

DEPARTMENT OF CHEMISTRY
RANI RASHMONI GREEN UNIVERSITY
M.Sc. COURSE IN CHEMISTRY
Semester I Examination, 2024
Course ID: CHEM-C-12

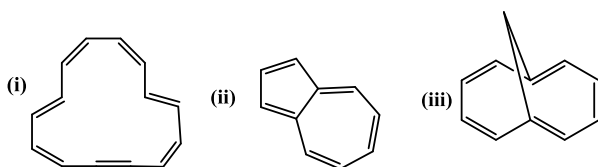
Full Marks: 40

Time: 2 hours

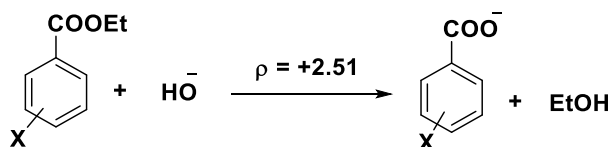
Answer all the questions. Candidates are required to write answers in their own words and with proper scientific representations, if needed.

Unit-1: Structure-Activity Relationship

Q-1. (a) Identify the aromaticity of the following compounds with suitable explanation.



(b) Explain the significance of given ρ value for base catalyzed hydrolysis of *m*- and *p*-substituted ethyl benzoates. Describe the influence of X (X = electron withdrawing or donating group placed at the *m*- or *p*-position) on the rate of reaction.



(c) Discuss the Huckel treatment to calculate the optimized energy and secular determinant for cyclobuta 1,3-diene. [3+3+2 = 8]

Q-2. (a) Discuss alternant and non alternant hydrocarbons with suitable example

(b) Discuss the Huckel treatment to calculate the optimized energy and explain stability of allylic systems (cation, anion and radical).

(c) Why base catalyzed hydrolysis of *m*-methoxy ethylbenzoate ($\sigma_{m-MeO} = +0.12$) is faster than the corresponding unsubstituted ester? Draw the mechanism and explain the significance of σ value for this reaction.

[2+3+3 = 8]

Unit-2: Stereochemistry-1

Q-3. (a) What will happen when *cis*- and *trans*-2-acetoxycyclohexyl tosylates are individually reacted with NaOAc in AcOH?

(b) What will happen when *cis*-1,2-dimethyl cyclohexane-1,2-diol is reacted with dilute acid? [5 + 3 = 8]

Q-4. a) Indicate the preferred conformation of each of the following compounds with appropriate reasons:

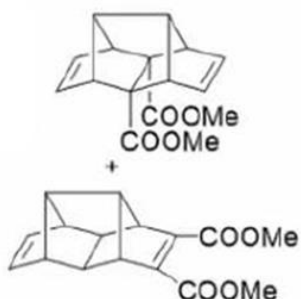
(i) *trans*-1,3-di-*tert*-butylcyclohexane (ii) *trans*-2-bromo-4-methylcyclohexane

(b) Both *cis*- and *trans*-1,2-dibromocyclohexane, on reaction with iodide give cyclohexene.

Explain. [5 + 3 = 8]

Unit-3: Pericyclic Reactions

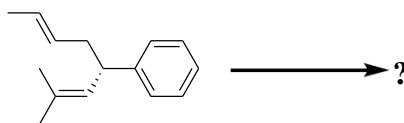
Q-5. (a) Explain the formation of following products from an easily available starting material:



(b) Carry out the following conversion:



(c) What will be the major product when the following molecule is heated?

