



RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. Honours in Chemistry
Fourth Year – Semester I Examination – July / August 2023

CHE 4309 – ADVANCED ORGANIC CHEMISTRY

Answer all questions.

Time: Three (03) hours

1. a) Discuss the factors that should be considered in order to select a suitable solvent for a reaction.
(40 marks)
 - b) Draw the molecular orbital diagram for the following allylic free radical. Clearly indicate HOMO and LUMO levels.

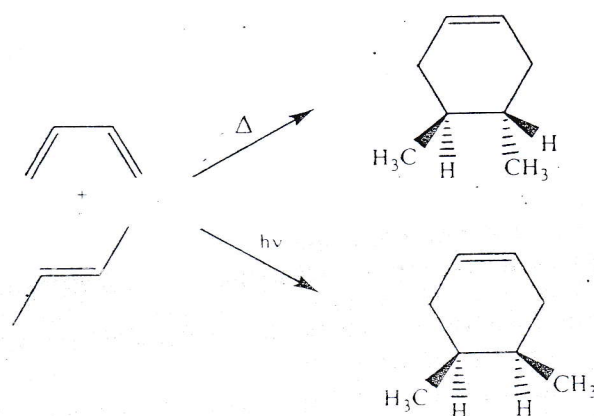
$$\text{H}_2\text{C}=\text{CH}-\dot{\text{C}}\text{H}_2$$
(20 marks)
 - c) Discuss the applications of Kinetic Isotope Effect in discovery of reaction mechanisms with respect to S_N^1 and S_N^2 .
(40 marks)
2. Following data are for the ionization of phenols.

Substituent	pK_i	σ
H	10	0.00
p-Me	10.26	-0.17
p-Cl	9.33	0.23
m-Cl	9.02	0.37
m-OMe	9.65	0.12
m-Me	10.09	-0.07
m-F	8.72	0.92

- a) Define the Hammett equation.
(10 marks)
- b) Based on above data, construct the Hammett plot.
(20 marks)
- c) Hence, calculate the reaction constant, ρ for the process.
(10 marks)
- d) If $\sigma_{\text{p-CN}} = 0.66$, what is the predicted K_i for p-cyanophenol?
(10 marks)

- e) σ values for p-F and m-F are 0.062 and 0.337 respectively: Account for values. (20 marks)
- f) What observations can you make from this data regarding the correlation? Explain. (30 marks)

3. a) Cycloaddition of following reactants may give two products depending on the reaction conditions. Explain the results by means of Hückel-Möbius analysis.

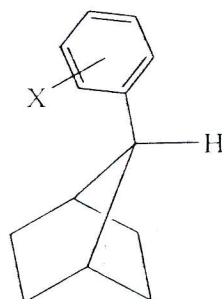


(20 marks)

- b) Suggest reasonable mechanisms for the hydrolysis of a carboxylic ester in both dilute acid bases and explain how mechanism might account for ρ values of the reaction.
- c) Draw the correlation diagram for conrotatory interconversion of cyclobutene-butadiene system.

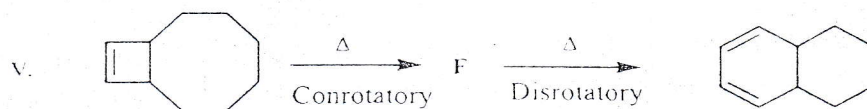
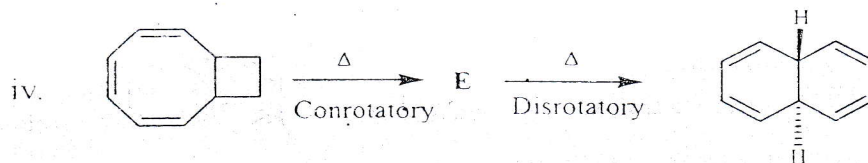
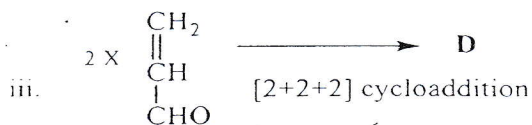
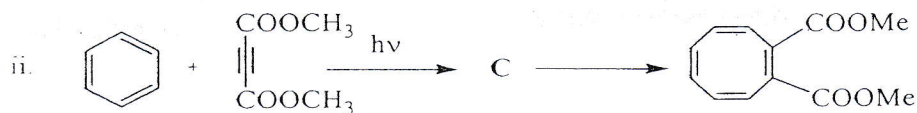
(30 marks)

- b) Following compound can undergo both S_N1 and S_N2 mechanisms. Draw possible intermediates. Clearly indicate the charges on the reaction centers. How do you identify the two reactions on the Hammett plot? Justify your answer.



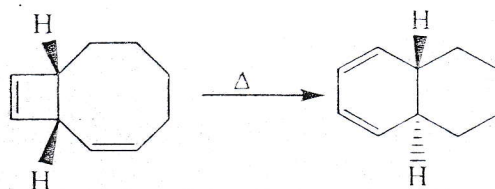
(20 marks)

a) Predict the intermediates of the following concerted photochemical cyclization.



