

IIT-JAM: 2011

Chemistry

Instructions: Q.1-30 (Objective questions) carry three marks each and Q.31-44 (Subjective questions) carry fifteen marks each.

❖ Question Paper

Part I: Objective Questions

Q.1 – Q.30 carry three marks each.

Q.1 The pair of semimetals in the following is:

- (a) Al, Si (b) Ge, As (c) Sb, Te (d) Ca, B

Q.2 Most probable oxidation states for both Cr and Mo are

- (a) +2, +3, +4 (b) +2, +3, +5 (c) +2, +3, +6 (d) +3, +4, +5

Q.3 The correct order of acidic character is:

- (a) $\text{Al}_2\text{O}_3 > \text{MgO} > \text{SiO}_2 > \text{P}_4\text{O}_{10}$ (b) $\text{P}_4\text{O}_{10} > \text{Al}_2\text{O}_3 > \text{MgO} > \text{SiO}_2$
(c) $\text{P}_4\text{O}_{10} > \text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{MgO}$ (d) $\text{SiO}_2 > \text{P}_4\text{O}_{10} > \text{Al}_2\text{O}_3 > \text{MgO}$

Q.4 The pair of amphoteric oxides is:

- (a) VO, Cr₂O₃ (b) V₂O₃, Cr₂O₃ (c) VO₂, Cr₂O₃ (d) V₂O₅, CrO₃

Q.5 In the structure of $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$

- (a) All four B atoms are trigonal planar
(b) One B atom is tetrahedral and other three are trigonal planar
(c) Three B atom are tetrahedral and other one is trigonal planar
(d) Two B atom are tetrahedral and other two are trigonal planar

Q.6 The pH of an aqueous solution of Al^{3+} is likely to be

- (a) Neutral (b) Acidic (c) Slightly basic (d) Highly basic

Q.7 Hydrolysis of $(\text{CH}_3)_2\text{SiCl}_2$ and CH_3SiCl_3 leads to

- (a) Linear chain and cross-linked silicones, respectively
(b) Cross-linked and linear chain silicones, respectively
(c) Linear chain silicones only
(d) Cross-linked silicones only

Q.8 The oxide that has the inverse spinel structure is:

- (a) FeCr_2O_4 (b) MnCr_2O_4 (c) CoAl_2O_4 (d) Fe_2CoO_4

Q.9 The transition metal monoxide that shows metallic conductivity is:

- (a) NiO (b) MnO (c) TiO (d) CoO

Q.10 The metal that is extracted by the reduction method is:

- (a) Al (b) Au (c) Hg (d) Mg

Q.11 The most viscous liquid is:

- (a) Water (b) Methanol (c) Ethylene glycol (d) Glycerol

Q.12 In ammonical buffer, oxine (8-hydroxyquinoline) forms yellow precipitate with

- (a) Mg(II) (b) Ca(II) (c) Ba(II) (d) Sr(II)

Q.13 Addition of an aqueous solution of Fe(II) to potassium hexacyanochromate(III) produces a brick-red coloured complex, which turns dark green at 100°C . The dark green complex is:

- (a) $\text{Fe}_4[\text{Cr}(\text{CN})_6]_3$ (b) $\text{KFe}[\text{Cr}(\text{CN})_6]$ (c) $\text{KCr}[\text{Fe}(\text{CN})_6]$ (d) $\text{Fe}[\text{Cr}(\text{CN})_6]$

Q.14 In the following equation X is ${}^{241}_{95}\text{Am} + \alpha \rightarrow {}^{243}_{97}\text{Bk} + X$

- (a) $2{}^1_0\text{n}$ (b) $1{}^1_0\text{n}$ (c) $2{}^1_1\text{H}$ (d) $4{}^2_2\text{He}$

Q.15 Based on the principle of equipartition of energy, the molar heat capacity of CO_2 at constant volume $C_{v,m}$ is:

- (a) $3.5R$ (b) $6R$ (c) $6.5R$ (d) $9R$

Q.16 One mole of a Vander Waal gases undergoes reversible isothermal transformation from an initial volume V_1 to a final volume V_2 . The expression for the work done is:

