



WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 2nd Semester Examination, 2022

CEMACOR04T-CHEMISTRY (CC4)

ORGANIC CHEMISTRY-II

Time Allotted: 2 Hours

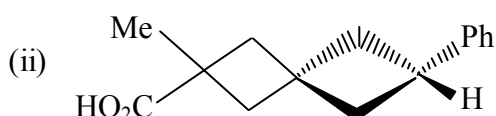
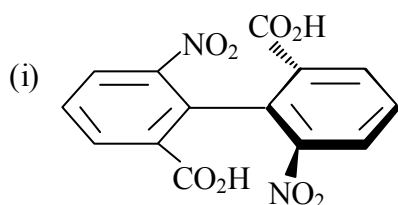
Full Marks: 40

*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

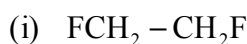
Unit-I

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

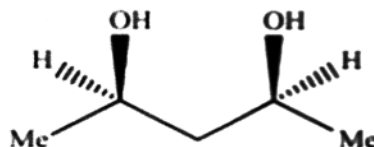


- (b) Draw the Newman projections of all six conformations and show their position in the potential energy diagram for the rotation about the C2–C3 bond in (*R*)-2-iodobutane. 3

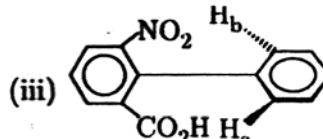
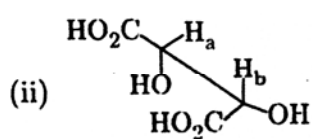
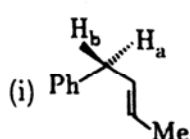
- (c) Draw the most populated conformer of the following molecules. 1+2



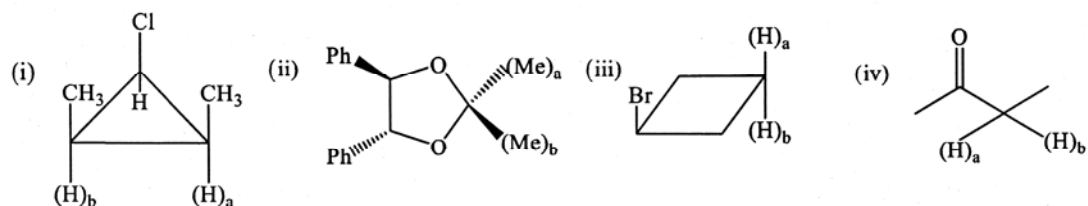
- (d) Write down the compound obtained by substitution of pro-s hydrogen of the following compound by Cl. Also find out the configuration of the chlorine substituted Carbon. 2



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



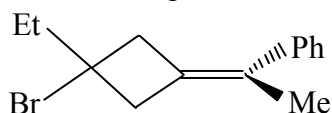
2. (a) Identify the topic relationships (homotopic, enantiotopic or diastereotopic) between the ligands marked 'a' and 'b' in the following compounds. (any *three*) 3



- (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 *meso*-butan-2,3-diol; 2
- (e) Label the marked hydrogen atom (H*) as *pro-R*, *pro-S*, *pro-E* or *pro-Z*. 2



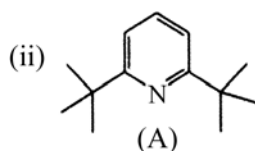
- (f) Find out (*R/S*) configurational descriptor for the following molecule. 1



Unit-II

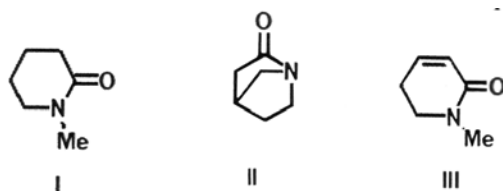
3. (a) Explain the following: 3

- (i) A reaction will not take place at all if ΔH° is positive and ΔS° is negative.

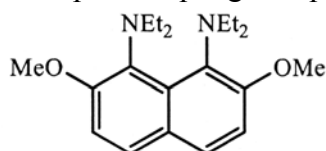


(A) is known as an excellent scavenger of protons.

