This question paper contains **8** printed pages] (15)

2018

Roll No. | | | | | | | | | | | |

S. No. of Question Paper : **6490**

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**

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

Answer *six* questions in all.

Question No. **1** is compulsory.

1. Attempt any *five* :

(*a*) Giving reasons, arrange the following carbanions in increasing order of stability :

$C_6H_5\bar{C}H_2$ (I) , $(C_6H_5)_3\bar{C}$ (II) , $(C_6H_5)_2\bar{C}H$ (III)

P.T.O.

(*b*) Explain the following :

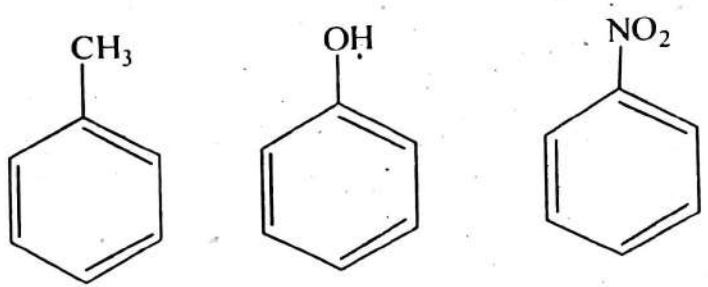
(*i*) Benzylamine is more basic than aniline.

(*ii*) α-bromobutanoic acid is stronger acid than β-bromobutanoic acid.

(*c*) Define the terms enantiomers and diastereoisomers. Explain with suitable examples.

(*d*) Explain why 1, 3-pentadiene is more stable than 1, 4-pentadiene.

(*e*) Giving reasons, arrange the following in increasing order of reactivity towards ring bromination :



(*f*) How would you distinguish 1-butyne from 1-butene chemically ?

(*g*) Draw all conformations of 1, 2-dimethylcyclohexane. Which conformer is most stable and why ?

(*h*) Why is nitration of toluene faster than nitration of nitrobenzene ? 5×3=15

2. (*a*) Carry out the following conversions (any *three*) :

(*i*) 2-Pentanone from 1-pentene

(*ii*) Chloroprene from acetylene

(*iii*) 2, 3-Dimethylbutane from propane

(*iv*) 1-Phenylethane from bromobenzene

(*v*) Propyne to tert.-butylalcohol.

(*b*) Write down the mechanism involved in bromination of aromatic hydrocarbons.

(*c*) Giving reasons, arrange the following in increasing order of boiling points :

Neopentane, *n*-hexane, 2-methylpentane, 2, 3-dimethylbutane. 6,3,3

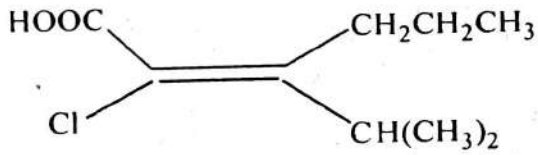
P.T.O.

3. (*a*) Draw the Fischer projections for all possible stereoisomers of butane-2, 3-diol. What is the correlation among these stereoisomers ? Comment on the optical activity of these isomers.

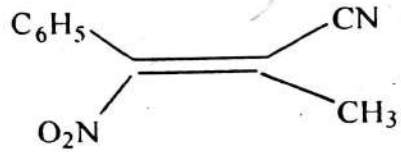
(*b*) Explain why the chair conformation of cyclohexane is more stable than the boat conformation.

(*c*) Assigning priority order, explain how you will designate E/Z to the following :

(*i*)



(*ii*)



4,4,4

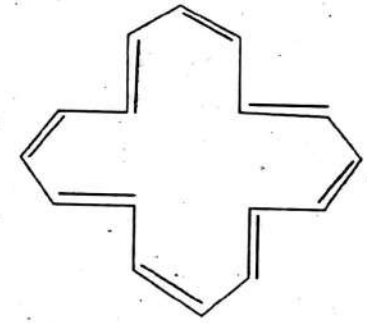
4. (*a*) Discuss the stereochemistry of addition of bromine to cis-2-butene.

(*b*) Chlorine is more reactive but bromine is more selective in halogenation of alkanes. Explain.

(*c*) Which of the foflowing compound/s is/are aromatic ? Give reasons (any *two*) :

(*i*)

(*ii*)



[16] annulene

(*iii*)

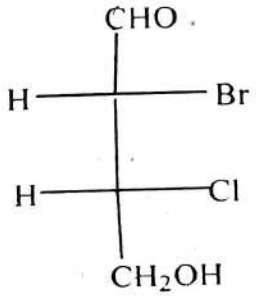
4,4,4

5. (*a*) 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.