- (a) $RT \ln \frac{V_2}{V_1} + a(V_2 - V_1)$ (b) $-RT \ln \frac{V_2 - b}{V_1 - b} + a \left\{ \frac{1}{V_1} - \frac{1}{V_2} \right\}$
 (c) $RT \ln \frac{P_2}{P_1}$ (d) $RT \ln \frac{V_2 - b}{V_1 - b} - a \left\{ \frac{1}{V_1} - \frac{1}{V_2} \right\}$

Q.17 The scalar product of two vectors u and v , where $u = 2\hat{i} + 3\hat{j} - 5\hat{k}$ and $v = \hat{i} + \hat{j} + 3\hat{k}$, is:

- (a) -10 (b) $2\hat{i} + 3\hat{j} - 15\hat{k}$ (c) $3\hat{i} + 4\hat{j} - 2\hat{k}$ (d) 10

Q.18 The minimum concentration of silver ions that is required to start the precipitation of Ag_2S ($K_{sp} = 1 \times 10^{-51}$) in a 0.1 M solution of S^{2-} is:

- (a) $1 \times 10^{-49} \text{ M}$ (b) $1 \times 10^{-50} \text{ M}$ (c) $1 \times 10^{-26} \text{ M}$ (d) $1 \times 10^{-25} \text{ M}$

Q.19 Identify the correct statement regarding Einstein's photoelectric effect

- (a) The number of electrons ejected depends on the wavelength of incident radiation
 (b) Electron ejection can occur by any wavelength of incident radiation.
 (c) The number of electrons ejected at a given incident wavelength depends on the intensity of the radiation.
 (d) The kinetic energy of the ejected electrons independent of the wavelength of incident radiation.

Q.20 The hydrolysis constant (K_h) of NH_4Cl is 5.6×10^{-10} . The concentration of H_3O^+ in a 0.1 M solution of NH_4Cl at equilibrium is:

- (a) $\sqrt{5.6 \times 10^{-11}}$ (b) $\sqrt{5.6 \times 10^{-10}}$ (c) 5.6×10^{-10} (d) 2.8×10^{-5}

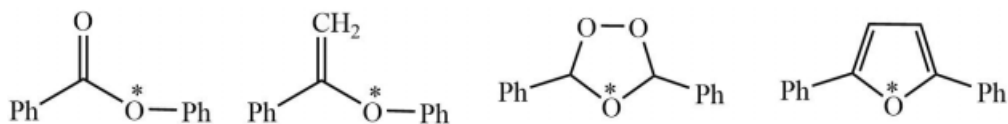
Q.21 The acid dissociation constant (K_a) for HCOOH , CH_3COOH , CH_2ClCOOH and HCN at 25°C are 1.8×10^{-4} , 1.8×10^{-5} , 1.4×10^{-3} and 4.8×10^{-10} , respectively. The acid that gives highest pH at the equivalence point when 0.2 M solution of each acid is titrated with a 0.2 M solution of sodium hydroxide is:

- (a) HCOOH (b) CH_3COOH (c) CH_2ClCOOH (d) HCN

Q.22 For an ideal gas undergoing a reversible Carnot cycle, the plot of enthalpy (H) versus entropy (S) is:

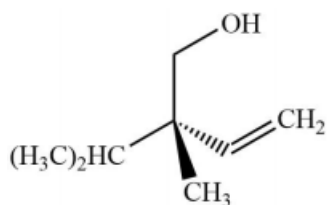


Q.23 Hybridizations of the atoms indicated with the asterisk in the following compounds sequentially are



