WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2024

CEMACOR10T-CHEMISTRY (CC10)

ORGANIC CHEMISTRY-IV

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 *four* questions taking *one* from each unit

Unit-I

1. (a) Identify the products **A**, **B** and **C** in the following sequence of transformations. Suggest a mechanism for the conversion of **B** to **C**. 3

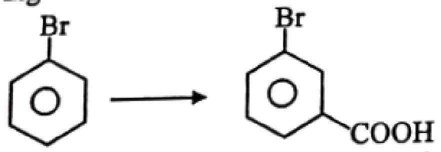
$$PhCHO \xrightarrow[NaOEt]{MeNO_2} \mathbf{A} \xrightarrow{LiAlH_4} \mathbf{B} \xrightarrow{HNO_2} \mathbf{C}$$

(b) Predict the product(s) of the following reaction with plausible mechanism. $1\frac{1}{2}$

(c) State the action of $NaNO_2$ / HCl on (only the product): $1\frac{1}{2}$

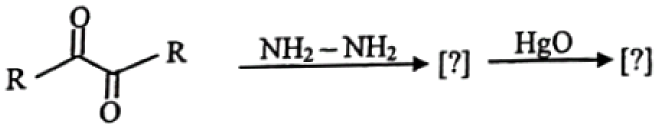
(i) *N*-methylaniline (ii) *N*, *N*-dimethylaniline and (iii) benzylamine

2. (a) Carry out the following conversion: 2



(b) Illustrate the use of diazomethane for the preparation of pyrazole and conversion of cyclopentanone to cyclohexanone. 2

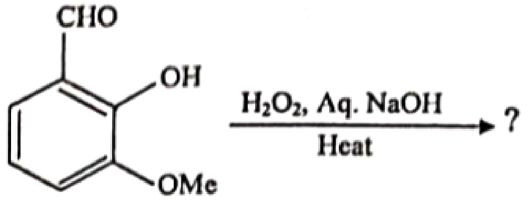
(c) Write down the product in the following scheme. 2



Unit-II

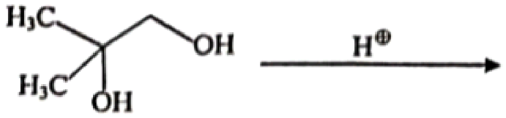
3. (a) "In the Arndt-Eistert synthesis two equivalent of diazomethane is used." — Explain the statement showing mechanism of the reaction. 2

(b) Predict the product of the following reaction: 3



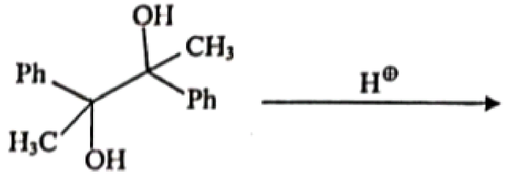
(c) Complete the following reactions and give reasons for your answer: $1\frac{1}{2}\times 2=3$

(i)



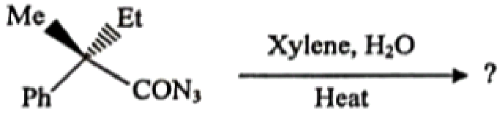
2 / 4

(ii)



4. (a) Two isomeric α-halo ketones A and B on treatment with NaOMe (separately) gave the same product $PhCH_2CH_2CO_2Me$. Identify A and B. 2

(b) Predict the product (with proper stereochemistry) in the following reaction with suitable mechanistic explanation. 3

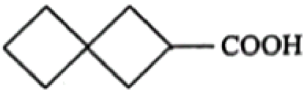


(c) Show that Hofmann, Curtius and Lossen reactions proceed through a common intermediate. Give proper evidence in favour of your answer. 3

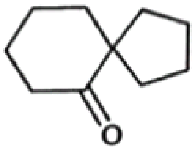
Unit-III

5. (a) Analyse the following molecules retro synthetically and suggest plausible synthetic route to them. (any *two*) $3\times 2=6$

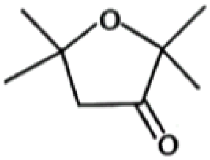
(i)



(ii)



(iii)



(b) Explain the terms "functional group interconversion" and 'illogical nucleophile' with suitable examples. 2+2

