(1)   Your Roll No. 2022

Sr. No. of Question Paper : 730   B

Unique Paper Code   : 32171201

Name of the Paper   : Organic Chemistry – I

Name of the Course   : **B.Sc. (H) Chemistry**

Semester   : II

Duration : 3 hours   Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.

2. Attempt **six** questions in all.

3. **All** questions carry equal marks.

1. Give reasons for the following statements. Attempt any **five** :

    (a) Methyl group in Toluene is ortho-para directing.

    (b) Chair conformation of cyclohexane is more stable than boat conformation.

    (c) Both racemic mixture and meso compound are optically inactive.
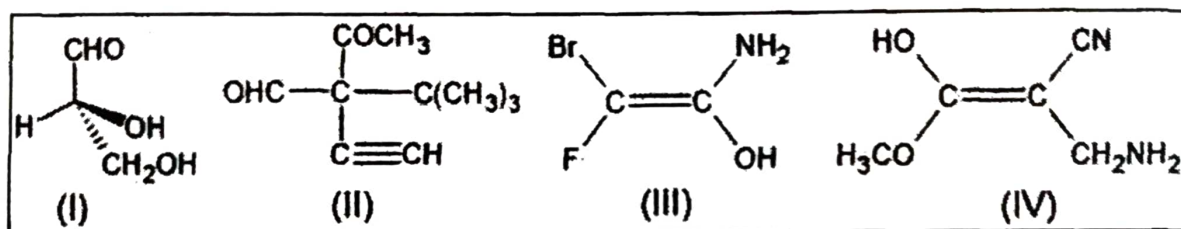
(d) Phenols are less acidic than carboxylic acids.

(e) Terminal alkynes are acidic in nature.

(f) Alkenes are more reactive than alkynes towards electrophilic addition reactions. $(2.5 \times 5 = 12.5)$

2. (a) Assigning priorities, determine the configuration (E/Z or R/S) for the following compounds

(b) An alkene on reductive ozonolysis yields a mixture of two isomers with molecular formula C_3H_6O. Identify the structure of the alkene and the products. Write the product of the reaction between alken e with HBr.   (8,4.5)

3. (a) Comment on the aromaticity of the following compounds

     (i) Naphthalene

     (ii) Cyclopentadienyl cation

     (iii) Cycloheptatriene

     (iv) Pyridine

(b) A compound (4.25 g in 100 mL)'s solution in chloroform was taken in a polarimeter tube of length 5 cm and its optical rotation (at 25°C) was observed to be −1.2°. Calculate the specific rotation. (8,4.5)

4. (a) Carry out the following conversions :

   (i) Propane to 2,3-Dimethyl butane

   (ii) Propyne to Pent-2-yne

   (iii) But-1-yne to Butan-2-one
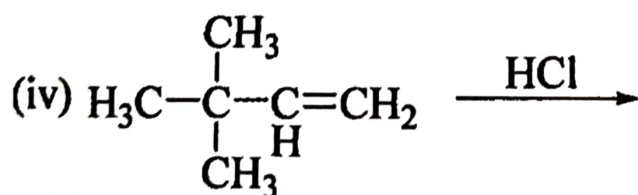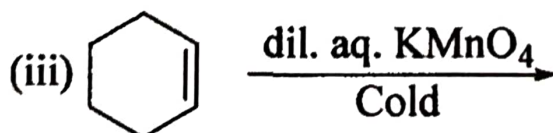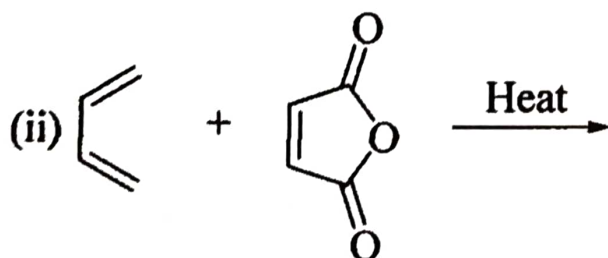
   (iv) But-1-ene to But-2-ene

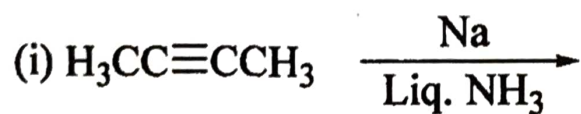   (b) Write down the mechanism involved in Friedel Craft's alkylation of benzene with propyl chloride. (8,4.5)

5. (a) Draw the Fischer projection for all the possible stereoisomers of butane-2,3-diol. State the correlation among these stereoisomers? Comment on the optical activity of these isomers.

   (b) In halogenation of alkanes why chlorination is more reactive but less selective than bromination?