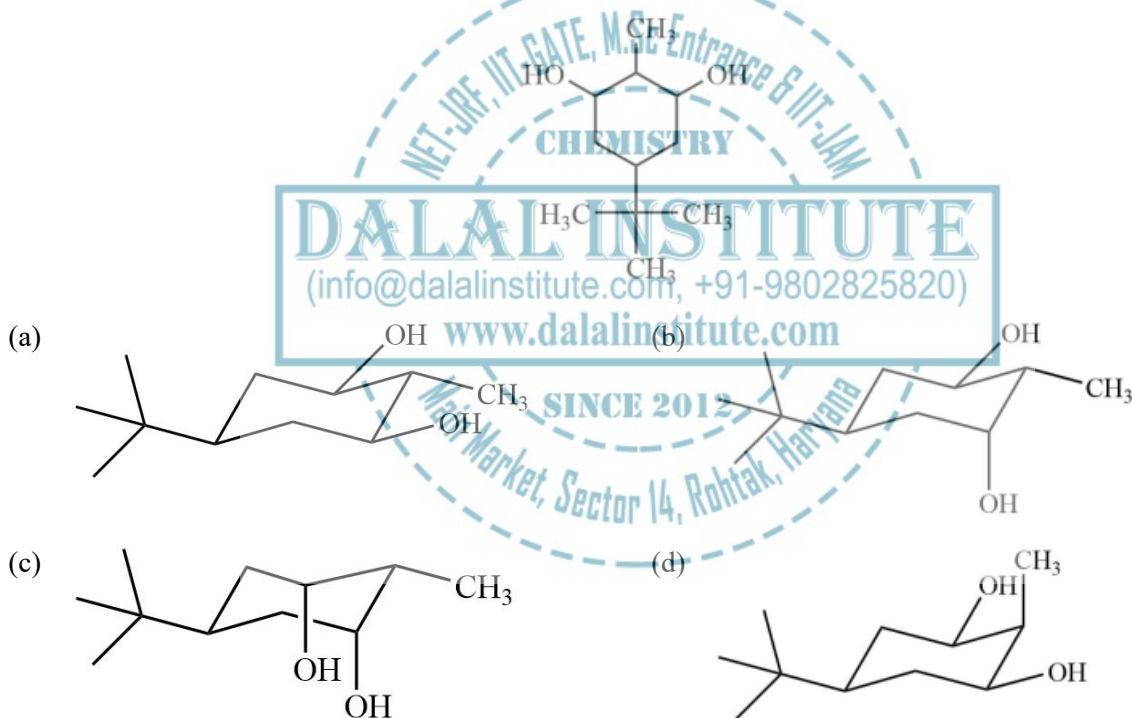
- (a) $\text{sp}^2, \text{sp}^2, \text{sp}^3, \text{sp}^2$ (b) $\text{sp}^2, \text{sp}^3, \text{sp}^3, \text{sp}^2$ (c) $\text{sp}^3, \text{sp}^3, \text{sp}^3, \text{sp}^2$ (d) $\text{sp}^2, \text{sp}^2, \text{sp}^3, \text{sp}^3$

Q.24 The Cahn-Ingold-Prelog (CIP) priorities of the groups and the absolute configuration (R/S) of the following compound are



- (a) $\text{CH}_2\text{OH} > \text{CH}(\text{CH}_3) > \text{CH}=\text{CH}_2 > \text{CH}_3$ and S (b) $\text{CH}_2\text{OH} > \text{CH}=\text{CH}_2 > \text{CH}(\text{CH}_3) > \text{CH}_3$ and S
 (c) $\text{CH}_2\text{OH} > \text{CH}=\text{CH}_2 > \text{CH}(\text{CH}_3) > \text{CH}_3$ and R (d) $\text{CH}_2\text{OH} > \text{CH}(\text{CH}_3) > \text{CH}=\text{CH}_2 > \text{CH}_3$ and R

Q.25 The optical active stereoisomer of the following compound is:

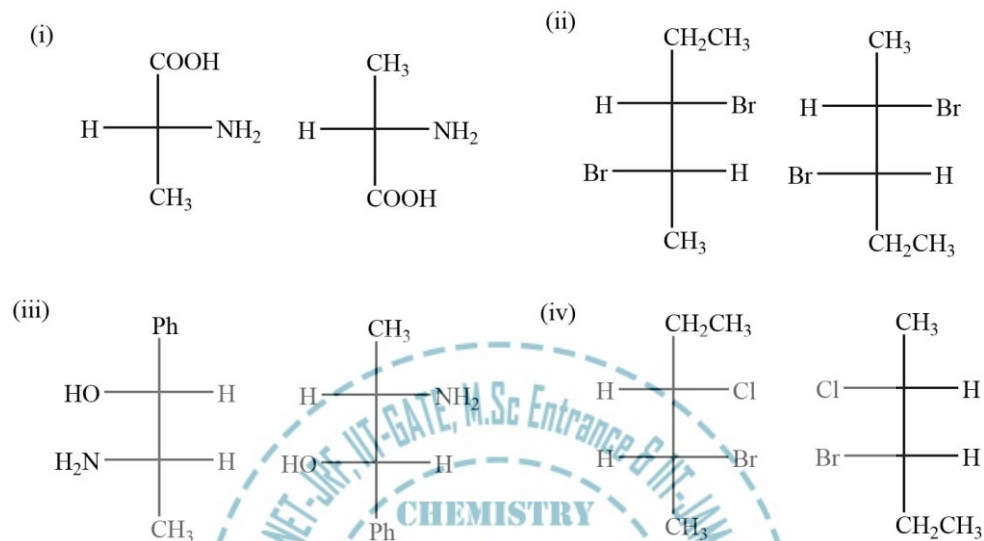


Q.26 The correct relationship within each pair of the natural products is:

- (a) Camphor–terpene; insulin–protein; nicotine–alkaloids; streptomycin–carbohydrate
 (b) Camphor–terpene; insulin–carbohydrate; nicotine–alkaloids; streptomycin–lipid
 (c) Camphor–alkaloids; insulin–protein; nicotine–terpene; streptomycin–carbohydrate

(d) Camphor– carbohydrate; insulin–protein; nicotine–alkaloids; streptomycin–terpene

Q.27 The correct sequence of relationships between the compounds of the following pairs i-iv is:



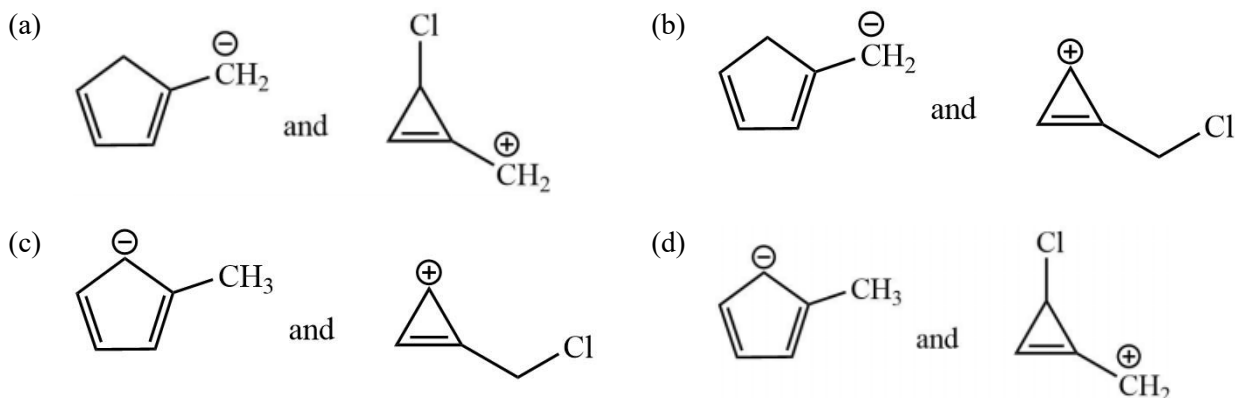
- (a) Identical, enantiomers, diastereomers and structural isomers.
 (b) Enantiomers, Identical, structural isomers and diastereomers.
 (c) Enantiomers, Identical, diastereomers and structural isomers.
 (d) Identical, identical, diastereomers and structural isomers.

Q.28 The incorrect statement in the following is:

- (a) The nucleobase pairs are aligned perpendicular to the helical axis in DNA.
 (b) RNA contains uracil and thymine, but DNA contains only thymine.
 (c) All naturally occurring amino acids with the exception of glycine are chiral.
 (d) All enzymes are proteins, but all proteins are not necessarily enzymes.

