

## GATE – 2009 – Chemistry



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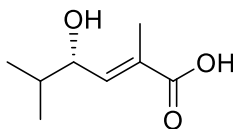
### Features

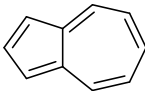
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**Q.1 – Q.20 Multiple Choice Question (MCQ), carry ONE mark each (for each wrong answer: – 1/3).**

- 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
- For the given compound the **stereochemical notations** are

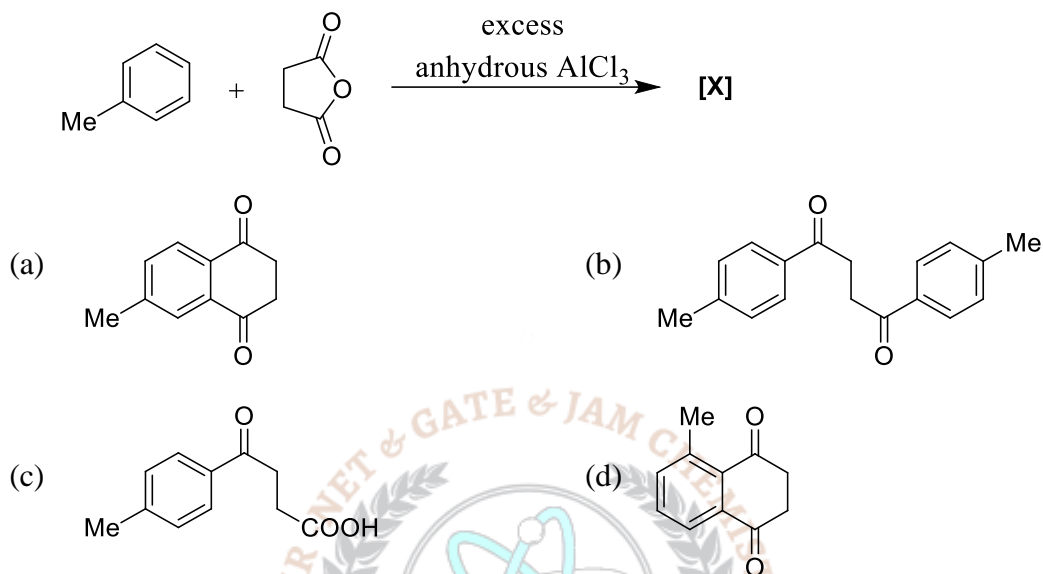


- 2Z, 4R
  - 2Z, 4S
  - 2E, 4R
  - 2E, 4S
9. The compound  is
- aromatic and has high dipole moment
  - aromatic and has no dipole moment

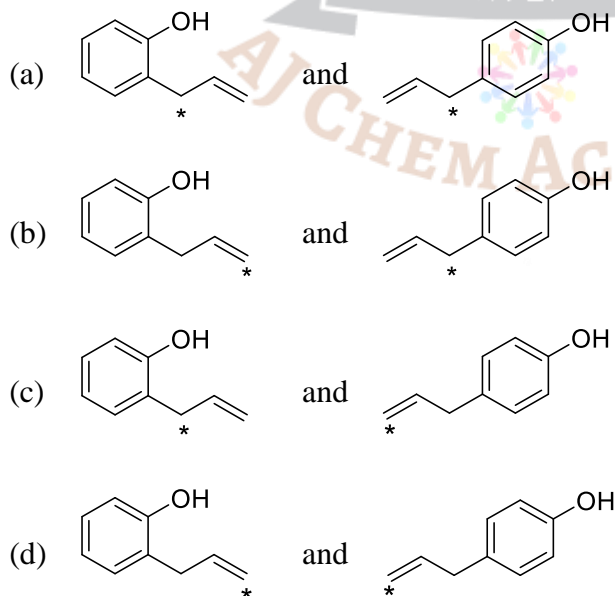
(c) non-aromatic and has high dipole moment