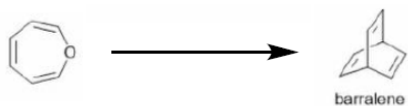


(d) Carry out the synthesis of the following molecule:

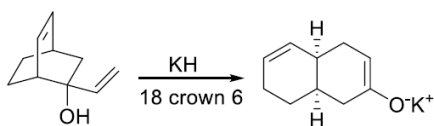


[2 + 2 + 2 + 2 = 8]

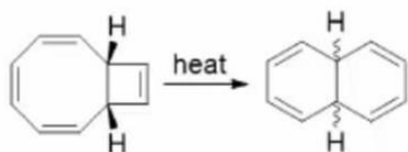
Q-6. (a) Carry out the following conversion:



(b) Depict the mechanism of the following reaction



(c) Suggest a suitable mechanism and identify the stereochemistry of the product formed for the following reaction

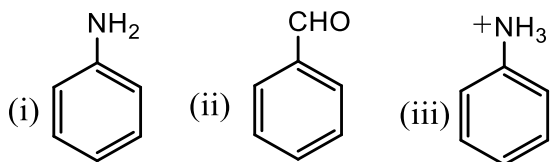


[3+2+3 = 8]

Unit-4: NMR Spectroscopy-1

Q-7. (a) Discuss an AMX spin system in ¹H NMR with a suitable example including spectral pattern, chemical shift and coupling constant.

(b) Comment on the chemical shift value of all aromatic protons (*ortho*, *meta* and *para*) in the following compounds by ¹H NMR spectroscopy.



(c) Explain spin decoupling technique with a suitable example. [3+3+2 = 8]

Q-8. (a) NMR spectrometer contains 2.5 T magnet and Larmor precession frequency of ¹H is 100 MHz. The radio frequency used in this spectrometer has an associated magnetic field strength of 2.5 x 10⁻⁴ T. What will be the time duration of 90° pulse for this spectrometer.

(b) Discuss an ABX spin system in ¹H NMR with suitable example including spectral pattern, chemical shift and coupling constant.

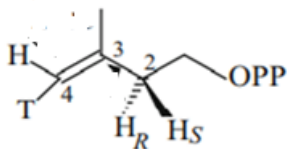
(c) Illustrate spin tickling technique with suitable example.

(d) Explain the NMR concept of aromaticity.

[2+3+1.5+1.5 = 8]

Unit-5: Natural Products-I

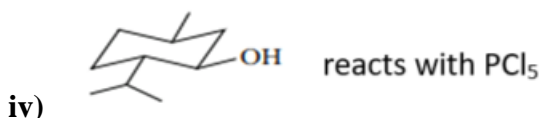
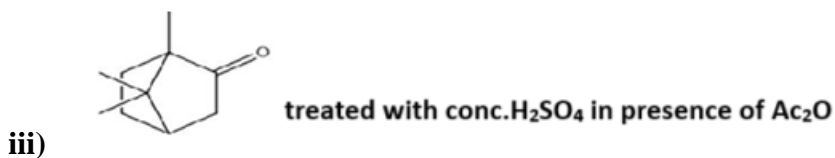
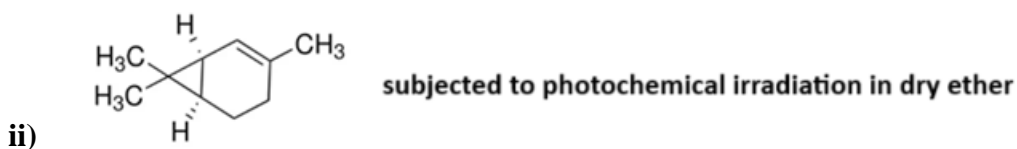
Q-9. (a) What happens when the following compound is treated with D₂O in presence of IPP isomerase enzyme? Explain the mechanism of the enzyme on the basis of the structure of the product formed.



- (b) Acetyl CoenzymeA CH_3COSCoA undergoes Claisen Ester Condensation type reaction to yield Acetoacetyl CoenzymeA $\text{CH}_3\text{COCH}_2\text{SCoA}$ as the first step of biosynthesis followed in MVA pathway. Justify the choice of thioester group by Nature.
- (c) Give example of a monoterpene which is formed from the unusual coupling between two units of DMAPP and indicate the respective coupling pattern.

[3 + 3 + 2 = 8]

Q-10. Predict the product(s) of the following reactions. Explain the mechanism of the reaction in each case. (Any four)



[2+2+2+2=8]