(c) Why peroxide effect is observed in case of addition of HBr?   (5,4.5,3)

6.   (a) Complete the following reaction with product(s) (including stereochemistry wherever applicable)

(i) $H_3CC{\equiv}CCH_3$ $\xrightarrow[\text{Liq. } NH_3]{\text{Na}}$

(ii) $+$ $\xrightarrow{\text{Heat}}$

(iii) $\xrightarrow[\text{Cold}]{\text{dil. aq. } KMnO_4}$

(iv) $H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{H}{\overset{|}{C}}{=}CH_2$ $\xrightarrow{HCl}$

(b) Calculate the percentage of isomers formed on monochlorination of n-butane. Relative rates of hydrogens $3°:2°:1°$ towards chlorination at room temperature are $5.0:3.8:1$.   (8,4.5)

7. (a) Comment on the stereochemistry of the products formed when cis and trans isomers of but-2-ene reacts with bromine solution. Explain the reaction with mechanism.

   (b) State limitations of Wurtz reaction. How Corey-House synthesis overcomes these limitations? Give with suitable examples.

   (c) Which is more acidic, p-nitrophenol or o-nitrophenol? Give reasons. (5,4.5,3)

8. (a) How will you chemically distinguish between 1-butyne and 2-butyne?

   (b) Convert the following structures to standard Fischer projections :

   (I) (II)
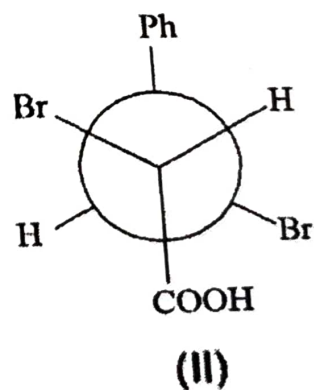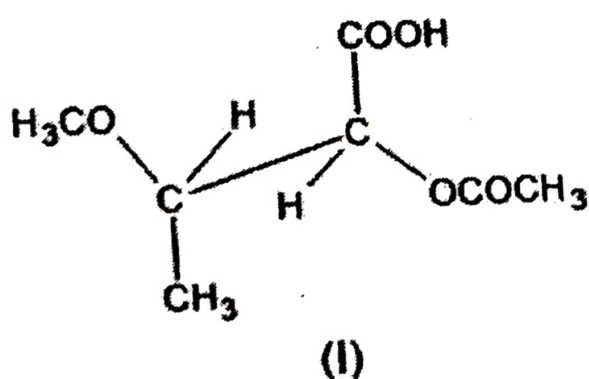
   (c) Explain why 1,3-pentadiene is more stable than 1,4-pentadiene?

(d) Why nitration of toluene is faster than nitration of benzene?

(2,4,3,3.5)

9.   Write short notes on the following : **(any four)**

(a) E1 and E2 reactions (including mechanism)

(b) D,L system of configuration (including limitations)

(c) Oxymercuration – Demercuration Reaction (including mechanism)

(d) Allylic Halogenation using NBS (including mechanism)

(e) Nucleophilic addition reactions in alkynes

(3.5,3,3,3)

[This question paper contains 8 printed pages.]

② Your Roll No. 2022

Sr. No. of Question Paper : 748   **B**

Unique Paper Code   : 32171202

Name of the Paper   : Physical Chemistry II

Name of the Course   : **B.Sc. (Hons.)**

Semester   : II

Duration : 3 hours   Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.

2. Answer any **six** questions.

3. Use of calculator is allowed.

1. (a) Why ΔG is used more compared to ΔA to express the condition of spontaneity of the reaction?

(2)

(b) Give reason why reversible processes are ideal processes & cannot be carried out in practice.

(2)

P.T.O.

(c) How equilibrium constant K_p is a dimensionless quality? (2)

(d) Why it is necessary to make standard solutions in standard flasks instead of a beaker? (2)

(e) Explain Q is a path function and not a state function. (2)

(f) Predict whether the following variables are intensive or extensive :

mass, enthalpy, mole fraction, boiling point, entropy (2.5)

2. (a) A 25 g mass of ice at 273 K is added to 150 g of liquid water at 360K at constant P. What is the final state of the system? Calculate ΔS for the process. Given $\Delta H_{fus.}$ (H_2O) = 6.0095 kJ mol^{-1}, C_p $(H_2O, 1)$ = 75.29 JK^{-1} mol^{-1} & T_m (H_2O, S) = 273 K. (4)

(b) Derive the relation : (4)

$$\left(\frac{\partial V}{\partial S}\right)_T = \left(\frac{\partial T}{\partial p}\right)_V$$
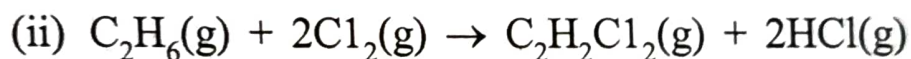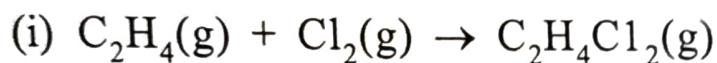
(c) Show that entropy is a state function & dS is an exact differential using first law of thermodynamics. (4.5)