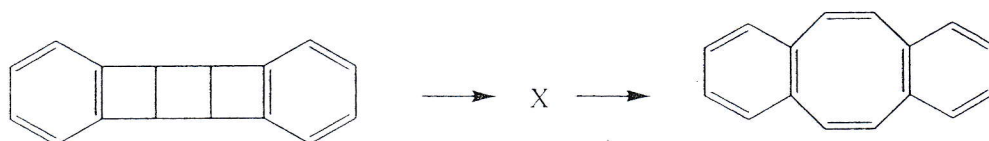
(50 marks)

b) Write down the mechanism for the following electrocyclic reaction under thermal conditions.



(20 marks)

c) Draw the structure of the intermediate (X) for the following electrocyclic reaction in the presence of silver catalyst.



(30 marks)

5. a) The dependence of energy separation between α and β states on the NMR magnetic field and the nucleus concerned can be expressed as

$$\Delta E = h\nu = \frac{h\gamma}{2\pi} B_0$$

Describe " γ " and graphically explain the states when $\gamma < 0$ and $\gamma > 0$

(20 marks)

- b) Define "Chemical shift" of NMR and express the relevant equation. (20 marks)

- c) Discuss the detailed ^1H NMR spectrum of $\text{CH}_3\text{OCHClCH}_2\text{Cl}$. Draw the relative spectrum in draft form.

(20 marks)

d)

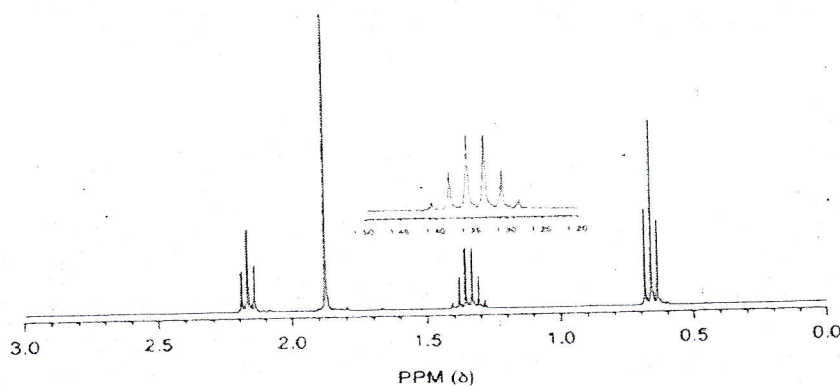
- i. Match the ^1H NMR spectrum below to its corresponding compound from the list given below. Assign all of the signals and explain your answer.

k). cyclopentanone
p). 4-heptanone

l). 3-pentanone
q). 1-butene

m). butanaldehyde

o). 2-pentanone



(20 marks)

- ii. Draw the ^{13}C NMR spectrum of the above-selected compound.

(20 marks)

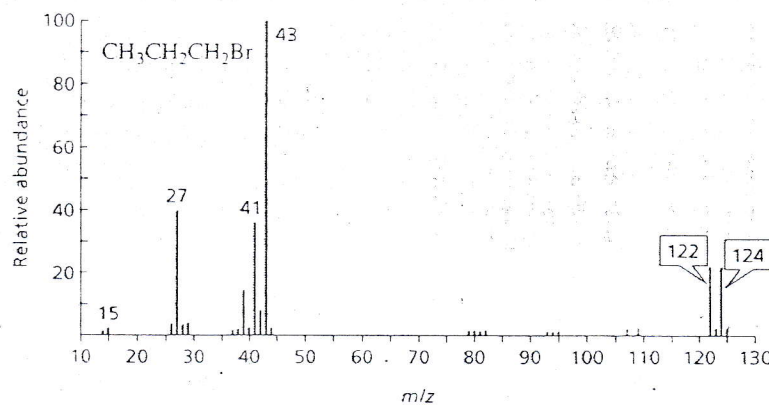
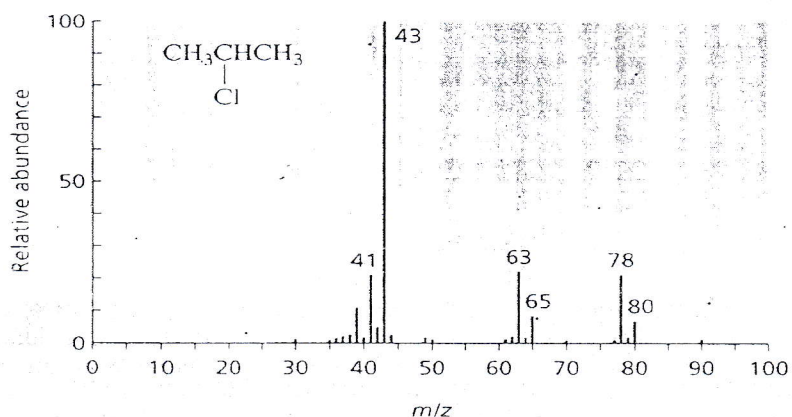
5. a). Describe the Time-of-flight mass spectrometry (TOF-MS)

(20 marks)

- b). Write a short note on different detectors used in Gas chromatography and compare their advantages / disadvantages over Mass detector.