(d) anti-aromatic and has no dipole moment

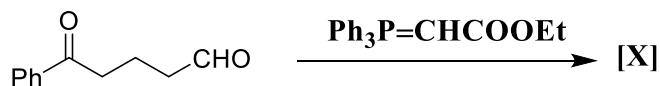
10. In the given reaction, the **major product-X** is:

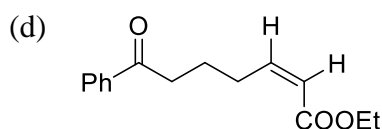
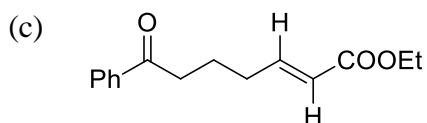
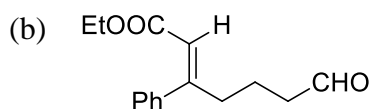
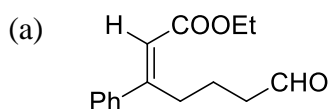


11. In the given reaction the **major products X and Y** are,

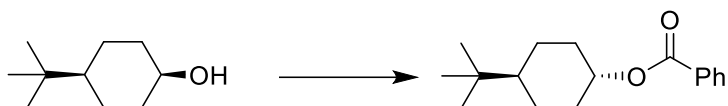


12. In the given reaction, the **major product-X** is:





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



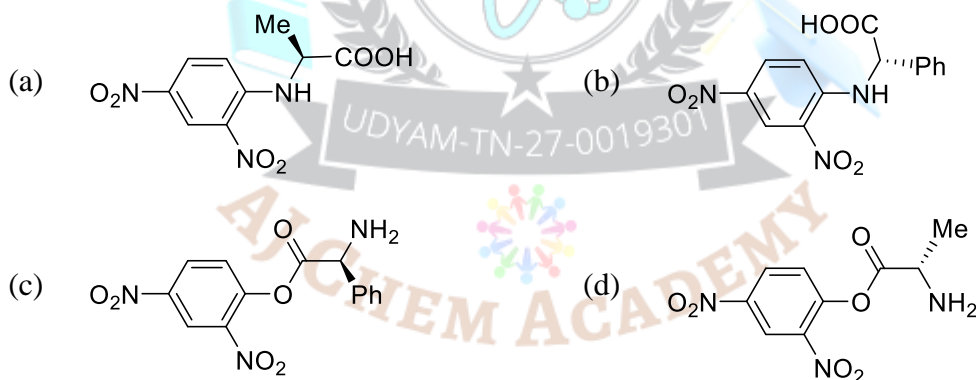
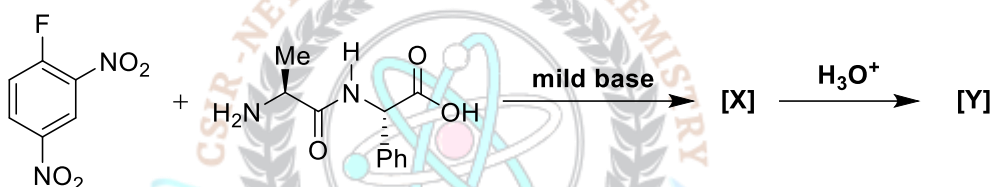
(a)  $\text{PhCOCl}$  and pyridine

(b) DCC and  $\text{PhCOOH}$

(c)  $\text{PhBr}$ ,  $\text{CO}$  and  $\text{Pd(PPh}_3)_4$

(d)  $\text{EtOOC-N=N-COOEt}$ ,  $\text{PPh}_3$  and  $\text{PhCOOH}$

14. In the given **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:

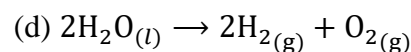
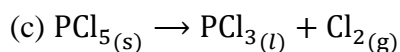
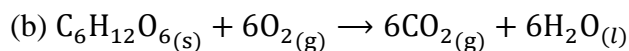
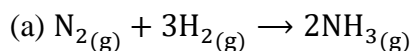
(a) 200 g of water at  $40^\circ\text{C}$