Q.29 The product P and Q in the following reactions, respectively, are





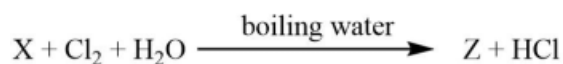
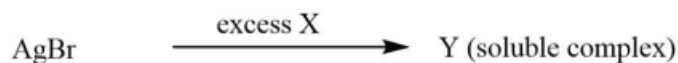
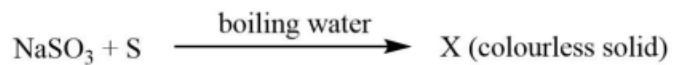
Q.30 The major product of the following reaction is



Part II: Subjective Questions

Q.31 – Q.44 carry fifteen marks each.

Q.31 (a) In the following reactions, identify X, Y and Z.



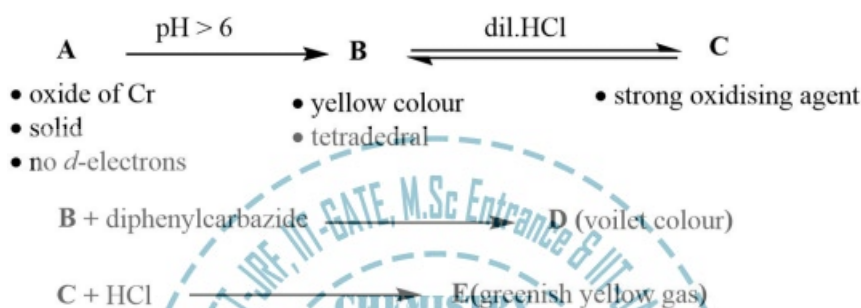
(b) Draw the structures of $\text{S}_4\text{N}_4\text{H}_4$ and $\text{N}_4\text{S}_4\text{F}_4$.

Q.32 (a) The magnetic moment of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ varies with temperature. The magnetic moments at 200K and 50K are 4.9 BM and 0 BM, respectively. Write the d-electron configurations of Fe at both temperatures and given reason for the observed change in the magnetic moment. (phen = 1,10-phenanthroline)

(b) PCl_5 exists as a discrete covalent molecule in the gaseous state, but is ionic in the solid state. Draw the structures of PCl_5 in gaseous and solid states.

Q.33 In the following equilibrium and reactions, identify species B and E.

Write the balanced chemical equation for the conversion of C to E.



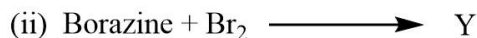
Q.34 (a) Identify species A and C in the following.

Write the balanced chemical equation for the conversion of A to A^{3+} .



Hint: C on the dilution with water gives B

(b) Draw the structures of X and Y in the following reactions.



Q.35 (a) The molar conductances at infinite dilution for BaCl_2 , KCl , K_2SO_4 and Cl^- are 280, 150, 300 and 76 $\text{ohm}^{-1}\text{m}^2\text{mol}^{-1}$, respectively. Calculate the transport number of Ba^{2+} in BaSO_4 solution at infinite dilution.

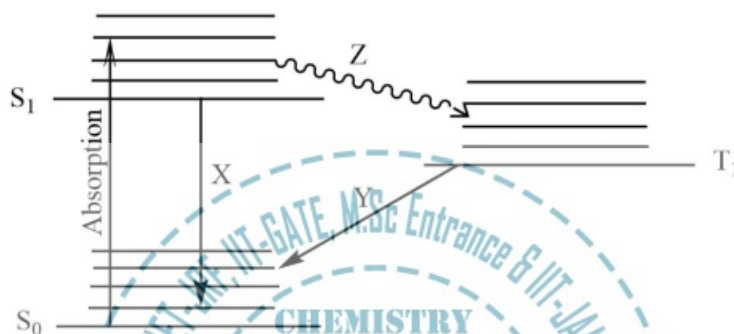
(b) If 4 moles of a MX_2 salt in 1 kg of water raises the boiling point of water by 3.2 K. calculate the degree of dissociation of MX_2 in the solution.