6. (a) Write down the synthetic equivalents of the following synthons. 3

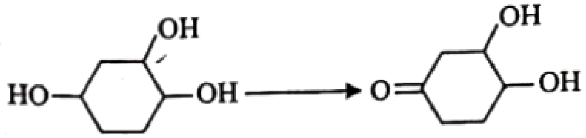
(i) $\bar{C}O_2H$ (ii) $\overset{+}{C}HCH_2OH$ (iii) $Ph-\bar{C}=O$

(b) Predict the major diastereomeric product when *S*-3-bromo-2-butanone is treated with sodium borohydride. 3

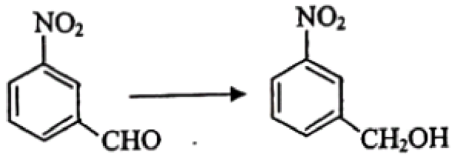
(c) Illustrate the use of acyloin condensation for the synthesis of large rings. Does the method require the high dilution technique? 2

(d) Give the reagents for the following transformations. 2

(i)

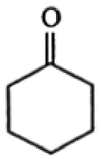


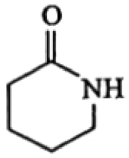
(ii)



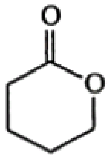
Unit-IV

7. (a) Consider the following carbonyl compounds. Suggest the correct increasing order of $C=O$ stretching frequency. 3


I



II



III

(b) Distinguish the following pair of compounds on the basis of their IR spectroscopic data: 2+2+2

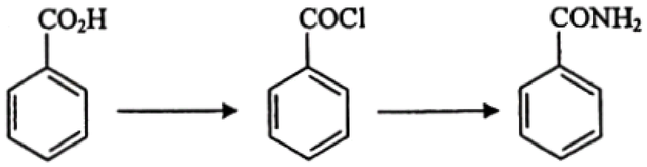
(i) Acetone and benzophenone

(ii) Salicylic acid and *o*-chloro benzoic acid

(iii) Phenyl acetate and methyl benzoate.

(c) What will be the change in ^{1}H-NMR spectrum of pure ethanol by the addition of D_2O? 2

(d) How do you study the progress of the following transformations using IR spectroscopy? 2



(e) Comment on the effect of polarity of solvent on $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in UV spectroscopy. 2

(f) Mention one solvent, other than $CDCl_3$, that acts as NMR solvent. 1

8. (a) An organic compound with molecular formula $C_6H_{12}O$ gives positive iodoform test. Its UV, IR and ^1H-NMR data are given below: 3+1

UV: λ_{max} 282 nm , ε_{max} 22

IR: ν_{max} 1710 cm^{-1}

^1H NMR: δ 2.1 (3H, s) and 1.1 (9H, s)

Deduce the structure of the compound with proper explanation.

Explain the spectroscopic data.

(b) Write down the structure of the compound $C_5H_{11}Cl$ which shows two singlets in its ^1H NMR spectrum. Predict the chemical shift. 2

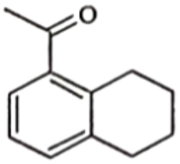
(c) Toluene is oxidized to benzaldehyde. What changes would you expect in PMR spectral feature for the product with respect to that of the starting material? 2

(d) "The nature of H-bonding present in a molecule can be identified by IR spectroscopy." — Explain with examples. 2

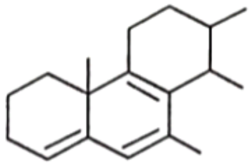
(e) The stretching absorption maxima for C–H and C–D are approximately 2900 cm^{-1} and 2200 cm^{-1} respectively. — Explain why. 2

(f) Calculate λ_{max} values for the following compounds using Woodward Fieser rule. 2+2

(i)



(ii)



—×—

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2024

CEMACOR09T-CHEMISTRY (CC9)

INORGANIC CHEMISTRY-III

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) Write down the name of one ore from which Ti metal can be extracted. How would you extract Ti metal from this ore by Kroll process? 1+3

(b) Mention the differences between roasting and calcination. 2

(c) Using Ellingham diagram explain the nature of stability of the metal oxides at high temperature. 2

(d) What is the role of fluorspar and cryolite during the extraction of Al from Bauxite by Baeyer's Process? 2

2. (a) Describe the principle of refining nickel by Mond's process. 4

(b) What is the principle of hydrometallurgy? Mention one advantage of using this process. 2

(c) What is leaching? Name one basic leaching reactor. 2

(d) Which metals are generally extracted by electrolytic reduction and why? 2

Unit-II

3. (a) Compare and contrast the chemistry of N, P, As, Sb and Bi with special references to: 6

(i) Oxidation states
(ii) Hydrides
(iii) Halides.