(b) 100 g of water at  $20^\circ\text{C}$

(c) 150 g of water at  $50^\circ\text{C}$

(d) 300 g of water at  $30^\circ\text{C}$

16. Among the following, the reaction that is accompanied by a **decrease in the entropy** is,



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  $\ln \gamma_{\pm}$  will

( $\gamma_{\pm}$  is the molal mean ionic activity coefficient)

- (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:

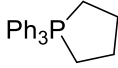
- (a)  $1 \times 10^{-4} \text{ s}^{-1}$  (b)  $2.5 \times 10^{-5} \text{ s}^{-1}$  (c)  $4 \times 10^{-4} \text{ s}^{-1}$  (d)  $4 \times 10^4 \text{ s}^{-1}$

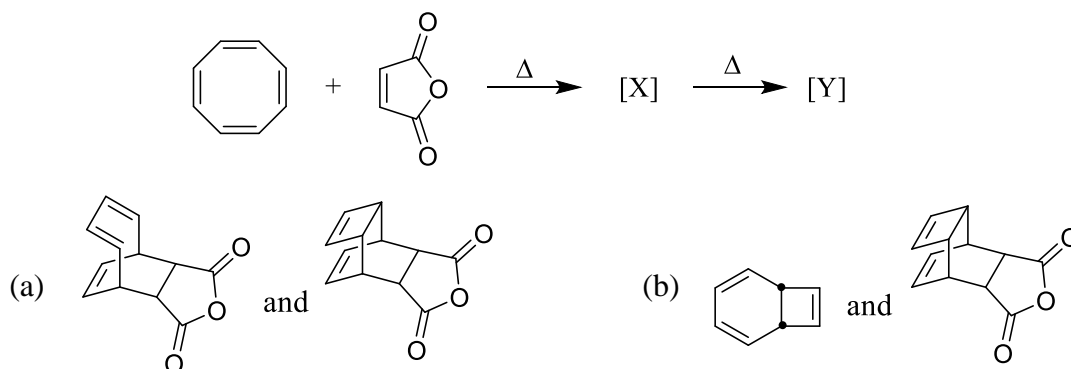
**Q.21 – Q.60 Multiple Choice Question (MCQ), carry TWO marks each (for each wrong answer: – 2/3).**

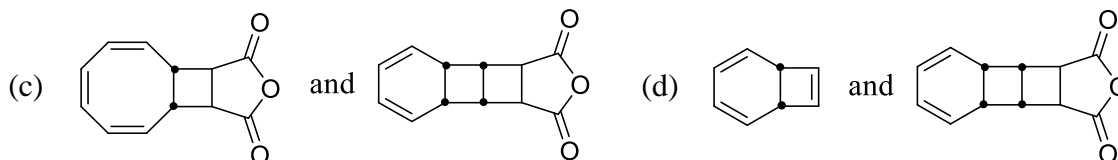
21. The **correct order of  $\nu_{\text{CO}}$**  for the following compounds, in the **IR spectrum** is:
- $[\text{Mo}(\text{CO})_3(\text{NMe}_3)_3]$   
I

$[\text{Mo}(\text{CO})_3(\text{P}(\text{OPh})_3)_3]$   
II
- $[\text{Mo}(\text{CO})_3(\text{PMe}_3)_3]$   
III