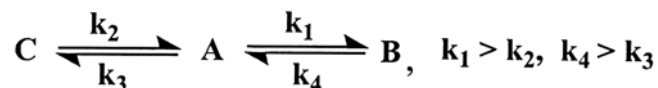
- (b) Cyclic 1, 2-diketones exist mainly in the enol form; Explain. 1
- (c) The enol content of 4, 4, 4-trifluoro-2-butanone is larger than that of 2-butanone. Explain the fact. 2
- (d) Compare the basicity of the following compounds with explanation; 2



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

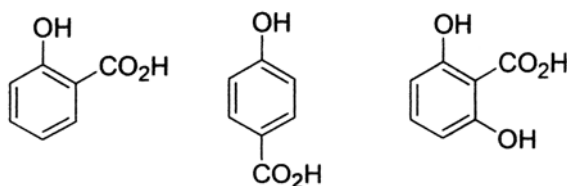


- (f) Reactions of HBr with 1,3-butadiene give the 1,4- and 1,2-addition products at different temps; Explain the mechanism of the reaction stating the reaction conditions for Kinetically controlled product and thermodynamically controlled product. 2
- (g) Why ethyl acetoacetate exist in the enol form 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?

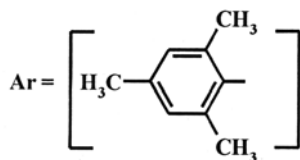
- (b) Arrange the following compounds in increasing order of acid strength and explain. 2



- (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) $[\text{Me}_3\text{CO}]_3\text{CH}$ 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



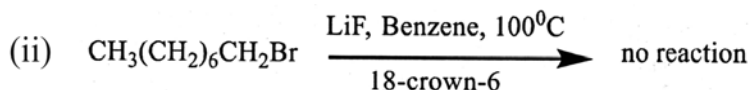
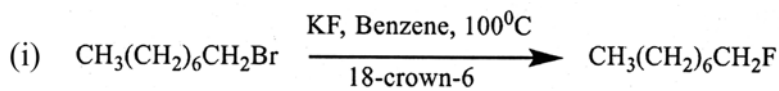
- (f) Arrange the following compounds in the increasing order of basicity and nucleophilicity. 2



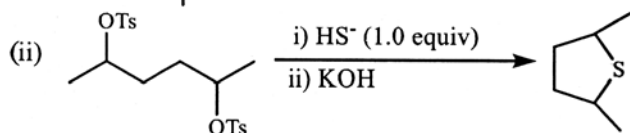
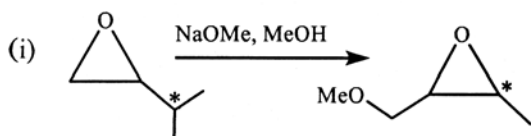
Unit-III

5. Explain the following observations: 2
- (a) Me_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 (+) $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Cl}$ leads to 98% racemisation whereas solvolysis of (+) $\text{C}_6\text{H}_{13}\text{CH}(\text{CH}_3)\text{Cl}$ gives only 34% racemisation. 2

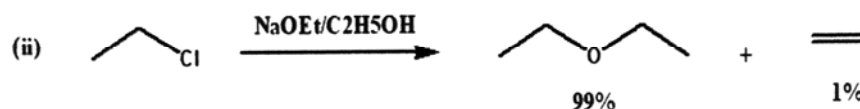
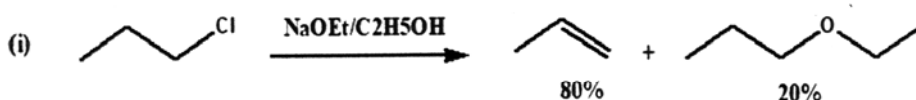
- (c) BF_3 accelerates the unimolecular substitution reactions of alkyl fluorides but not those of alkyl chlorides. The reverse is true for AgF . 2
- (d) The reaction rate of CH_3I with N_3 at 0°C is increased 4.5×10^4 fold on change of solvent from methanol to DMF. Explain. 2
- (e) $\text{C}_6\text{H}_5\text{SNa}$ 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