3.   (a) Prove the Kirchhoff s relations: (4)

         (i) $\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$

         (ii) $\Delta U_2 - \Delta U_1 = \Delta C_v (T_2 - T_1)$

   (b) Calculate the enthalpy change for the following reactions :

         (i) $C_2H_4(g) + Cl_2(g) \rightarrow C_2H_4Cl_2(g)$

         (ii) $C_2H_6(g) + 2Cl_2(g) \rightarrow C_2H_2Cl_2(g) + 2HCl(g)$

         Given B.E. (C-C) = 348 kJ mol^{-1}

         B.E. (C=C) = 610 kJ mol^{-1}

         B.E. (C–H) = 413 kJ mol^{-1}

         B.E. (Cl–Cl) = 242 kJ mol^{-1}

         B.E. (C–Cl) = 328 kJ mol^{-1}

         B.E. (H–Cl) = 432 kJ mol^{-1} (4)

   (c) Define enthalpy of neutralization. Enthalpy of neutralization of HCl by NaOH is 257.32 kJ mol^{-1} and by NH_4OH is –51.34 kJ mol^{-1}. Calculate the enthalpy of dissociation of NH_4OH.   (4.5)

4.   (a) Prove thermodynamic equation of state :

$$\left(\frac{\partial U}{\partial V}\right)_T + p = T\left(\frac{\partial p}{\partial T}\right)_V$$

                                                            (4)

    (b) For an ideal gas $C_{pm} = (5/2\ R)$. Calculate the change in entropy when 3 moles of gas is heated from 300K to 600K at

        (i) constant pressure

        (ii) constant volume   (4)

    (c) Show that :

        (i) $\left(\dfrac{\partial U}{\partial V}\right)_T = 0$ for an ideal gas.

        (ii) $C_p - Cv = R$ for one mole of an ideal gas.

                                                            (4.5)

5.   (a) Derive Gibbs – Helmholtz equation,

$$\frac{\Delta G}{T} = \frac{\Delta H}{T} + I.$$

    Where I is the constant of integration.   (4)

(b) Starting from the fundamental expressions of first and second laws of thermodynamics derive the following relations :

    (i) $dA = -SdT - pdV$

    (ii) $dG = -SdT + Vdp$

                                               (4)

(c) Derive Gibbs Duhem equation and prove :

$$\sum_i n_i dV_{i,pm} = 0$$

                                              (4.5)

6. (a) (i) Show that the pressure for a gas obeying

$$\left(p + \frac{a}{V^2}\right)(V) = RT$$

        is a state function.   (2)

    (ii) Prove that :

$$\left(\frac{\partial H}{\partial P}\right)_T = 0$$

                                          (2)

(b) In the following reactions, involving change in number of mol, what will be the effect of increase

in pressure from external source on the equilibrium of the reactions :

$$N_2O_4(s) \rightarrow 2NO_2(g)$$

$$2SO_2(s) + O_2(g) \rightarrow 2 SO_3(g) \tag{4}$$

(c) 1 mole of an ideal gas at 300K expands isothermally and reversible from an initial volume of 2 litres to a final volume of 20 litres. Calculate q, w, ΔU, ΔH, ΔS and ΔG. (4.5)

7. (a) The boiling point of chloroform was raised by 0.325K when 5.141×10^{-4} kg of anthracene was dissolved in 3.5×10^{-2} kg of chloroform. Calculate the molar mass of solute.

$$K_b = 3.9 \text{ K kg mol}^{-1}. \tag{4}$$

(b) van't Hoff factor, i, for aqueous solution of both NaCl and CH_3COOH depends on the concentration of the solution. Explain. (4)

(c) At 480K and a total pressure of 1 atmosphere, a mixture consisting of nitrogen and hydrogen in the mole ratio of 1:3 contains 16% ammonia at equilibrium. Calculate K_p for the reaction. (4.5)

8. (a) What is the Osmotic pressure at 25°C when 72.5 mL of a solution containing 4.25 grams of electrolyte $CaCl_2$ (molar mass = 111 g/mol) is prepared? (4)

(b) How much heat (in kJ) is needed to convert 100.0 grams of ice at −10°C to steam at 115°C?

(4)

(c) Prove that :

(i) $TV^{\gamma-1}$ = constant

(ii) PV^{γ} = constant (4.5)

9. (a) How many grams of non-electrolyte sucrose (molar mass = 342 g/mole) must be added to 450 g of water (molar mass = 18.0 g/mole) to change its vapour pressure of 745 mm Hg at 100°C? (4)

(b) State the third law of thermodynamics. Write the expressions for the change in entropy per mole of a substance undergoing each of the phase transitions – fusion, vaporization and (4) sublimation.

(c) Explain :

    (i) Criteria for spontaneity and equilibrium

    (ii) Le Chatelier's principle.   (4.5)