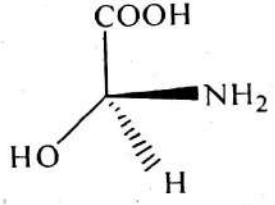
(*b*) What happens when isobutylene is heated with Conc. H_2SO_4 ? Explain giving the mechanism.

(*c*) Assigning priority order, explain how you will designate R/S configuration to the following :

(*i*)



(*ii*)



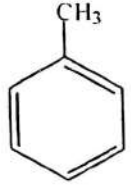
4,4,4

6. (*a*) Complete the following reactions :

(*i*)

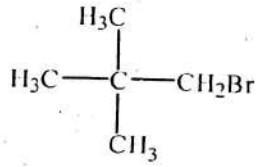
+ CH_2=CHCHO ⟶ A

(*ii*)



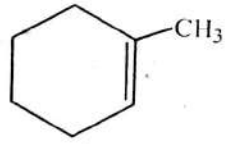
+ C_6H_5COCl $\xrightarrow{\text{anhyd. } AlCl_3}$ B + C

(*iii*)



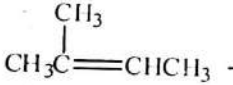
$\xrightarrow[\Delta]{\text{Alc. KOH}}$ D + E

(*iv*)



$\xrightarrow[NaBH_4]{(CH_3COO)_2Hg/\ H_2O,\ r.t}$ F

(*v*)



$\xrightarrow[Zn/H_2O]{O_3/CCl_4}$ G + H

(*vi*)

$\xrightarrow{HBr}$ I

(*b*) An optically active compound "A" with molecular formula C_6H_{10} decolorizes bromine solution and gives white precipitate with ammonical solution of silver nitrate. Compound "A" on ozonolysis gives two compounds "B" and resolvable "C". Identify A, B and C.

(*c*) Define resolution. How would you resolve a racemic mixture of lactic acid ?

6,3,3

7. (*a*) Write short notes on (any *three*) :

(*i*) Friedel-Crafts' alkylation reaction

(*ii*) Ozonolysis of alkenes

(*iii*) Mechanism of allylic substitution

(*iv*) Hyperconjugation and its applications.

(*b*) Define specific rotation. A solution of compound (7.14 g in 100 mL) in chloroform was taken in a polarimeter tube (5 cm) and its optical rotation at 25°C was found to be −1.3°. Calculate its specific rotation. 9,3

This question paper contains 7 printed pages]

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S. No. of Question Paper : **6491**

Unique Paper Code : **32171202**

Name of the Paper : **Physical Chemistry-II**

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

Semester : **II**

Duration : **3 Hours** Maximum Marks : **75**

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

Answer *six* questions in all. Question No. **1** is compulsory.

Use of scientific calculators is allowed.

Logarithmic tables can be provided, if required.

1. Explain, giving reasons, any *five* of the following :

   (*a*) An ideal gas does not heat or cool on expansion or compression. Explain.

   (*b*) The limiting partial molar volume of $MgSO_4$ in water is $-1.4\ cm^3mol^{-1}$. Explain

(*c*) What are the shortcomings of Joule's experiment?

(*d*) While stating the enthalpy change of a chemical reaction, the temperature and pressure of both the reactants and products are considered identical. Explain

(*e*) Crystallization process is attended by a decrease in entropy of the system yet it occurs spontaneously. Comment.

(*f*) It is not necessary to specify the pressure in third law. Explain.

(*g*) Integral enthalpy of solution is positive for NaCl and negative for KCl. Explain.

(*h*) Why is the value of C_p always greater than C_v? 5×3

2. (*a*) Two moles of an ideal monatomic gas ($C_{v,m}$ =12.55 $JK^{-1}mol^{-1}$) expands irreversibly and adiabatically from an initial pressure of 1.013 MPa against a constant external pressure of 0.1013 MPa, until the temperature drops from the initial value of 325 K to a final value of 275 K. Determine the final volume of the gases system and the work involved in the expansion process.

(*b*) Derive the relation $C_p - C_v = TV\frac{\alpha^2}{\beta}$.

(*c*) Show that the magnitude of work involved in a reversible adiabatic expansion of an ideal gas is less than that of the isothermal one, when the expansion is carried out between the same initial and final pressures 4, 4, 4

3. (*a*) The Joule-Thompson coefficient of a gas can be positive, negative or zero. Comment.

