WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 2nd Semester Examination, 2022

CEMACOR04T-CHEMISTRY (CC4)

ORGANIC CHEMISTRY-II

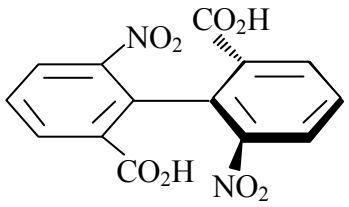
Time Allotted: 2 Hours | Full Marks: 40

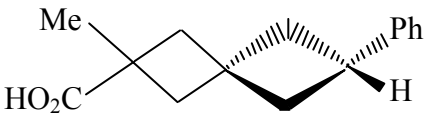
The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.

Answer any *three* questions taking *one* from each unit

Unit-I

1. (a) Find out (R/S) configurational descriptors for the following molecules. 2

(i) 

(ii) 

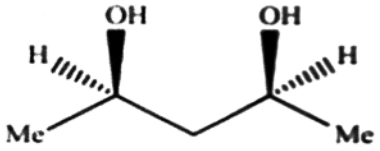
(b) Draw the Newman projections of all six conformations and show their position in the potential energy diagram for the rotation about the C2–C3 bond in (R)-2-iodobutane. 3

(c) Draw the most populated conformer of the following molecules. 1+2

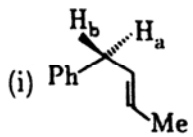
(i) FCH_2-CH_2F

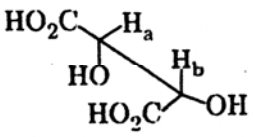
(ii) $ClCH_2-C(CH_3)(Br)-C(CH_3)_2Br$ (along $C-1/C-2$ bond)

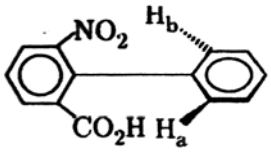
(d) Write down the compound obtained by substitution of pro-s hydrogen of the following compound by Cl. Also find out the configuration of the chlorine substituted Carbon. 2



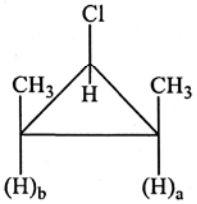
(e) Identify $\mathbf{H_A}$ and $\mathbf{H_B}$ in each of the following structures as homotopic, enantiotopic or diastereotopic ligands with explanation. 3

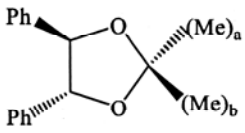
(i) 

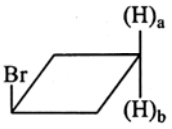
(ii) 

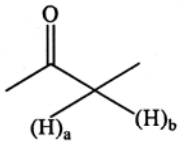
(iii) 

2. (a) Identify the topic relationships (homotopic, enantiotopic or diastereotopic) between the ligands marked 'a' and 'b' in the following compounds. (any ***three***) 3

(i) 

(ii) 

(iii) 

(iv) 

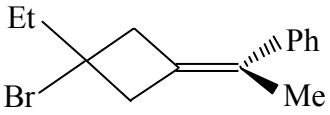
(b) Draw the three staggered conformations of 1,2-dichloroethane and label each of those with Klyne-Prelog system of conformational terminology. 3

(c) Draw the s-cis and s-trans conformations of (2S, 3E, 5E, 7S)-2, 7-dibromoocta-3, 5-diene. 2

(d) Explain the following: The intramolecular H-bonding in *active*-butan-2,3-diol is relatively stronger than that in *messo*-butan-2,3-diol; 2

(e) Label the marked hydrogen atom (H*) as *pro-R*, *pro-S*, *pro-E* or *pro-Z*. 2

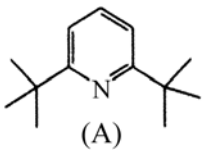
(f) Find out (R/S) configurational descriptor for the following molecule. 1



Unit-II

3. (a) Explain the following: 3

(i) A reaction will not take place at all if $\Delta \mathbf{H}^{\circ}$ is positive and $\Delta \mathbf{S}^{\circ}$ is negative.

(ii) 

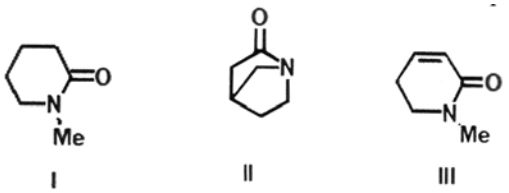
(A)

(A) is known as an excellent scavenger of protons.