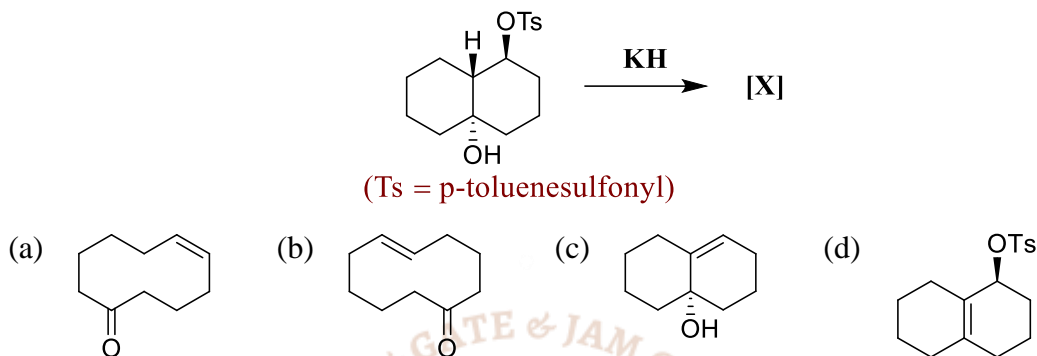
$[\text{Mo}(\text{CO})_3(\text{PCl}_3)_3]$   
IV
- (a) I > II > III > IV (b) IV > I > II > III (c) IV > II > III > I (d) III > I > IV > II
22. **2.5 g of an iron compound upon suitable treatment yielded 0.391 g of iron(III) oxide. The percentage of iron in the compound is (Atomic weight of Fe: 55.847, O: 15.994)**  
 (a) 10.94 (b) 12.15 (c) 11.31 (d) 9.11
23. In the reaction,  $\text{Ph}_3\text{P} \xrightarrow{\text{Mel}} [\text{X}] \xrightarrow{\text{n-BuLi}} [\text{Y}]$ ; 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)  $[\text{Ph}_3\text{P}(\text{Me})][\text{I}];$  
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  $\text{HSO}_4^- (\text{aq}) + \text{OH}^- (\text{aq}) \leftrightarrow \text{SO}_4^{2-} (\text{aq}) + \text{H}_2\text{O} (\text{l})$ , 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:  
 X Y Z  
 $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$   $[\text{V}(\text{H}_2\text{O})_6]^{2+}$   $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$   
 (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