(*b*) Show that the expression for expansion work for expansion of a van der Waals gas is given by :

$$w = -nRT\ln\frac{V_2 - nb}{V_1 - nb} - n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right).$$

(*c*) 20 g of N_2 at 300 K is compressed reversibly and adiabatically from 20 dm^3 to 10 dm^3. Calculate the final temperature, q, w, ΔU and ΔH. 4,4,4

4. (*a*) Show, with suitable example, that the standard enthalpy of formation of an element in its most stable state of aggregation is immaterial in calculation of enthalpy of a reaction.

(*b*) 91 kJ of heat was evolved when one mole of $MgSO_4$ was dissolved in a specified amount of water. When the solution of the same composition was formed by dissolution of one mole of $MgSO_4.7H_2O$ in suitable quantity of water, 13 kJ of heat was absorbed. Determine the enthalpy of hydration for the reaction

$$MgSO_4\ (s) + 7H_2O\ (l) \rightarrow MgSO_4.7H_2O\ (s)$$

(*c*) Derive the Kirchhoff equation for the enthalpy change of a reaction when :

(*i*) C_p independent of temperature

(*ii*) C_p depends on temperature. 3,4,5

5. (*a*) To predict the spontaneity of a process both ΔS_{sys} and ΔS_{surr} are considered but ΔG alone is sufficient for the same. Explain.

(*b*) One mole of an ideal monatomic gas at 298 K, occupying a volume of 3 dm^3, is expanded adiabatically and reversibly to a pressure of 101.325kPa. Calculate q, w, ΔU, ΔH, and ΔS.

(*c*) Show that $dS = \frac{C_v}{T}dT + \frac{\alpha}{\beta}dV$,

where α and β are the coefficient of thermal expansion and compressibility factor respectively. 3,4,5

6. (*a*) Show that for an ideal gas undergoing reversible isothermal expansion; $\Delta G = \Delta A$.

(*b*) Derive the following relations :

$$\left\{\frac{\partial(\frac{\Delta G}{T})}{\partial(\frac{1}{T})}\right\}_p = \Delta H$$

(*c*) Calculate $\Delta_r S$ for the process

1 mole H_2O (l, 293K, 101.325 kPa) ⟶

1 mole H_2O (g, 523K, 101.325 kPa)

Given the following data :

$C_{p,m}(l) = 75.312\ JK^{-1}mol^{-1}$; $C_{p,m}(g) = 35.982\ JK^{-1}\ mol^{-1}$

$\Delta_{vap}H$ at 373 K, 101.325 kPa = 40.668 kJ mol^{-1} 3,4,5

7. (*a*) Derive the relation $\left(\frac{\partial \mu_i}{\partial p}\right)_{T,n_j,s} = -V_{i,pm}$

(*b*) Show that the chemical potential of an ideal gas in a mixture of ideal gases is lesser than the chemical potential of the pure ideal gas maintained at the same temperature and total pressure.

(c) Calculate the $\Delta_{mix}G$, $\Delta_{mix}S$ and $\Delta_{mix}H$ when 20 mol of gas A is mixed in a gases mixture formed by mixing 20 mol of gas A and 20 mol of gas B, at 298 K and 1 atm pressure. 3,4,5

8. (a) For the following reaction, predict and explain the change in extent of reaction upon an increase in pressure :

$$1/2\ I_2(g) + 1/2\ Br_2(g) \rightleftharpoons IBr(g)$$

(b) Show that for an endothermic reaction, an increase in extent of reaction increases the equilibrium extent of reaction at equilibrium.

(c) $PCl_5(g)$ dissociates according to the reaction,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

At 523 K, the equilibrium constant K_p^o for the reaction is 1.80. Determine the degree of dissociation of PCl_5. 3,4, 5

9. (a) When 0.1 M aqueous solution of $K_4[Fe(CN)_6]$ is separated from 0.1 M $FeCl_3$ solution by a semipermeable membrane, predict whether the blue color will appear in either of the compartments as a result of the reaction between $K_4[Fe(CN)_6]$ and $FeCl_3$ due to osmosis. Give reasons in support of your answer.

(b) Calculate the depression in freezing point of CCl_4 upon dissolution of a non-volatile substance in it, if the relative vapor pressure lowering is recorded as 0.04. The molar mass and freezing point depression constant for CCl_4 is 342 $gmol^{-1}$ and 31.8 K $kgmol^{-1}$, respectively.

(c) Derive thermodynamically :

$$\Delta T_f = \frac{RT_0^2 M_1}{\Delta H_{fus}} \times m$$ 3,4,5