PAPER : IIT-JAM 2010

CHEMISTRY-CY

NOTE: Attempt ALL the **44 questions.** Questions 1-30 **(Objective questions)** carry ***three*** marks each and questions 31-44 **(Subjective questions)** carry ***fifteen*** marks each.

1. The molar internal energy of a gas at temperature T is $U_m(T)$. The molar internal energy at T = 0 is $U_m(0)$. The correct expression that relates these two with appropriate contributions is:

   (a) $U_m(T) = U_m(0) + 3RT$ [Linear molecule, translation only]

   (b) $U_m(T) = U_m(0) + \frac{5}{2}RT$ [Linear molecule, translation and rotation only]

   (c) $U_m(T) = U_m(0) + \frac{3}{2}RT$ [Nonlinear molecule, translation and rotation only]

   (d) $U_m(T) = U_m(0) + RT$ [Non linear molecule, translation only]

2. If a particle has linear momentum $\vec{p} = -2\vec{i} + \vec{j} + \vec{k}$ at position $\vec{r} = 3\vec{i} - \vec{j} + \vec{k}$, then its angular momentum is:

   (a) $\vec{i} + 2\vec{k}$ (b) $-2\hat{i} - 5\hat{j} + \hat{k}$ (c) $5\hat{i} - 2\hat{j}$ (d) $2\hat{i} + 5\hat{j} - \hat{k}$

3. If ψ is the eigenfunctions to the Hamiltonian operator with α as the eigenvalue, then α MUST be

   (a) Positive (b) Negative (c) An integer (d) Real

4. A quantum mechanical particle of mass m free to rotate on the surface of a sphere of radius r is in the state with energy $\frac{10\hbar^2}{mr^2}$. The degeneracy of this state is:

   (a) 20 (b) 10 (c) 9 (d) 4

5. Choose the **INCORRECT** statement among the following:

   (a) When ideal gases are mixed, the entropy of mixing is always positive.
   (b) At equilibrium, the chemical potential of a species is the same in all of the phases of the system.
   (c) The total pressure of a mixture of a ideal gases is equal to the sum of the partial pressure of each gas in the mixture
   (d) When a gas is allowed to expand, the maximum work is obtained when the process is carried out irreversibly.

6. The work done during the free expansion of one mole of an ideal gas at 27ºC to twice its original volume is (given: RT = 2494 J mol^{-1}, ln 2 = 0.7, log 2 = 0.3)

   (a) 1746 J mol^{-1} (b) –1746 J mol^{-1} (c) zero (d) 748.2 J mol^{-1}.

7. Choose the correct order of the diffusion coefficients of the following at 298 K.

   $P: H^+$ in water

   $Q: OH^-$ in water

   R: H_2O in water

   S: Sucrose in water

   (a) P > Q > R > S (b) S > R > Q > P (c) S > Q > R > P (d) P > R > Q > S

8. Two matrices are given as $X = \begin{pmatrix} 1 & 5 \\ 3 & 7 \end{pmatrix}$ and $Y = \begin{pmatrix} 2 & 4 \\ 6 & 0 \end{pmatrix}$. If X^T is the transpose of X then what would be X^TY?

(a) $\begin{pmatrix} 20 & 52 \\ 4 & 20 \end{pmatrix}$ (b) $\begin{pmatrix} 20 & 4 \\ 52 & 20 \end{pmatrix}$ (c) $\begin{pmatrix} 32 & 4 \\ 48 & 12 \end{pmatrix}$ (d) $\begin{pmatrix} 44 & 28 \\ 12 & 12 \end{pmatrix}$

9. Addition of 1.0 g of a compound to 10 g of water increases the boiling point by 0.3ºC. The amount of compound needed to prepare a 500 ml of 0.1 M solution is (given: assume negligible dissociation or association of the compound, boiling point constant K_b of water = 0.513 Kkg mol^{-1})
(a) 0.855 g (b) 17.1 g (c) 8.55 g (d) 85.5 g

10. The molar conductivity of 0.009 M aqueous solution of a weak acid (HA) is 0.005 S m^2 mol^{-1} and the limiting molar conductivity of HA is 0.05 S m^2 mol^{-1} at 298 K. Assuming activity coefficients to be unity, the acid dissociation constant (K_a) of HA at this temperature is:
(a) 1×10^{-4} (b) 0.1 (c) 9×10^{-4} (d) 1.1×10^{-5}

11. The colour of potassium dichromate is due to
(a) d-d transition (b) transition in K^+ ion.
(c) Ligand to metal charge transfer (d) Metal-to-ligand charge transfer.