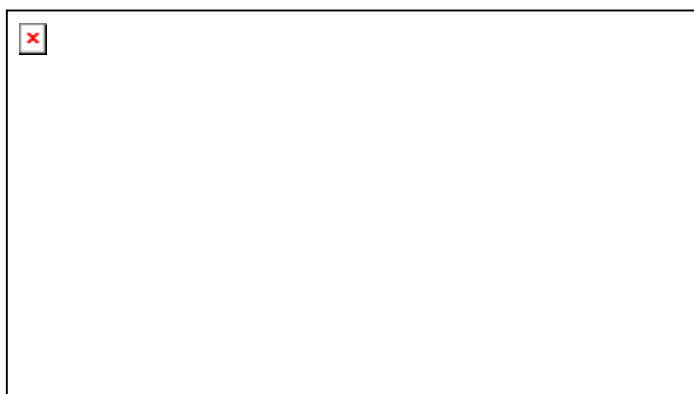
6. (a) Account for the following observations: $2 \times 2 = 4$



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



- (c) Predict the product(s) with plausible mechanism in the following cases— $2 \times 3 = 6$



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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B.Sc. Honours 2nd Semester Examination, 2022

CEMACOR03T-CHEMISTRY (CC3)

INORGANIC CHEMISTRY-I

Time Allotted: 2 Hours

Full Marks: 40

*The figures in the margin indicate full marks.
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All symbols are of usual significance.*

Answer any four questions taking one from each unit

Unit-I

1. (a) What is the exchange energy? From the concept of exchange pair of electrons, how ground state electronic configuration of chromium can be determined? 1+3
- (b) What electronic transition in He^+ spectrum would have the same wavelength as the first Lyman transition of hydrogen? 3
- (c) Explain the significance of different m_l (magnetic quantum number) values corresponding to Azimuthal quantum numbers (l) = 1. 2
- (d) Determine the ground state term symbol of Cu^{2+} ion. 2
2. (a) Mention the limitation of Bohr's theory of atomic structure and discuss the Sommerfeld's extension on it. 3
- (b) State Hund's rule and hence find out the ground term for gaseous Cr atom. 3
- (c) How do the shapes of s and p orbitals can be obtained from angular functions? Give reasons. 3
- (d) Calculate the de-Broglie wavelength of $6s$ electron of Hg moving with a speed nearly $1/6^{\text{th}}$ that of light. Velocity of light = $3.0 \times 10^8 \text{ ms}^{-1}$. 2

Unit-II

3. (a) Explain the causes of Lanthanide-contraction. 2
- (b) The ionization energies follow the sequence in the following cases as shown — Justify. 3
 - (i) $\text{IE}_1(\text{Cu}_{29}) < \text{IE}_1(\text{Zn}_{30}) > \text{IE}_1(\text{Ga}_{31})$
 - (ii) $\text{IE}_1(\text{Au}_{79}) < \text{IE}_1(\text{Hg}_{80}) > \text{IE}_1(\text{Tl}_{81})$

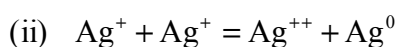
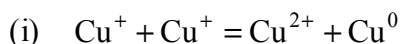
- (c) Calculate the electronegativity of hydrogen from the following data: 3
 $E_{\text{H-H}} = 458 \text{ kJ/mol}$, $E_{\text{F-F}} = 155 \text{ kJ/mol}$, $E_{\text{H-F}} = 565 \text{ kJ/mol}$, $\chi_p(\text{F}) = 4.0$
4. (a) Nitrogen is more electronegative than phosphorus but the electron affinity of phosphorus is more than that of Nitrogen — Explain. 2
- (b) Explain the sequence of ionization energies. 3
 kJmol^{-1} : Cu (746), Zn (906), Ga (579)
- (c) Calculate the electronegativity of As atom ($Z = 33$) in the Allred-Rochow Scale having covalent radius 1.21 \AA . 2
- (d) Write the IUPAC names of the elements with atomic numbers 190 and 107. 1

