



RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

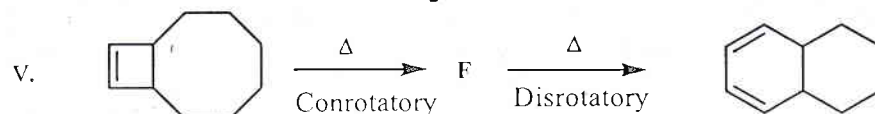
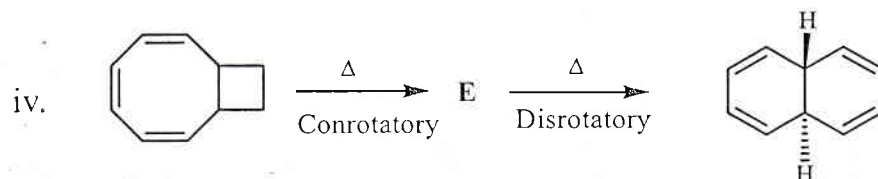
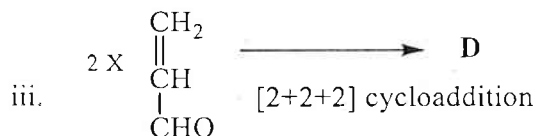
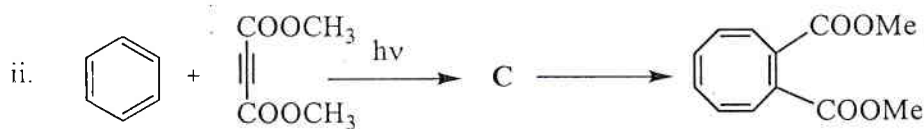
B.Sc. Honours in Chemistry
Fourth Year – Semester I Examination – January / February 2021

CHE 4309 – ADVANCED ORGANIC CHEMISTRY

Answer all questions.

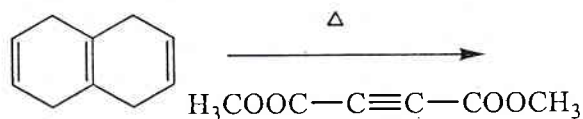
Time: Three (03) hours

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



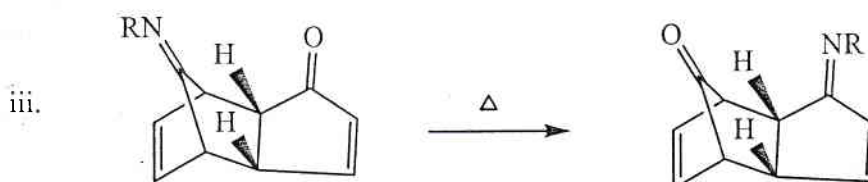
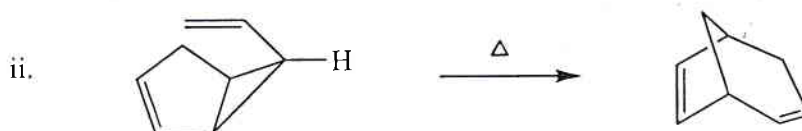
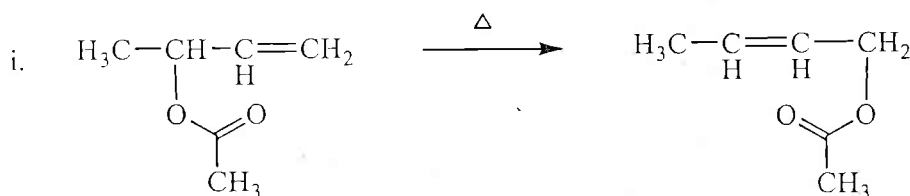
(60 marks)

b) Suggest the product of the following reaction.



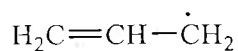
(10 marks)

c) Explain the following concerted rearrangements.



(30 marks)

2. a) Draw the molecular orbital diagram for the following allylic free radical. Clearly indicate HOMO and LUMO levels.



(40 marks)

b) Draw correlation diagrams for both (i) conrotatory and (ii) disrotatory ring closures of 2,4 pentadienyl anion separately and find out whether these reactions are allowed or forbidden.

(60 marks)

3. a) Suggest a reasonable mechanism for the hydrolysis of a carboxylic ester in dilute acid and explain how that mechanism might account for the small value of ρ for the reaction.

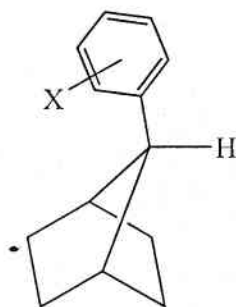
(30 marks)

- b) The following are the acidity constants (in water, 25 °C) for some substituted benzeneseleninic acids, ArSeO_2H .