(b) Explain the structure and bonding of polyphosphazenes. 3

(c) The acidity of boric acid may be enhanced in presence of polyhydric alcohols. — Explain. 3

(d) PbO_2 is an oxidizing agent whereas SnO_2, GeO_2, SiO_2 are not. — Explain. 2

(e) Discuss the hydrolytic behaviour of xenon fluorides by mentioning the balanced chemical equations. 3

(f) What are polyhalides? Why do they form? Mention one example each for homo and hetero nuclear polyhalide. 1+1+1

4. (a) How would you prepare borazine? Why is it called inorganic benzene? Indicate the hybridisation of B and N in this compound. 2+2+1

(b) $AlCl_3$ is covalent but AlF_3 is ionic. — Why? 2

(c) Freons deplete the ozone layer of upper atmosphere. — Explain. 2

(d) Among the so called inert gases, Xenon is most suitable to form chemical compounds. — Explain. 2

(e) Give one example each to show that hydroxylamine acts both as oxidizing and reducing agent. 2

(f) Discuss the structure and bonding of the following compounds: 4

(i) XeO_3 (ii) XeF_2

(g) Discuss the structure and bonding of $(SN)_x$ $[x = 4]$. 3

Unit-III

5. (a) Write the IUPAC Nomenclature of $[(NH_3)_5Cr-OH-Cr(NH_3)_5]Cl_5$ and formula for bromopentanitratocobalt (II) sulphate. 1+1

(b) Chromium (III) chloride forms three different hydrates of the same mole ratio $Cr : Cl : H_2O = 1 : 3 : 6$. A violet form does not lose water over concentrated H_2SO_4 and gives 3 equivalents of AgCl on treatment with $AgNO_3$. Two other forms, both green, lose 1 and 2 mols of H_2O over concentrated H_2SO_4 and give 2 and 1 equivalents of AgCl respectively with $AgNO_3$. 3

Write the coordination structures of three isomeric complexes.

(c) Draw the possible geometrical isomers of $[Co(en)_2(NCS)(NH_3)]^{2+}$ and hence predict which of them would be optically active. 3

(d) Mention two major drawbacks of Werner's theory. 2

6. (a) Write down the structures of different isomeric forms of $[Cr(ox)_3]^{3-}$. 2

(b) The solubility of the first-order inner metallic complex is very poor in water. Explain with example. 2

(c) How will you chemically distinguish between *cis* and *trans* isomer of $[Pt(NH_3)_2Cl_2]$? 2

(d) Between $K_4[Fe(CN)_6]$ and KCN, mention which one is toxic and which one is not. — Explain. 2

(e) Why metal chelates are more stable than non-chelated complexes? 2

$3NH_4Cl + 3LiBH_4 \rightarrow B_3 + 3LiCl + 9H_2$

——×——

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2024

CEMACOR08T-CHEMISTRY (CC8)

PHYSICAL CHEMISTRY-III

Time Allotted: 2 Hours Full Marks: 40

Att: 4b 3

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) Using the Clausius-Clapeyron equation show that the slope of the solid-gas coexistence curve is greater than the slope of the liquid-gas coexistence curve at the triple point. 3

(b) Derive thermodynamically using chemical potential a relation between Osmotic Pressure of a very dilute solution with its molal concentration. Also, mention the assumptions and approximations. 4+2

(c) Why molality is taken for the calculation of colligative properties instead of molarity? 2

(d) Vapour pressure of water at its boiling point changes by 27.6 mm per degree. Calculate the molal boiling point elevation constant of water. 3

2. (a) Using Duhem-Margules Equation, deduce the Konowaloff's Rule. 3

(b) A mixture of 100 g water and 80 g phenol separates into two layers at 60°C. One layer L_1, consists of 44.9% water by mass, the other layer L_2, consists of 83.2% water by mass. Calculate the total number of moles in L_1 and L_2. [Given: molar mass of Phenol is 94.4 gmol^{-1}]. 4

(c) Show that the van't Hoff factor i and the degree of dissociation α of an electrolyte $AxBy$ in aqueous solution are related by the expression:

$$\alpha = \frac{i-1}{n-1} \quad \text{, where } n = x + y$$

(d) Indicate the number of components, number of phases and the degree of freedom in the following systems: 2

(i) $NH_4Cl\ (\text{vapour}) \rightleftharpoons NH_3\ (g) + HCl\ (g)$

(ii) A solution of potassium chloride in water, containing some undissolved salt in equilibrium with water vapour.

