## Ex/SC/CHEM/UG/CORE/TH/12/2023

## B. Sc. Chemistry Examination, 2023

(5th Semester, CBCS)

## **CHEMISTRY (CORE)**

PAPER: CORE/CHEM/TH/12

Time: Two Hours Full Marks: 40

(20 marks for each unit)

Use a separate answer script for each unit.

## UNIT - 5121 - O

- 1. (a) Outline Bardhan-Sengupta synthesis of phenanthrene. How can you explain the formation of a common spiran intermediate in both Bardhan-Sengupta and Bogert-Cook method for the synthesis of phenanthrene.  $1\frac{1}{2} + \frac{1}{2}$ 
  - (b) What are the possible products when phenylhydrazone of  $H_3C-C-CH_2CH_3$  is heated with anhydrous O
    - ZnCl<sub>2</sub>? Mention the major product and decide which of the nitrogen atom of phenylhydrazone is lost using isotope labelling.  $1\frac{1}{2} + \frac{1}{2}$
  - (c) Predict the product(s) in the following reactions with plausible mechanism (any *four*).  $1\frac{1}{2} \times 4$

iii)  $MeCOCH_2COOEt + MeCOCH_2Cl \xrightarrow{aq. NaOH} rt \rightarrow$ 

iv) 
$$CH_2OH \longrightarrow m$$
-CPBA  $CH_2Cl_2 \longrightarrow OH$ 

v) 
$$Me \xrightarrow{CO_2Et}$$
  $MeCHO, HCl$   $EtOH, 100°C$ 

$$\begin{array}{c|c} vi) & & \xrightarrow{PoCl_3} & \\ \hline & CH_2Cl_2, & reflux \end{array}$$

2. (a) 'Amines usually undergo conjugate addition to unsaturated esters.' In view of the above statement and on the basis of Baldwin rules for ring closure, predict the product formed when the following molecule C cyclises. What is the stereochemical basis of your answer?

$$H_2N$$
  $CO_2E$ 

(b) Comment on the optical activity of *trans* – 1,3-dimethylcyclohexane. Justify your answer with proper pictorial presentation(s).

(iii) The following isomer of toluene has been synthesized. Although it is much less stable than toluene, it has a surprisingly long life-explain.

- 4. (a) Draw the structure of heterocyclic bases observed in DNA double helix structure and discuss how base pairing occurs.
  - (b) Discuss with a suitable mechanism how the hydantoins could be synthesized from carbonyl compounds.
  - (c) Outline a synthetic sequence of reactions by which an aldohexose can be converted into 2-ketohexose *via* an osone intermediate.
  - (d) Explain the following conversion mechanistically. 2

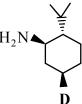
(e) Write a scheme with reagents and conditions for the conversion of D-glucose to L-Gulose. 2

$$\begin{array}{ccc} \text{iv)} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & \\ & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

- (b) Answer *any two* of the following questions: 2x2
  - (i) On standing, cyclopentadiene spontaneously forms two possible dicyclopentadiene. Draw the strucgtures and identify the major isomer and explain their formation with FMO approach.
  - (ii) Using FMO approach, explain the product formed when *trans*, *cis*, *trans* –2,4,6- octatrine is heated.

(c) A compound **E** (molecular formula  $C_{10}H_{20}O$ ) is obtained in high yield when the following molecule **D** is treated with sodium nitrite in aqueous hydrochloric acid. On treatment with sodium hydride and carbon disulfide followed by methyl iodide, compound **E** gives an intermediate compound **F** which on heating produces two isomeric molecules, **G** (major) and **H** (minor), with molecular formula  $C_{10}H_{18}$ . The isomer **H** is formed as the sole product, though very slowly, when either molecule **I** (molecular formula  $C_{10}H_{19}Cl$ ) or its isomer **J** is heated with sodium ethoxide.

Identify the compounds **E** to **J** with proper stereochemistry and explain their formations with appropriate mechanistic and stereochemical interpretations.



**UNIT: 5122 - O** 

3. (a) Predict the product(s) with proper stereochemistry of the following reactions and explain their formation by FMO consideration (Answer *any three*) 2x3