CSM: 17

CHEMISTRY PAPER - II

Time Allowed: 3 hours Full Marks: 100

Marks for each question is indicated against it.

Attempt any 5 (five) questions taking not more than 3 (three) questions from each Part.

PART-A

(a) Designate each of the following compounds as aromatic, anti-aromatic and non-aromatic.
 Justify your answer.
 (10)

(b) Write the products of the following reactions with proper mechanism: $(2\times5=10)$

(i)
$$H^{\oplus}$$
 ?

(ii)
$$-$$
 BrCH₂COOEt $\xrightarrow{\text{(i) Zn, ether}}$?

- 2. (a) The E2 elimination reactions of unsymmetrical substrates yield more than one olefinic products. Two empirical rules, the Hofmann and Saytzeff's rules, govern the elimination in these reactions. State and explain these rules with suitable examples. (10)
 - (b) Discuss briefly the four factors influencing the relative reactivity in substitution reactions: $(4 \times 2\frac{1}{2} = 10)$
 - (i) The nature of the substrate
 - (ii) The nature of the solvent
 - (iii) The nature of the nucleophile
 - (iv) The nature of the leaving group

- 3. (a) Draw the π -molecular orbitals of (i) 1,3-butadiene (ii) 1,3,5-hexatriene. Show the symmetry element and number of nodes in the ground state and the first excited state and identify the HOMO and LUMO of the ground state and the first exited state. (10)
 - (b) In the thermal ring opening of trans-3,4-dimethyl Cyclobutene, two products can be formed by conrotatory motion, but only one is actually obtained. Identify the possible products. Which one is actually obtained and why? (10)
- 4. (a) How is terylene manufactured starting from dimethyl terephthalate? Give two properties and two uses of terylene. (10)
 - (b) Why is natural rubber elastic in nature? How does vulcanisation improve the qualities of natural rubber? (5+5=10)

PART - B

5. Complete the following reactions with suitable mechanism: (4×5=20)

(a)
$$H \xrightarrow{H} CH_2Cl_2$$
 ?

(b)
$$\phi$$
—CH₂—COOH $\frac{\text{(i) LiAlH}_4}{\text{(ii) H}_3\text{O}^+}$?

(c)
$$+$$
 N —Br CCl_4 hv ?

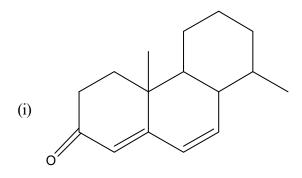
(d)
$$(i) \operatorname{CrO}_{3} \longrightarrow ?$$

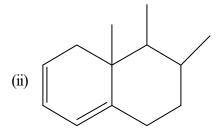
$$(ii) \operatorname{H}_{2}O/\operatorname{H}^{\oplus} \longrightarrow ?$$

(10)

- **6.** (a) Draw Jablonski diagram and define the following:
 - (i) Vibrational cascade (VC)
 - (ii) Intersystem crossing (ISC)
 - (iii) Internal conversion (IC)
 - (iv) Fluorescence (hv_c)
 - (v) Phosphorescence (hv_p)
 - (b) Describe the mechanism of Norrish type-II reactions taking suitable carbonyl compounds. (10)
- 7. (a) State and explain 'the rule of mutual exclusion' with reference to IR and Raman Spectroscopy. Why H_2 is Raman active whereas CO is IR active? (4+4=8)
 - (b) Draw Morse potential energy diagram for an anharmonic diatomic oscillator and explain anharmonicity. (6)
 - (c) The rotational spectrum of a diatomic molecule consists of series of lines that are equally spaced by a factor of 2B. Evaluate the value of 'B' assuming that diatomic molecule behaves as rigid rotator.

 (6)
- 8. (a) Predict the number of signals with relative intensities in the low resolution PMR spectrum of the following molecules: $(2\times2\frac{1}{2}=5)$
 - (i) CH₃CH₂OH
 - (ii) CH₃COCH₃
 - (b) The mass spectrum of diethylether gives a series of ions at m/z 29,31,45,59,74. Assign the fragmentation pattern. (5)
 - (c) Using Woodward's rule, predict the λ_{max} for the following compunds with proper justification. (2×5=10)





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