Q.36 (a) For the reaction $R \rightarrow P$, the plot of $\ln[R]$ versus time(t) gives a straight line with a negative slope. The half-life for the reaction is 3 minutes.

($\ln 2 = 0.693$, $\ln 0.1 = -2.303$)

- Derivative the expression for $t_{1/2}$.
- Calculate the slope of the straight line
- Calculate the time required for the concentration of R to decrease to 10% of its initial value.

(b) shown below is the Jablonski diagram that describes various photophysical processes. The solid arrow represents radiative transitions and the wavy arrow represents a non-radiative transition.



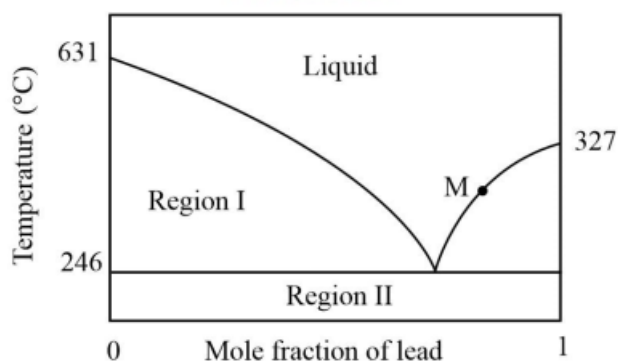
(i) Name the photophysical pathways X, Y and Z.

(ii) Which of the radiative decay is faster?

Q.37 (a)(i) Given that $\Delta G = -nFE$, derive the expression for the temperature dependence of the cell potential (E) in terms of change in entropy.

(ii) For a cell reaction, E (at 25°C) = 1.26 V, $n = 2$ and $\Delta S = -96.5 \text{ J K}^{-1} \text{ mol}^{-1}$. calculate E at 85°C by assuming ΔS to be independent of temperature. ($F = 96500 \text{ C mol}^{-1}$).

(b) The phase diagram for the lead-antimony system at a certain pressure is given below.



(i) Identify the phases and components in region I and region II.

(ii) Calculate the number of degree of freedom (variance) at point M.

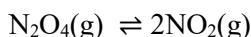
Q.38 (a) One mole of an ideal gas initially at 300K and at a pressure of 10 atm undergoes adiabatic expansion.

(i) Reversibly and

(ii) Irreversibly against a constant external pressure of 2 atm until the final pressure becomes equal to the external pressure.

Calculate ΔS_{system} for (i) and (ii). For (ii), express the final answer in terms of a R. Given :Molar heat capacity at constant volume $C_{v,m} = 3R/2$.

(b) For the following equilibrium at 300°C.



Calculate K_p when N_2O_4 is 30% dissociated and the total pressure is 2 bar.

Q.39 The Maxwell probability distribution of molecular speeds for a gas is:

$$F(v)dv = 4\pi v^2 \left\{ \frac{m}{2\pi kT} \right\}^{3/2} \exp \left\{ -\frac{mv^2}{2kT} \right\} dv$$

where 'v' is the speed, 'm' the mass of a gas molecule and k the Boltzmann constant.

(i) Use $F(v)$ to show that the most probable speed v_{mp} is given by the expression,

$$v_{mp} = \left\{ \frac{2RT}{M} \right\}^{1/2}$$

(ii) Use $R = 8 \text{ J K}^{-1} \text{ mol}^{-1}$ in the expression to calculate the v_{mp} is for $\text{CH}_4(\text{g})$ at 127°C.

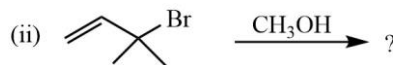
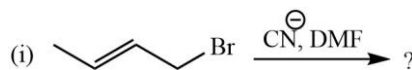
(b) The wavefunction of a quantum state of hydrogen atom with principal quantum number $n = 2$ is:

$$\Psi_{2lm}(r, \theta, \phi) = \frac{1}{\sqrt{32\pi}} \left\{ \frac{1}{a_0} \right\}^{3/2} \left\{ 2 - \frac{r}{a_0} \right\} \exp \left\{ -\frac{r}{2a_0} \right\}$$

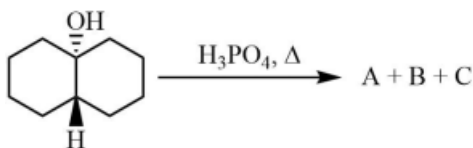
(i) Identify the values of quantum numbers l and m h. hence the atomic orbital.