(b) Cyclic 1, 2-diketones exist mainly in the enol form; Explain. 1

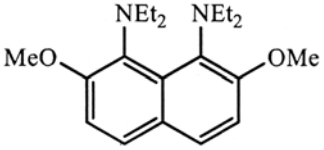
(c) The enol content of 4, 4, 4-trifluoro-2-butanone is larger than that of 2-butanone. Explain the fact. 2

(d) Compare the basicity of the following compounds with explanation; 2



I II III

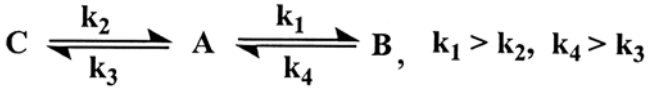
(e) The following compound acts as a proton-sponge. Explain. 2



(f) Reactions of HBr with 1,3-butadiene give the 1,4- and 1,2-addition products at different temps; Explain the mechanism of the reaction stating the reaction conditions for Kinetically controlled product and thermodynamically controlled product. 2

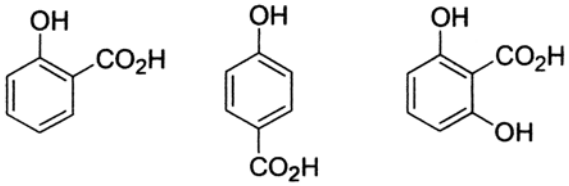
(g) Why ethyl acetoacetate exist in the enol form much more in hexane than in water? 2

4. (a) Draw the energy profile diagram of the following reaction and offer an explanation in favour of your answer. 4



Where A = reactant, B, C = stable products; k_1, k_2, k_3, k_4 = rates of reactions. Which product is formed at low temperature? Which is the thermodynamically more stable product?

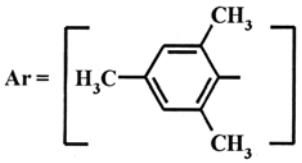
(b) Arrange the following compounds in increasing order of acid strength and explain. 2



(c) Bromination of methane is less exothermic than that of chlorination. Explain this statement. 2

[Bond energies (in kcal/mole): C–H = 104; Br–Br = 46; H–Br = 87.5; Cl–Cl = 58; H–Cl = 103; C–Cl = 83.5; C–Br = 71].

(d) $[Me_3CO]_3CH$ exists almost entirely in the keto form, whereas Ar_2CHCHO exists mainly in the enol form. Explain. 2



(e) Explain why the following two structures are tautomers but not the resonance forms. 2

(f) Arrange the following compounds in the increasing order of basicity and nucleophilicity. 2

NH_3, NH_2NH_2, NH_2OH

Unit-III

5. Explain the following observations:

(a) Mc_3CH on chlorination using chlorine in diffused sunlight gives primary halide as major monosubstituted product, while bromination by heating with bromine produces tertiary halide as the major product. 2

(b) Solvolysis of (+) $C_6H_5CH(CH_3)Cl$ leads to 98% racemisation whereas solvolysis of (+) $C_6H_{13}CH(CH_3)Cl$ gives only 34% racemisation. 2

(c) BF_3 accelerates the unimolecular substitution reactions of alkyl fluorides but not those of alkyl chlorides. The reverse is true for AgF. 2

(d) The reaction rate of CH_3I with N_3 at 0ºC is increased 4.5×10^4 fold on change of solvent from methanol to DMF. Explain. 2

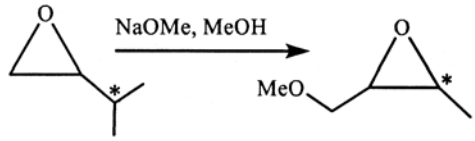
(e) C_6H_5SNa reacts with vinyl chloride in presence of NaOEt catalyst. Without NaOEt, the reaction does not occur at all. Explain. 2

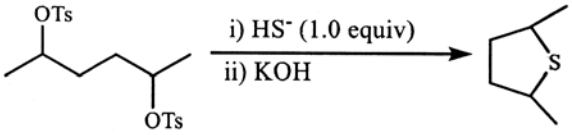
(f) Justify the following observations: 3

(i) $CH_3(CH_2)_6CH_2Br \xrightarrow[18\text{-crown-6}]{KF,\ Benzene,\ 100^0C} CH_3(CH_2)_6CH_2F$

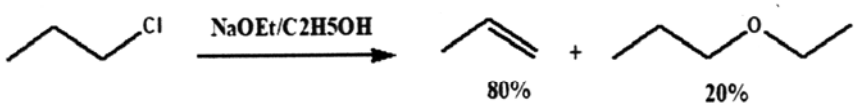
(ii) $CH_3(CH_2)_6CH_2Br \xrightarrow[18\text{-crown-6}]{LiF,\ Benzene,\ 100^0C}$ no reaction

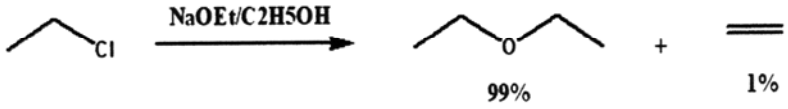
6. (a) Account for the following observations: 2×2 = 4

(i) 

(ii) 

(b) Explain with mechanisms of the following observations; 3

(i) 

(ii) 

(c) Predict the product(s) with plausible mechanism in the following cases— 2×3 = 6

N.B. : *Students have to complete submission of their Answer Scripts through E-mail / Whatsapp to their own respective colleges on the same day / date of examination within 1 hour after end of exam. University / College authorities will not be held responsible for wrong submission (at in proper address). Students are strongly advised not to submit multiple copies of the same answer script.*

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