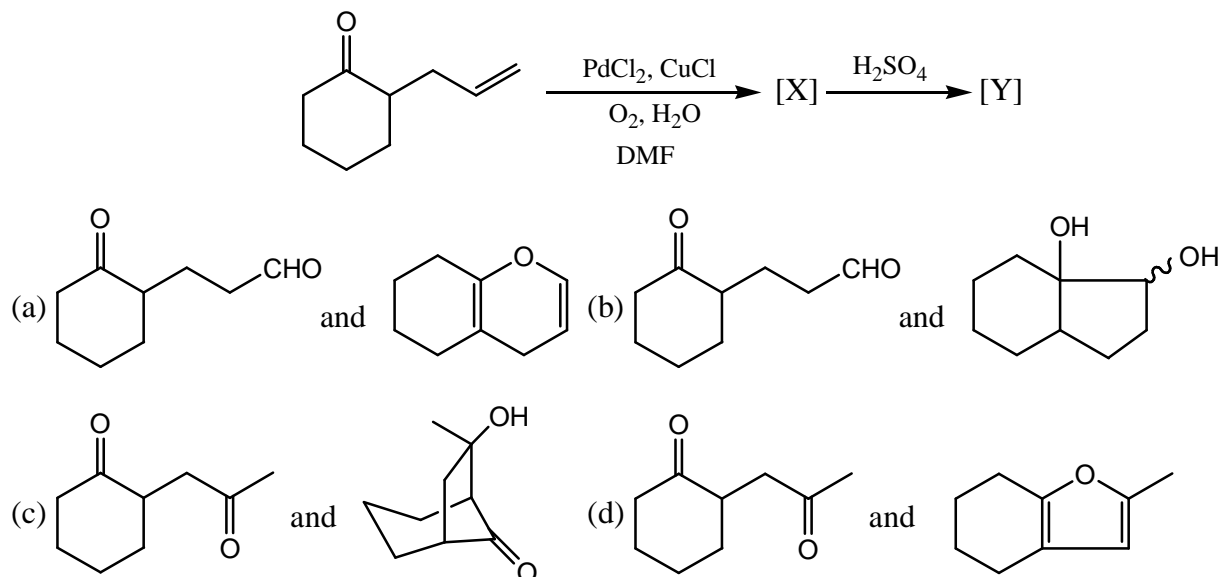
37. In the reaction sequence



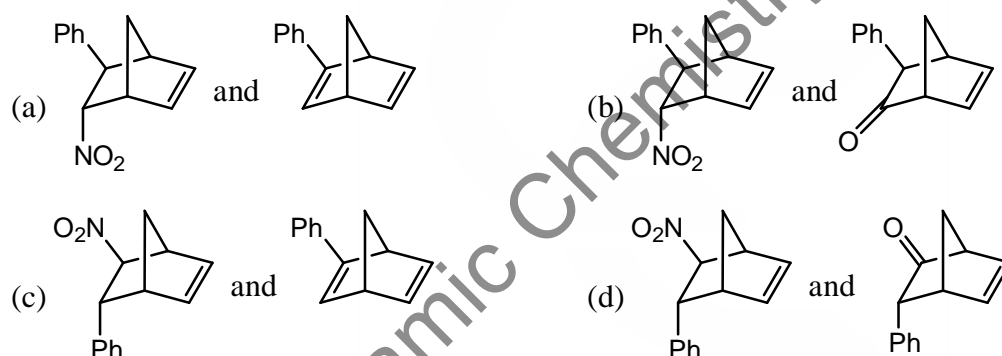
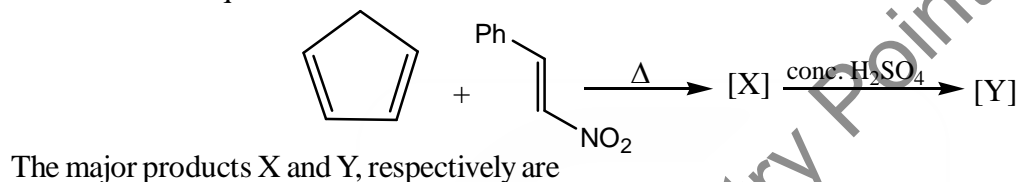
the major product respectively, are:



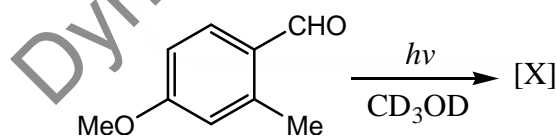
38. In the reaction sequence the major products X and Y, respectively are



39. In the reaction sequence



40. In the photochemical reaction



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

δ 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 ($[\text{E}]_0$) as follows:

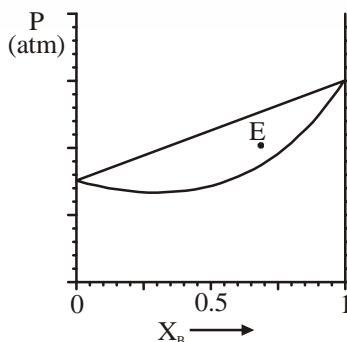
$[\text{E}]_0 / 10^{-2} \text{ mol L}^{-1}$ 5.0 4.0 3.0

$t_{1/2} / \text{s}$ 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 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 $^{19}\text{F}_2$ 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 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 kJ mol^{-1} and 33.2 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 (ΔG) 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.

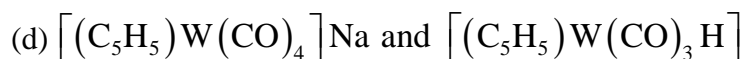
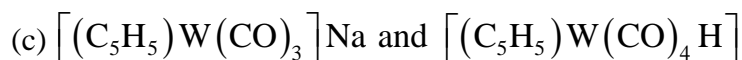
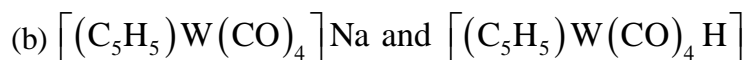
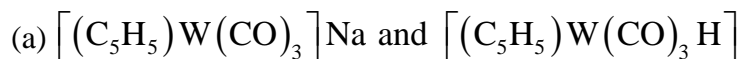


- Given a state of this vapour-liquid mixture whose overall composition corresponds to point E in the figure, the mole fraction of B in the vapour phase is approximately
 (a) 0.25 (b) 0.53 (c) 0.65 (d) 0.80

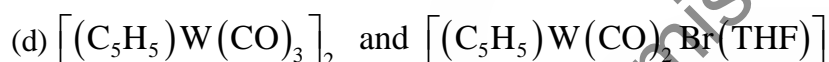
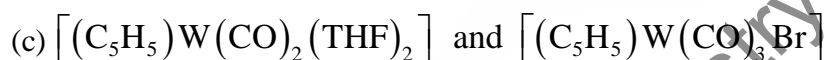
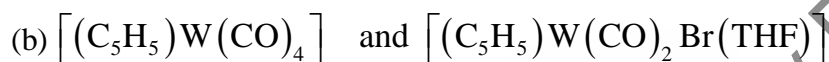
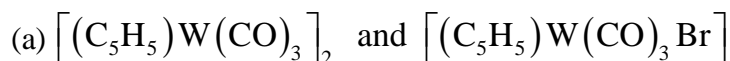
Common data for Q. 51 and Q. 52:

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



52. The compounds O and P, respectively, are

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

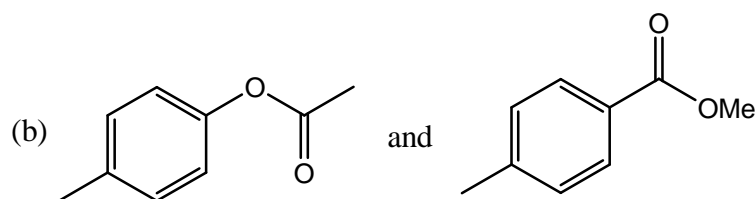
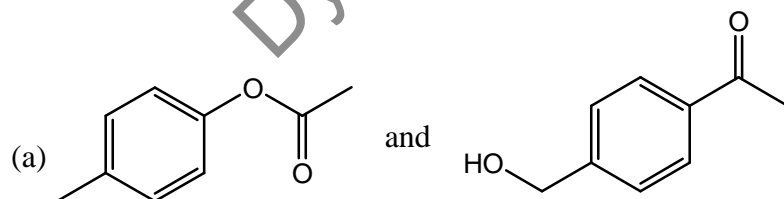
An organic compound X ($C_9H_{10}O$) exhibited the following spectral data.

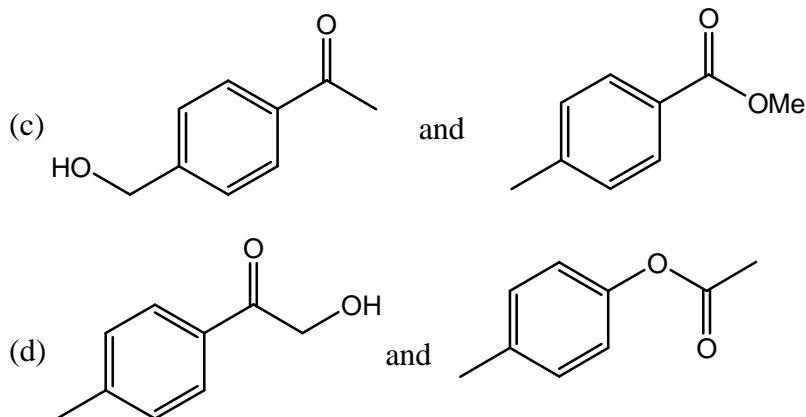
IR : 1680 cm^{-1} .

1H NMR : $\delta 7.8$ (2H, d, J 7.5 Hz), 7.2 (2H, d, J = 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





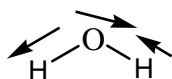
54. Compounds Y and Z can be differentiated by carrying out basic hydrolysis, because [GATE 2009]
 (a) Y produces 4-methylphenol and Z is unaffected.
 (b) Y produces 4-methylphenol and Z produces 4-methylbenzoic acid.
 (c) Y is unaffected and Z produces 4-methylbenzoic acid.
 (d) Y is unaffected and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



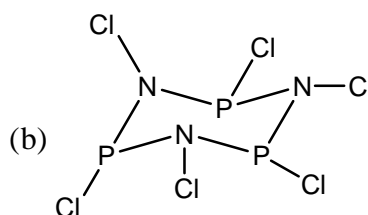
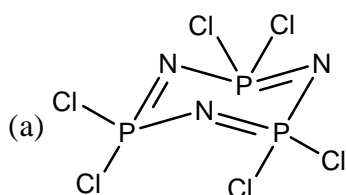
This vibration transforms as the irreducible representation

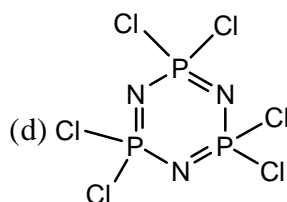
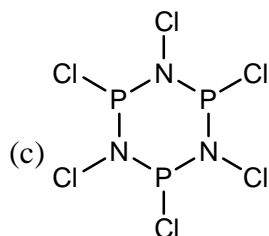
- (a) A_1 (b) B_1 (c) A_2 (d) B_2

Linked Answer type Q.57 and Q.58.

Triphosphazene is prepared by reacting X and Y in equimolar ratio at 120–150°C 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





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_A's represent activation energies, and $k_2 \gg k_3$

59. The overall rate constant (k_{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) $\frac{E_{A,1}}{E_{A,2} + E_{A,3}}$

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