Unit-III

5. (a) Write Wayland-Drago equation and explain the terms involved in it. What is the utility of this equation? 1+2
- (b) Predict the binding modes of CNS⁻ with reasons in the following complex ions. 2
 $[\text{Co}(\text{NH}_3)_5(\text{CNS})]^{2-}$ and $[\text{Co}(\text{CN})_5(\text{CNS})]^{3-}$
- (c) Can you develop a pH-like scale in liquid ammonia? What will be the span of that scale? 2
 Given: $K_{\text{H}_2\text{O}} = 10^{-14}$ at 25°C
 $K_{\text{NH}_3} = 10^{-33}$ at -50°C
- (d) Give the order of acidity of the following and rationalize the trend: 3
 $[\text{Na}(\text{H}_2\text{O})_x]^+$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
6. (a) SO_2 can act both as a Lewis acid and as a Lewis base. Explain with suitable examples. 2
- (b) Predict the direction of the following equilibria with explanation. 2
 (i) $2\text{CH}_3\text{MgF} + \text{HgF}_2 \rightleftharpoons (\text{CH}_3)_2\text{Hg} + 2\text{MgF}_2$
 (ii) $\text{BF}_3\text{H}^- + \text{BH}_3\text{F}^- \rightleftharpoons \text{BF}_4^- + \text{BH}_4^-$
- (c) Addition of SbF_5 enhances the acidity of pure HF while the addition of NaF reduces its acidity — Explain. 2
- (d) The B–F bond length in BF_3 is 130 pm. How will this bond length change in adducts H_3NBF_3 and Me_3NBF_3 ? Justify your answer. 2
- (e) What happens when bismuth nitride and ammonium chloride are allowed to react in liquid ammonia? 2

Unit-IV

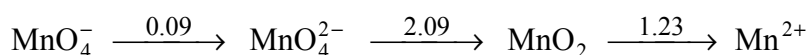
7. (a) Indicate the direction in which the following reactions spontaneously and assign them with appropriate name. 4



[E^0 in Volt :

$$\text{Cu}^{2+}/\text{Cu}^+ = 0.16, \text{Cu}^+/\text{Cu}^0 = 0.52, \text{Ag}^{++}/\text{Ag}^+ = 1.98, \text{Ag}^+/\text{Ag}^0 = 0.80]$$

- (b) From the following standard reduction diagram calculate the E^0 for $\text{MnO}_4^-/\text{Mn}^{2+}$ redox system and hence its formal potential at pH = 4. 3

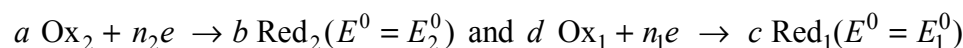


- (c) Balance the following redox reaction by ion electron method: 2

Oxidation of $\text{Mn}^{2+}(\text{aq})$ to MnO_4^- by sodium bismuthate in nitric acid medium.

- (d) Explain the separation of group II cations in qualitative analysis by solubility product principle and common ion effect. 2

8. (a) Show that for two general redox couples: 4



the overall reaction: $n_2 c \text{Red}_1 + n_1 a \text{Ox}_2 = n_2 d \text{Ox}_1 + n_1 b \text{Red}_2$ has the equilibrium constant K_{eq} where $\log K_{\text{eq}} = (E_2^0 - E_1^0)/(0.059/n_1 n_2)$.

- (b) Solutions containing cupric ions readily oxidize potassium iodide to iodine though E_{Red}^0 of the $\text{Cu}^{2+}/\text{Cu}^+$ system (-0.15 V) is lower than that of the I_2/I^- system (0.54). — Explain. (K_{sp} of $\text{CuI} = 10^{-12}$). 3

- (c) What is disproportionation reaction? Give an example. 2

- (d) Apply solubility product principle and common ion effect in separation of group IIIB metal sulphides in qualitative analysis. 2

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