12. Which one of the following configuration will show Jahn-Teller distortion in an octahedral field?
(a) High spin d^8 (b) High spin d^4 (c) High spin d^5 (d) Low spin d^6.

13. B_2H_6 and B_4H_{10}, respectively, are examples of
(a) Nido and arachno borans (b) Nido and closo boranes
(c) Closo and arachno boranes (d) Nido boranes.

14. Which of the following has a square planar geometry according to the VSEPR theory? Atomic number: B = 5, S = 16, Xe = 54.
(a) XeO_2F_2 (b) SF_4 (c) BF_4^- (d) XeF_4

15. The structure of rock salt consists of
(a) A cubic close-packed array of anions with cations in all the octahedral sites.
(b) A cubic close-packed array of cations with anions in all the tetrahedral sites.
(c) A hexagonal close-packed array of anions with cations in all the octahedral sites.
(d) A cubic close-packed array of anions with cations in all the tetrahedral sites.

16. Among lithium, nitrogen, carbon and oxygen, which element has the highest first ionization potential?
(a) Lithium (b) Nitrogen (c) Carbon (d) Oxygen

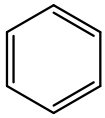
17. In which of the following C–H bond has the highest ‘s’ character?
(a) Acetylene (b) Ethylene (c) Methane (d) CH radical

18. Which one of the following is an electron deficient molecule according to the octet rule?
(a) CH_4 (b) $H_3N{:}BH_3$ (c) AlH_3 (d) GeH_4

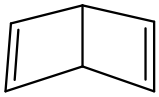
19. Which one of the following has the highest lattice energy?
(a) LiCl (b) $CaCl_2$ (c) LiF (d) KCl

20. At room temperature, HCl is a gas while HF is a liquid because
(a) Of a strong bond between H and F in HF
(b) HF is less acidic as compared to HCl
(c) Of strong intermolecular H-bonding in HF
(d) HCl is less acidic as compared to HF

21. Benzene and Dewar benzene are



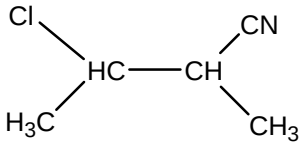
Benzene



Dewar benzene

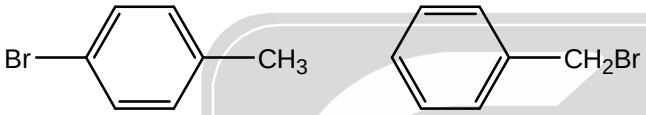
(a) Canonical forms (b) Structural isomers (c) Tautomers (d) Conformational isomers.

22. The IUPAC name of the following compound is:



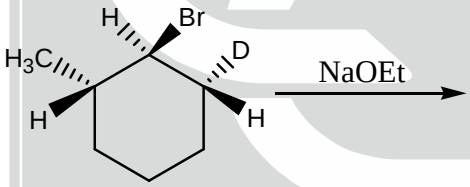
(a) 2-cyano-3-chlorobutane (b) 2-chloro-3-cyanobutane
(c) 2-methyl-3-chlorobutanenitrile (d) 3-chloro-2-methylbutanenitrile

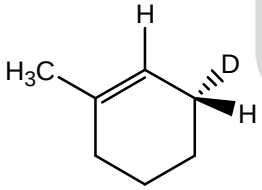
23. Which chemical test will distinguish the compounds shown below?

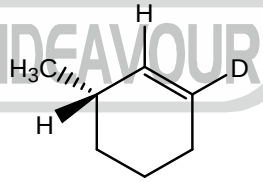


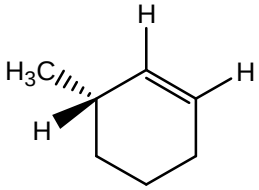
(a) Beilstein's flame test (b) Ethanolic silver nitrate test
(c) Sodium fusion test (d) Fehling's test

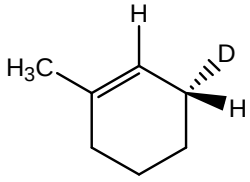
24. The reaction of the bromo compound shown below with sodium ethoxide gives predominantly