Unit-II

(a) Discuss the principle of determination of pH of a solution by using Quinhydrone electrode.

(b) Using the relevant equation, show that the total molar polarization varies linearly with $1/T$.

(c) Calculate the solubility product of AgCl at 298 K. Given, 3

(i) for half-cell oxidation reaction: $Ag\,(s) \rightarrow Ag^{+} + e^{-}$, $E^{\circ}_{Ag/Ag^{+}} = -0.799$ V at 298 K.

(ii) for half-cell reduction reaction: $AgCl\,(s) + e^{-} = Ag\,(s) + Cl^{-}\,(aq)$. $E^{\circ}_{Cl^{-}/AgCl/Ag} =$ 0.2223 V at 298 K.

(d) Set up the electrochemical cell where the following process takes place: 3+2

$$ZnCl_2\,(a_1) \rightarrow ZnCl_2\,(a_2)$$

Why are glass electrodes kept immersed in a slightly acidic solution when not in use?

4. (a) Show schematically the plots of $\log f_{\pm}$ versus $\sqrt{C}$ (Where C is the molar concentration) for the dilute aqueous solution of two strong electrolytes $AlCl_3$ and Na_2SO_4 in the same graph at 298 K and hence show that their slopes are in the ratio $3:\sqrt{2}$. 3

(b) Calculate the relative permittivity (ε_r) of HCl (g) at 1 atm and 25°C. 3

Given: dipole moment (μ) of HCl (g) $= 4.60 \times 10^{-30}$ (C.m)

distortion polarizability (α) of HCl (g) $= 2.95 \times 10^{-40}$ ($C^2m^2J^{-1}$)

permittivity of vacuum $(\varepsilon_0) = 8.85 \times 10^{-12}$ ($C^2N^{-1}m^{-2}$)

(c) Calculate the equilibrium constant for the reaction: $Cu^{2+} + Zn \leftrightarrow Cu + Zn^{2+}$ 2

[Given : $E^{0}_{Zn^{2+}/Zn} = -0.763$ V and $E^{0}_{Cu^{2+}/Cu} = 0.337$ at 25°C]

(d) The potential of the cell, $Zn\,(s) | ZnCl_2\,(m = 0.01021 \text{ mol Kg}^{-1}) \,|\, AgCl\,(s) \,|\, Ag\,(s)$ was found to be 1.1566 V. What is the mean ionic coefficient of $ZnCl_2$ in the solution? Given: $E^{0}_{Cl^{-}/AgCl(s)/Ag(s)} = +\,0.222$ (V); $E^{0}_{Zn^{2+}/Zn(s)} = -\,0.762$ (V). 4

(e) If the dipole moment of Chlorobenzene is 1.57 D, then find that for *m*-dichlorobenzene. 2

Unit-III

5. (a) (i) Define an orbital. 1+2+1

(ii) Find the number of radial nodes in the wave functions of the orbitals: 2*p* and 3*s*.

(iii) What is the significance of a node?

(b) Show that $[\hat{L}_x, \hat{L}_y] = \dfrac{ih}{2\pi}\hat{L}_z$. 2

(c) Find out the $\langle r \rangle$ for the 1*s* electron. 3

Given: $\psi_{1s} = \dfrac{1}{\sqrt{\pi}}\left(\dfrac{1}{a_0}\right)^{3/2} e^{-r/a_0}$.

(d) Use LCAO-MO method to H_2^{+} to find the ground state energy. 3

6. (a) Calculate the probability of finding a 1*s* electron of hydrogen within a distance $2a_0$ from the nucleus. What is the probability beyond $2a_0$? 3+

(b) Explain the concepts of molecular orbital theory and valence bond theory. State the strengths and limitations of valence bond approach to molecular bonding. 3+

(c) Write the Hamiltonian operator for the hydrogen molecule stating the meaning of the symbols.

——×——