Substituent	$K \times 10^{-6}$	σ
H	1.6	0
p-OCH ₃	0.89	-0.27
m-OCH ₃	2.2	0.12
m-Cl	3.5	0.37
p-Br	3.2	0.23
p-OC ₆ H ₅	1.3	-

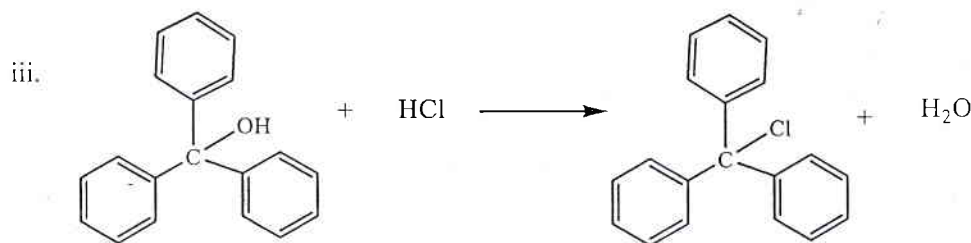
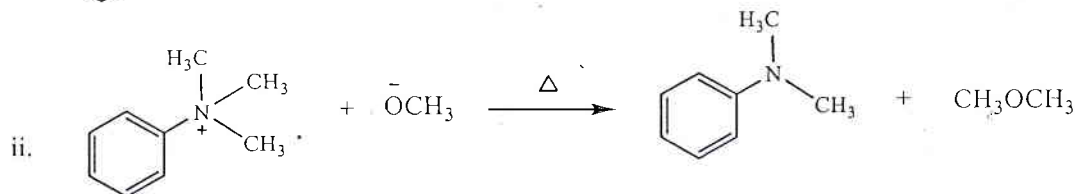
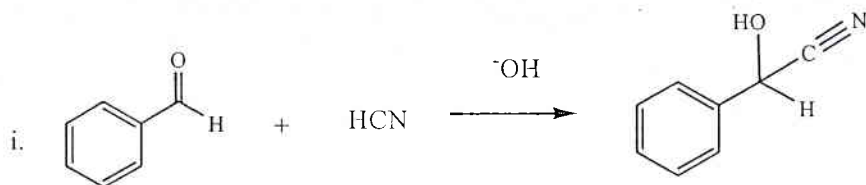
- i. Define the Hammett equation. (10 marks)
- ii. Show that the equilibria for ionization of these acids are governed by the Hammett equation. (20 marks)
- iii. Calculate ρ for this process. (10 marks)
- vi. Calculate the dissociation constant for p-OC₆H₅. (10 marks)
- v. σ values for p-OMe and m-OMe are -0.27 and 0.12 respectively. Account for values. (20 marks)

4. a) The Following compound can undergo both S_N^1 and S_N^2 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.



(40 marks)

- b) Indicate whether Hammett plots for rates of the following reactions should have positive or negative slopes. Decide whether the best fit to straight lines would be obtained by using values of σ , σ^+ , or σ^- . Explain your reasoning in each case.



(60 marks)

5. a) List four different features of a ^1H NMR spectrum that provide information about a compound's structure. Discuss two of them in detail. (20 marks)
- b) 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 $\gamma > 0$

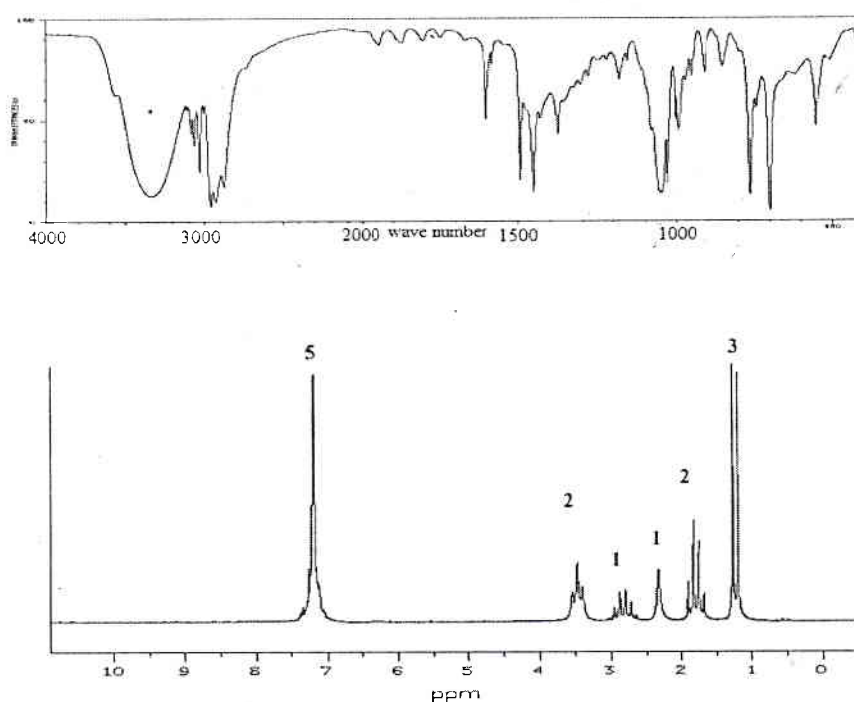
(20 marks)

- c) Draw the ^1H -NMR spectrum for each of the following compounds. Explain your answers.