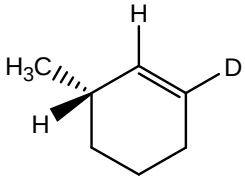


(a) 

(b) 

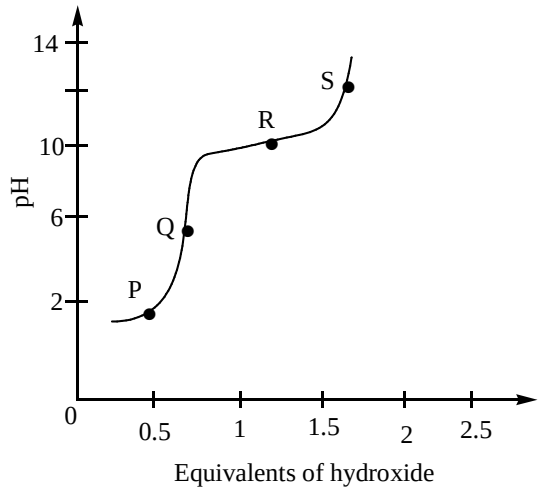
(c) 

(d) 

and 

25. Choose the correct order of reactivity for dehydration of the given alcohols using concentrated sulfuric acid.
(a) 2-methylpropan-2-ol > 2-butanol > 1-butanol
(b) 2-methylpropan-2-ol > 1-butanol > 2-butanol
(c) 2-butanol > 2-methylpropan-2-ol > 1-butanol
(d) 1-butanol > 2-butanol > 2-methylpropan -2-ol.

26. The titration curve of alanine hydrochloride is given below



The position in the graph that corresponds to the isoelectric point of alanine is:

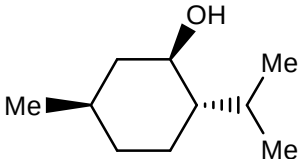
(a) P (b) Q (c) R (d) S

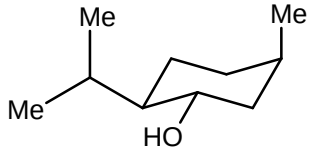
27. The absolute configurations at the two chiral centers in D-Ribulose are

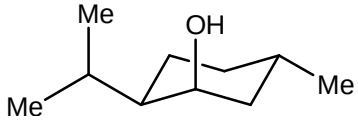
D-Ribulose

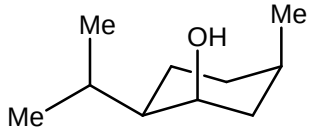
(a) 3R, 4R (b) 3R, 4S (c) 3S, 4R (d) 3S, 4S

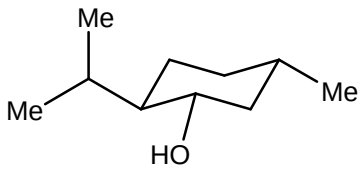
28. The most stable conformation of the molecule shown below is correctly represented by



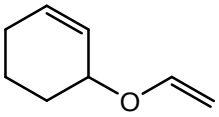
(a) 

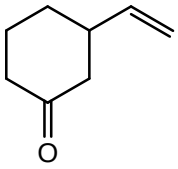
(b) 

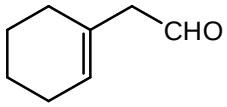
(c) 

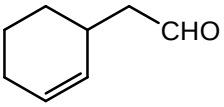
(d) 

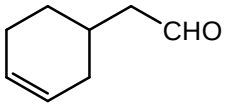
29. Thermal rearrangement of the following compound would give



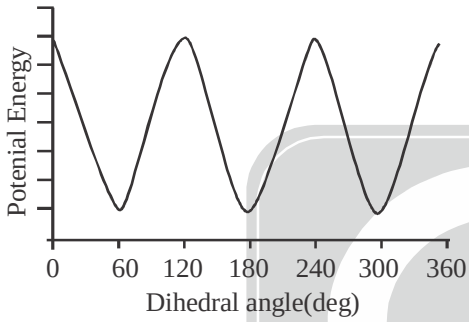
(a) 

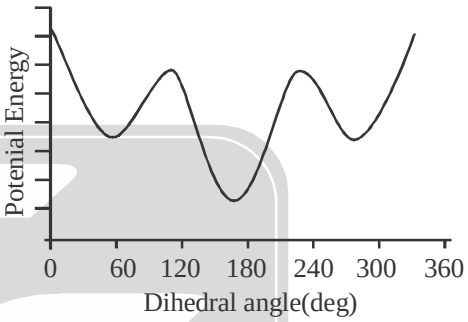
(b) 