(10 marks)

- c). Mass spectrums of 2-chloropropane and 1-bromopropane are given below. Discuss the ionizations and identify major peaks.

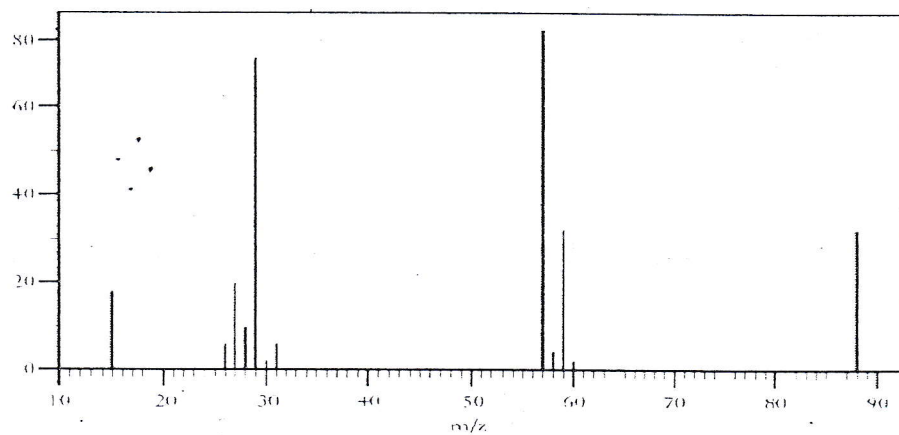


(40 marks)

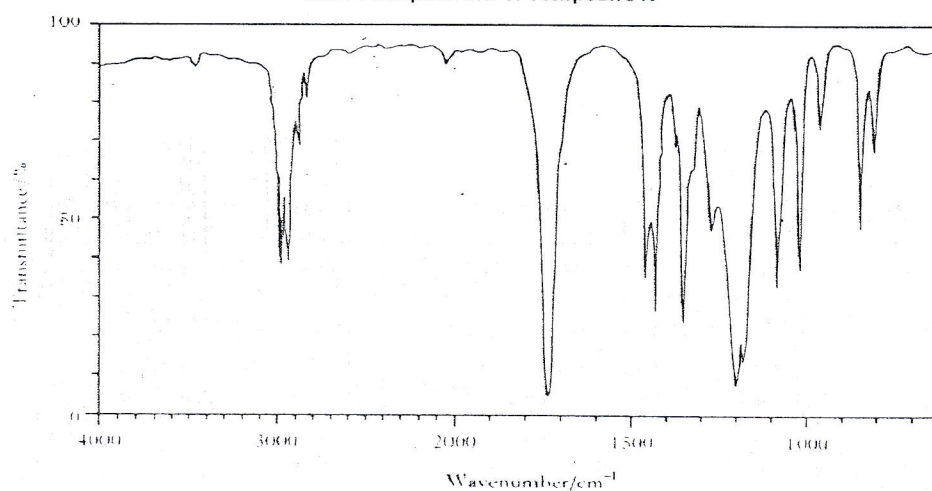
- d). Spectra of an organic compound, $\text{C}_4\text{H}_8\text{O}_2$, are given below.

- The absorption peak at 1745 cm^{-1} in the infrared spectrum can be used to help identify the compound. Which bond is responsible for this absorption?
- Draw the structure of the ion fragment responsible for the peak at m/z 57 in the mass spectrum
- Considering all the evidence, including the proton NMR spectrum, name the compound A.

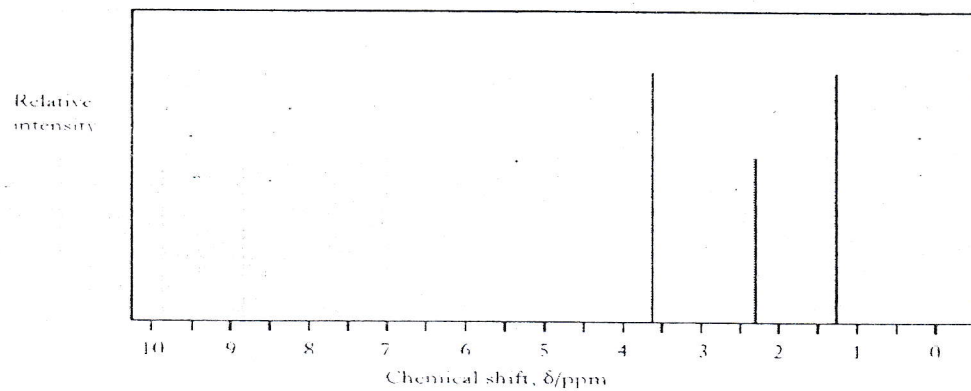
Mass spectrum of compound A



Infra-red spectrum of compound A



Proton nmr spectrum of compound A



(30 marks)

- End -