- Chlorocyclobutane
- 1-bromo-2,2-dimethylpropane
- Nitrobenzene
- 1-Phenyl-2-propanone

(60 marks)

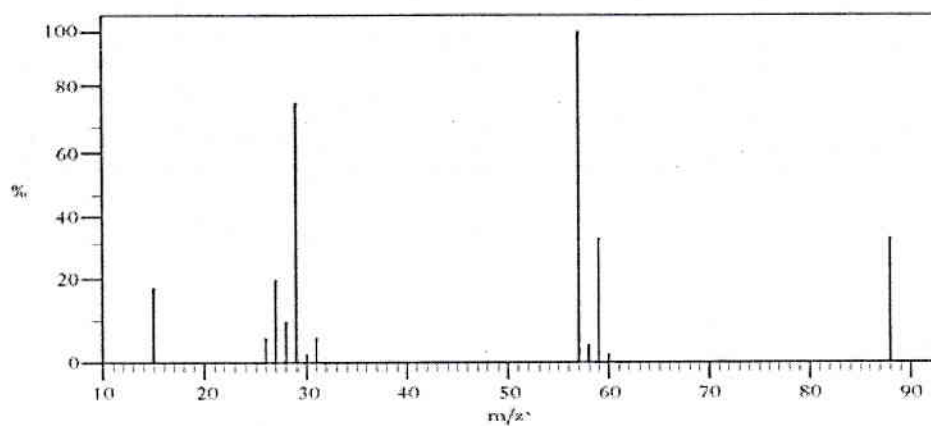
6. a) Write a short note on Gas Chromatography – Mass Spectrometry (GC-MS). (15 marks)
- b) Describe “Chemical Ionization” process in Mass Spectrometry. (15 marks)
- c) Given the IR and NMR spectra below, determine the chemical structure of the compound having an empirical formula of $C_{10}H_{14}O$. Justify your answer. (30 marks)



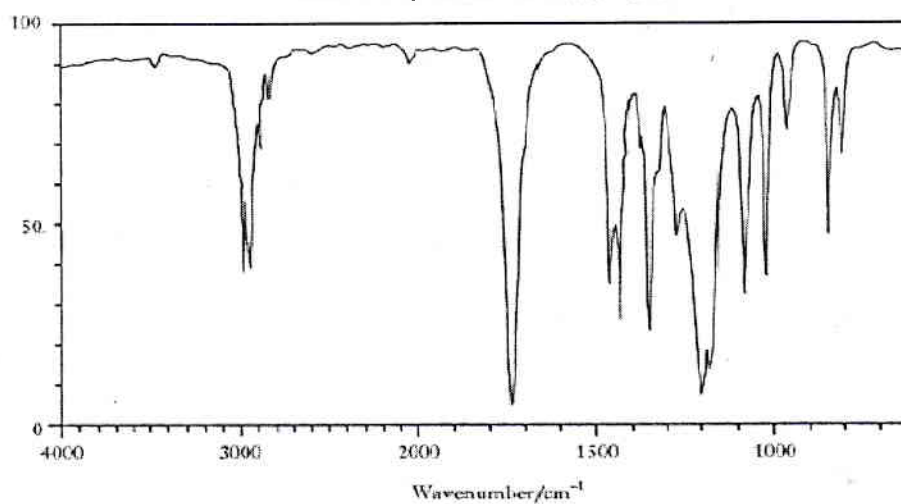
- d) Spectra of an organic compound A are shown below. Identify the compound using all information given herewith, and justify your answer. Draw the structure of the ion fragment responsible for the peak at m/z 57 in the mass spectrum.

Cont'd.

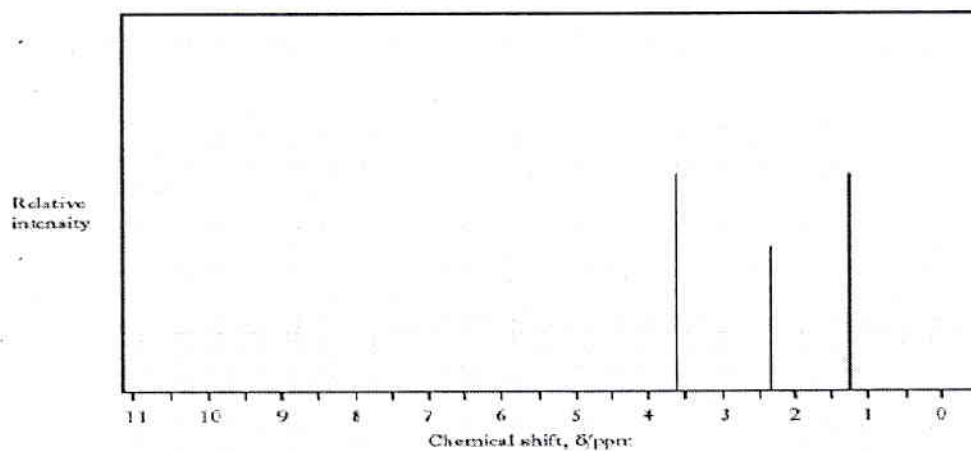
Mass spectrum of compound A



Infra-red spectrum of compound A



Proton nmr spectrum of compound A



(40 marks)

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