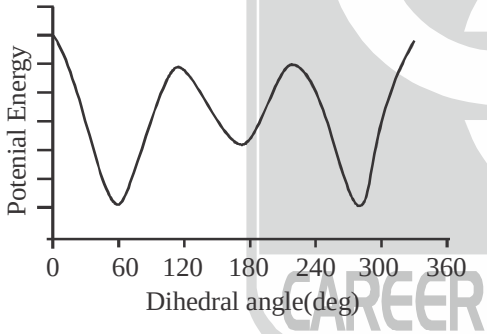
(c) 

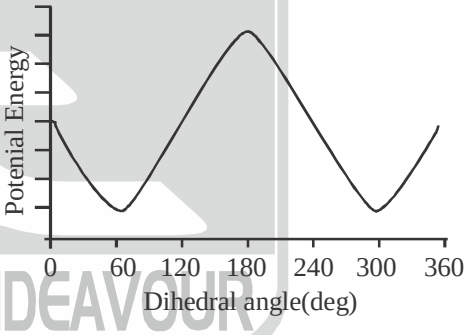
(d) 

30. The energy profile diagram that corresponds to 1, 2-dihydroxyethane for rotation around the C–C bond is

(a) 

(b) 

(c) 

(d) 

31. (a) Equilibrium constant for a reaction doubles as the temperature is increased from 300 K to 600 K. Calculate the standard reaction enthalpy (in kJ mol^{-1}) assuming it to be constant in this temperature range. (given R = 8.3 J K^{-1} mol^{-1}, ln2 = 0.7). **[9]**

(b) A 50 mL solution of 0.1 M monoprotic acid ($K_a = 1\times10^{-5}$ at 298 K) is titrated with 0.1 M NaOH at 298 K. Calculate the $[H^+]$ of the solution after the addition of 50 mL of NaOH at this temperature. (given $K_w = 1\times10^{-14}$ at 298 K) **[6]**

32. For the reaction, $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

the following mechanism has been proposed.

Initiation: $Br_2 + M \xrightarrow{k_i} Br^{\bullet} + Br^{\bullet} + M$

Propagation: $Br^{\bullet} + H_2 + \xrightarrow{k_p} HBr + H^{\bullet}$; $H^{\bullet} + Br_2 \xrightarrow{k_{p'}} HBr + Br^{\bullet}$

Retardation: $H^{\bullet} + HBr \xrightarrow{k_r} H_2 + Br^{\bullet}$

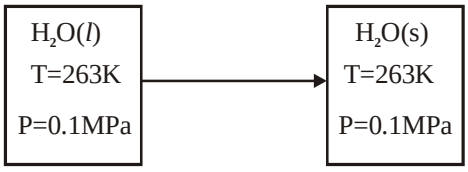
Termination: $Br^{\bullet} + Br^{\bullet} + M \xrightarrow{k_t} Br_2 + M + \text{energy}$

Where M is the initiator/terminator.

(a) Write the differential rate equations for the formation of the two intermediates $H^{\bullet}$ and $Br^{\bullet}$. **[6]**

(b) Using the steady-state approximate calculate the concentration of the intermediate $H^{\bullet}$ and $Br^{\bullet}$ and obtain the rate law for the formation of HBr. **[9]**

33. Calculate ΔH_m and ΔS_m for the process



Assume that at 273 K the molar enthalpy of fusion of ice is 6006 J mol^{-1}, the heat capacity $C_{p,m}(s)$ of ice is 38 J K^{-1} mol^{-1} and heat capacity $C_{p,m}(\ell)$ of liquid water is 76 J K^{-1} mol^{-1}. Consider the heat capacities to be constants. . **[15]**

(given: ln 263 = 5.57 and ln 273 = 5.61)

34. Two beakers, one containing 0.02 M $KMnO_4$, 0.2 M $MnSO_4$ and 0.5 M H_2SO_4 and another containing 0.15 M $FeSO_4$ and 0.05 M $Fe_2(SO_4)_3$, are connected by a salt-bridge Platinum electrodes are placed in each beaker and these two electrodes are connected via a wire with a voltmeter in between. H_2SO_4 is present in equal volumes in each beaker. Assume H_2SO_4 is completely ionized.