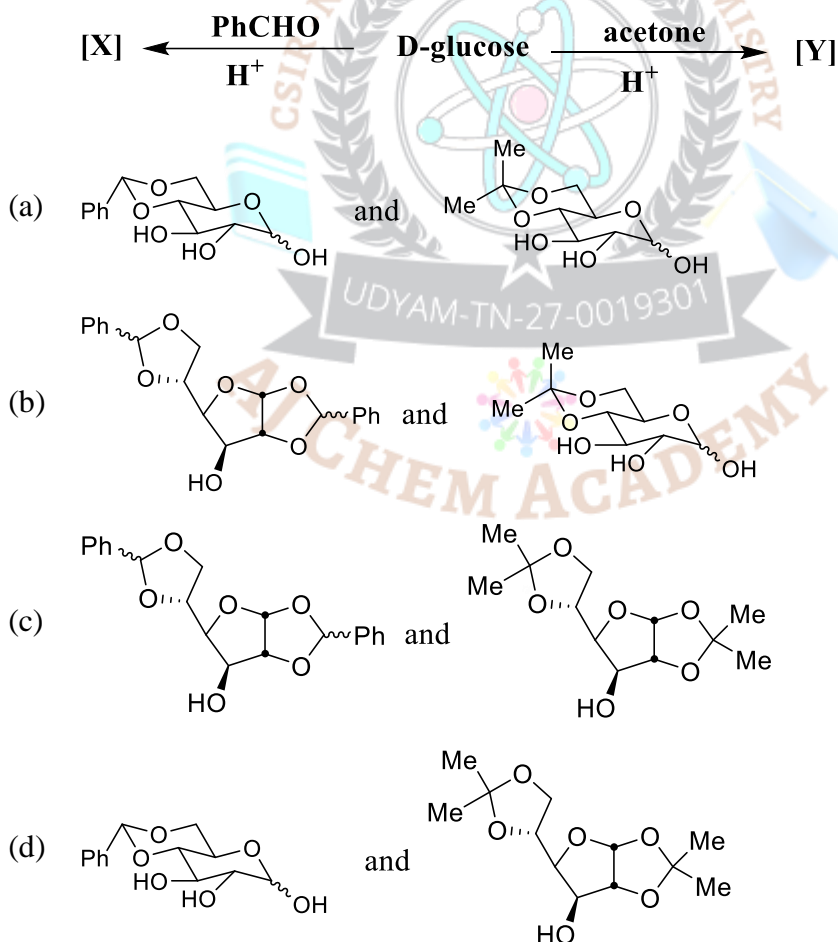




31. The major **product-X** in the given reaction is (based on the preferred conformation)

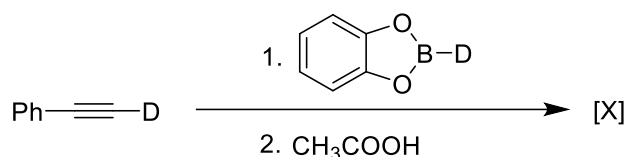


32. In the given reactions, the **major products X and Y**, respectively are



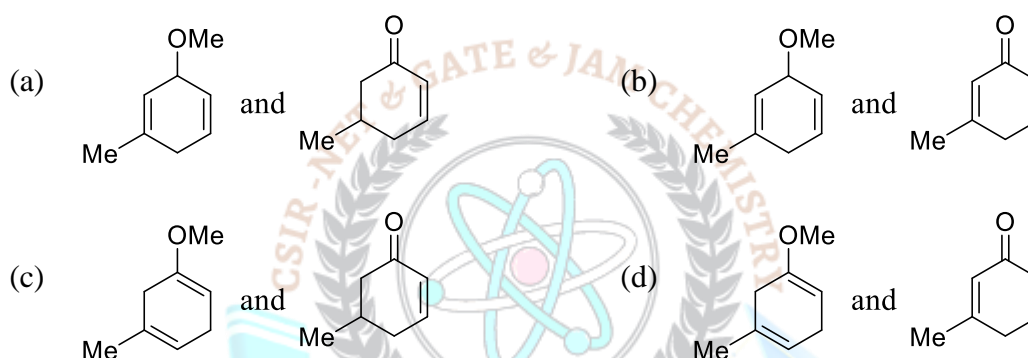
33. In the given reaction, the **major product-X** is



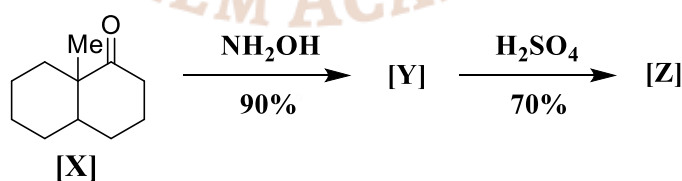


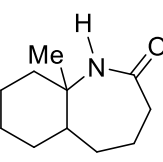
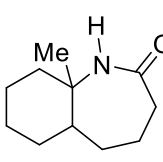
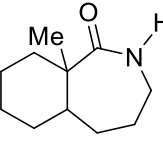
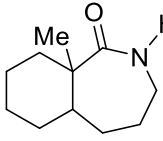
- (a)  (b)  (c)  (d) 

34. Reaction of *m*-methylanisole with lithium in liquid ammonia and *t*-butyl alcohol at  $-33^\circ\text{C}$  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



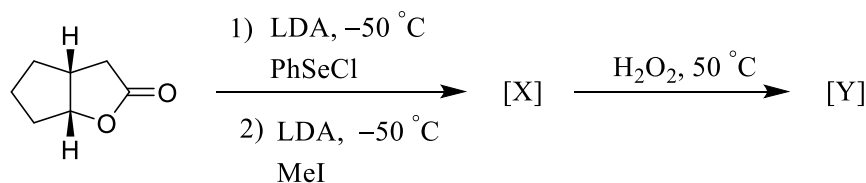
35. The number of signals that appear in the broad-band decoupled  $^{13}\text{C}$ -NMR spectrum of ortho-, meta- and para-dichlorobenzenes, respectively, are
- (a) 3, 4 and 2 (b) 3, 3 and 2 (c) 4, 4 and 2 (d) 3, 4 and 4
36. In the given reaction sequence, the structure of the major product-Z and the overall yield for its formation from the ketone-X, are



- (a)  and 80% (b)  and 63%
- (c)  and 63% (d)  and 80%

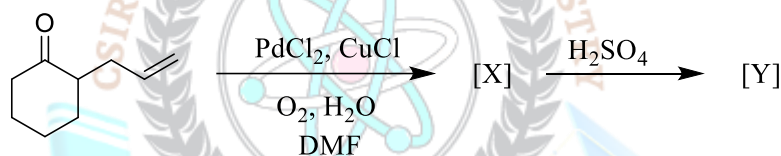
37. In the given reaction sequence, the major products X and Y respectively, are:





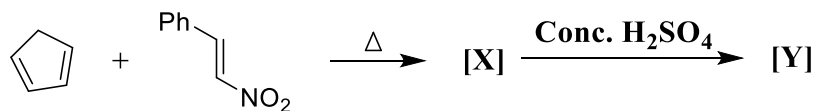
- (a) and (b) and (c) and (d) and

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



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

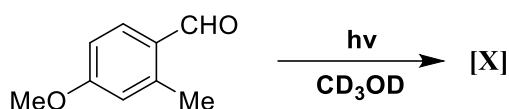
39. In the given reaction sequence, the **major products X and Y**, respectively are



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

40. In the given **photochemical reaction**, formation of the **compound-X** can be inferred

by the disappearance of the  $^1\text{H-NMR}$  signal at



$^1\text{H NMR}$  :  $\delta$  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

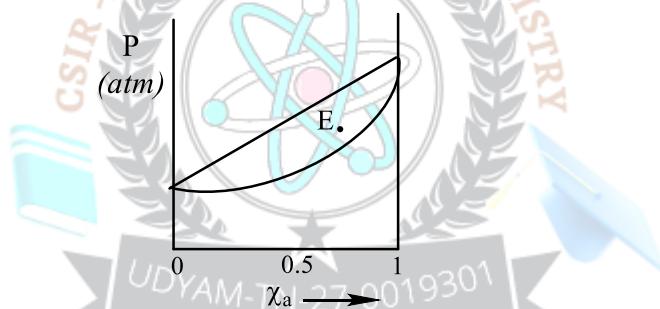
41. The half-life ( $t_{1/2}$ ) for the hydrolysis of an ester varies with the initial concentration of the reactant ( $[\text{E}]_0$ ) as follows:

$[\text{E}]_0/10^{-2} \text{ mol L}^{-1}$	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  $\text{H}_2$  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  $2\text{NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_{2(g)}$  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)  $2\text{SO}_{3(g)} \leftrightarrow 2\text{SO}_{2(g)} + \text{O}_{2(g)}$                       (b)  $\text{H}_{2(g)} + \text{I}_{2(s)} \leftrightarrow 2\text{HI}_{(g)}$
- (c)  $\text{C}_{(s)} + \text{H}_2\text{O}_{(g)} \leftrightarrow \text{CO}_{(g)} + \text{H}_{2(g)}$                       (d)  $3\text{Fe}_{(s)} + 4\text{H}_2\text{O}_{(g)} \leftrightarrow \text{Fe}_3\text{O}_{4(s)} + 4\text{H}_{2(g)}$
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  $\text{W}(\text{CO})_6$  with 1 equivalent of  $\text{Na}(\text{C}_5\text{H}_5)$  in THF solution gives the ionic compound-M. Reaction of M with glacial acetic acid results in product N. The  $^1\text{H}$  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  $\text{W}(\text{CO})_6$  with cyclopentadiene and  $\text{H}_2$  is also produced. Treatment of O with an equivalent of  $\text{Br}_2$  produces P. (Use the 18-electron rule as your guide).

51. The **compounds M and N**, respectively, are
- (a)  $[(\text{C}_5\text{H}_5)\text{W}(\text{CO})_3]\text{Na}$  and  $[(\text{C}_5\text{H}_5)\text{W}(\text{CO})_3\text{H}]$
- (b)  $[(\text{C}_5\text{H}_5)\text{W}(\text{CO})_4]\text{Na}$  and  $[(\text{C}_5\text{H}_5)\text{W}(\text{CO})_4\text{H}]$
- (c)  $[(\text{C}_5\text{H}_5)\text{W}(\text{CO})_3]\text{Na}$  and  $[(\text{C}_5\text{H}_5)\text{W}(\text{CO})_4\text{H}]$
- (d)  $[(\text{C}_5\text{H}_5)\text{W}(\text{CO})_4]\text{Na}$  and  $[(\text{C}_5\text{H}_5)\text{W}(\text{CO})_3\text{H}]$