(ii) Find where the radical node of the wavefunction occurs.

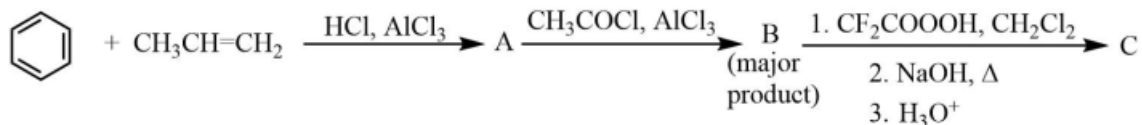
Q.40 (a) Write the possible substitution products in the following reactions. Indicate the types of mechanism (S_N1/S_N2) that is/are operative in each reaction.



(b) Write the elimination products A to C in the following reaction. Identify the major product



Q.41 (a) Write the structures of A to C in the following reaction sequence.



(b) Write the structures of D and E in the reactions given below.



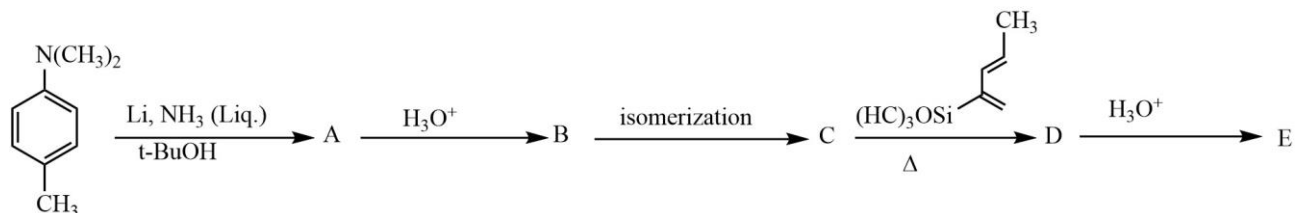
Q.42(a) Write the structures of A to C in the following reaction sequence.



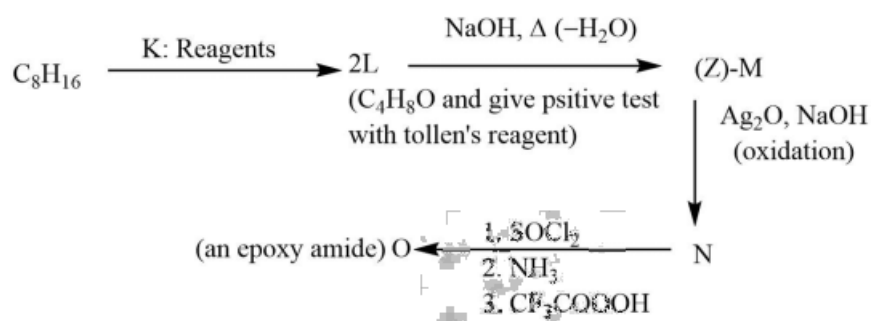
(b) Write the structures of D and E in the following reaction.



Q.43 Write the structures of products A to E in the following reaction sequence.



Q.44 Oxanamide O, a tranquilizer, is synthesized according to the following reaction scheme. Write the missing structures and reagents of K to O.



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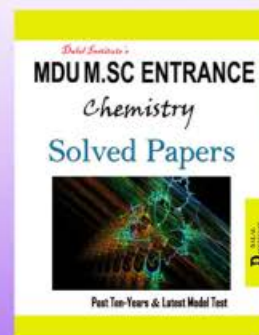
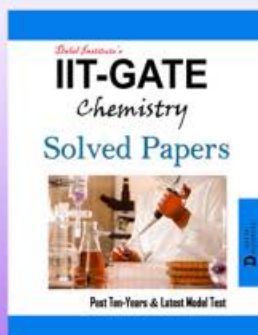
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