Given: $E^0_{Fe^{3+}/Fe^{2+}} = 0.8V$, $E^0_{MnO_4^-/Mn^{2+}} = 1.5\ V$, $\frac{2.303RT}{F} = 0.06V$ and log2=0.3

(a) Write the complete balanced redox reaction for this cell. **[6]**

(b) What would be the potential of each half-cell after the reaction has reached equilibrium? **[9]**

35. An atomic orbital is described by the wavefunction

$\psi(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\left(\frac{r}{a_0}\right)}$, where a_0 is the Bohr radius.

Given: $d\tau = r^2 \sin\theta dr d\theta d\phi$ and $\int_0^\infty r^n e^{-\beta r} d\tau = \frac{n!}{\beta^{n+1}}$ (n is a positive integer)

(a) Identify the atomic orbital and calculate the mean or the average radius of this orbital in terms of a_0. **[9]**

(b) Calculate the most probable radius (in terms of a_0) at which an electron will be found when it occupies this orbital. **[6]**

36. Identify W, X, Y and Z in the following sequence. **[15]**

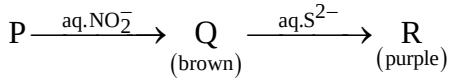
$$Li + W(g) \xrightarrow{\text{heat}} \underset{(\text{red})}{X} \xrightarrow{H_2O} Y(g) \xrightarrow{\text{alkaline } K_2HgI_4} \underset{(\text{brown})}{Z}$$

Y turns moist litmus paper blue. Write balanced chemical equation for the conversion of Y to Z.

37. (a) Draw the crystal field splitting diagram with appropriate labels for $[NiCl_4]^{2-}$. Determine the spin only magnetic moment and the crystal field stabilization energy (CFSE) for this complex. (given: atomic number of Ni = 28) **[9]**

(b) Write the balanced equations for the reactions involved in the iodometric estimation of Cu^{2+} using thiosulfate. **[6]**

38. (a) In the reaction sequence given below P is an anionic Fe(II) complex.



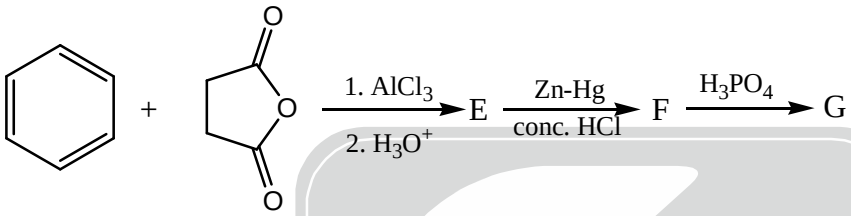
Identify P, Q and R. **[9]**

(b) Draw a properly labeled unit cell diagram of CsCl. Show through calculations that there is only one CsCl per unit cell. **[6]**

39. (a) Write the balanced chemical equations for the reactions involved in the synthesis of borazine using ammonium chloride as one of the starting materials. Write the structure of borazine. **[9]**

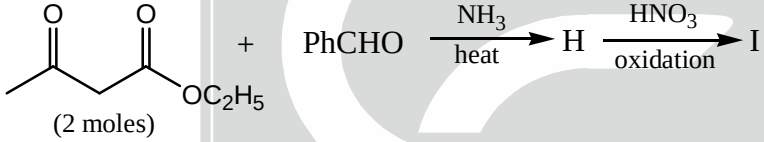
(b) Draw Lewis structures of SF_4 and NO_3^- **[6]**

40. (a) Complete the following sequence by identifying E, F and G.

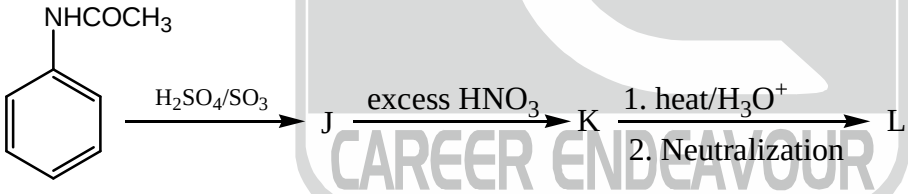


[9]

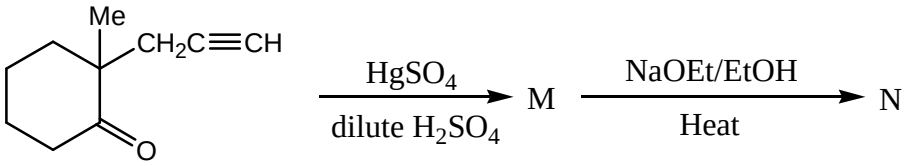
(b) Identify H and I in the reactions below **[6]**