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:**

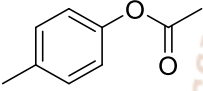
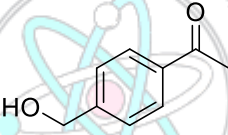
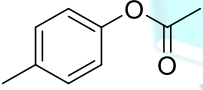
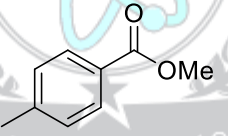
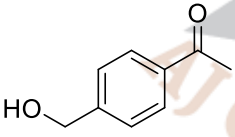
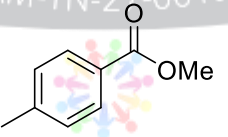
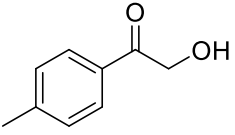
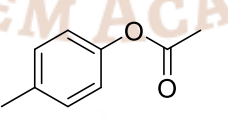
An organic compound-**X** ( $C_9H_{10}O$ ) exhibited the following spectral data.

**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

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

54. Compounds **Y** and **Z** can be differentiated by carrying out basic hydrolysis, because

- (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

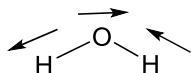
**Common data for Q. 55 and Q. 56:**

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

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v(yz)$		
$A_1$	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**,  $\Gamma_{tr}$ , 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  $z$ .



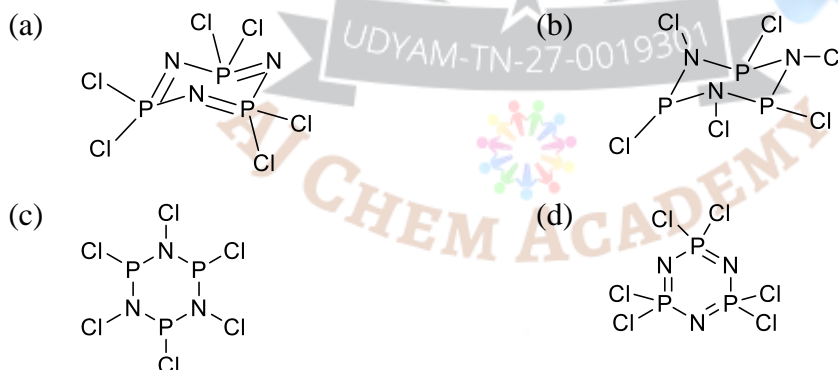
This vibration transforms as the **irreducible representation**

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

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

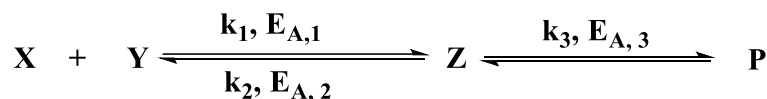
**Triphosphazene** is prepared by reacting **X** and **Y** in equimolar ratio at  $120-150^\circ C$  using appropriate solvents

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 below,



'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)  $\frac{E_{A,1}}{E_{A,2} + E_{A,3}}$

Answer Key

Q.No	Ans		Q.No	Ans		Q.No	Ans		Q.No	Ans
1.	c		16.	a		31.	b		46.	a
2.	d		17.	c		32.	d		47.	c
3.	b		18.	b		33.	c		48.	d
4.	c		19.	a		34.	d		49.	a
5.	b		20.	c		35.	a		50.	d
6.	b		21.	c		36.	b		51.	a
7.	a		22.	a		37.	a		52.	a
8.	d		23.	b		38.	c		53.	b
9.	a		24.	c		39.	b		54.	b
10.	c		25.	b		40.	a		55.	b
11.	b		26.	b		41.	c		56.	b
12.	c		27.	b		42.	c		57.	c
13.	d		28.	a		43.	b		58.	d
14.	a		29.	d		44.	c		59.	a
15.	c		30.	b		45.	a		60.	c

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