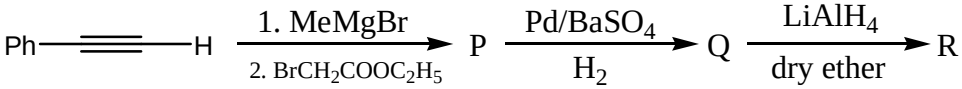
41. (a) Identify the products J, K, and L in the following reactions. Lassaigne's test for L shows the presence of nitrogen only. **[9]**



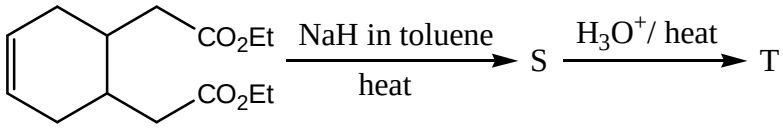
(b) Write the structure of M and N in the following reactions. **[6]**



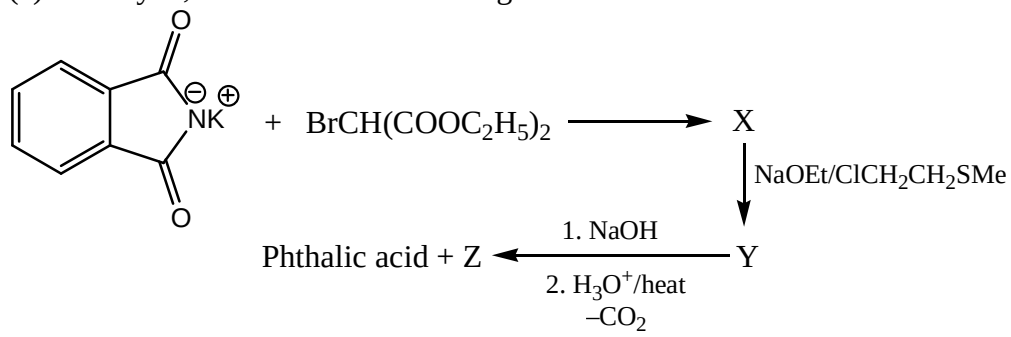
42. (a) Write the structures of P, Q and R in the given reaction sequence. **[9]**



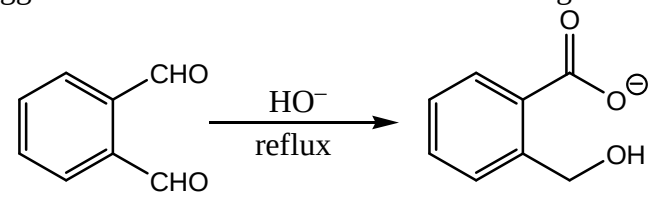
(b) Identify S and T in the reactions given below: **[6]**



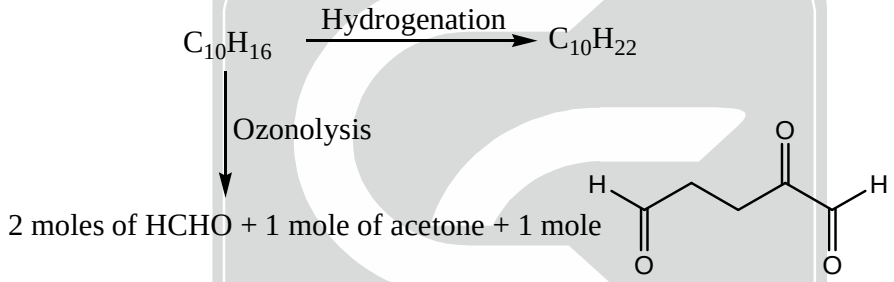
43. (a) Identify X, Y and Z in the following reactions. **[9]**



(b) Suggest a suitable mechanism for the following reaction. **[6]**



44. Consider the following reactions for a compound with molecular formula $C_{10}H_{16}$.



(a) Write structues that are consistent with the above data for the formula $C_{10}H_{16}$. **[9]**

(b) Given that myrcene is a terpene and has the molecular formula $C_{10}H_{16}$, using the isoprene rule identify the correct structure for myrcene among the structures elucidated in part(a). **[6]**