RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

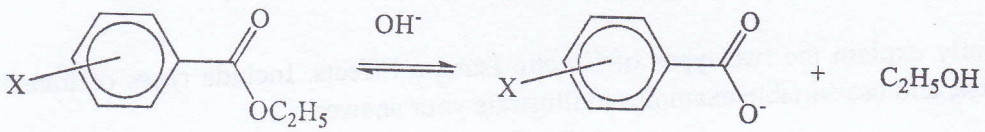
B.Sc. (Special) Degree in Chemistry
Fourth Year - Semester I Examination – October / November 2017

CHE 4309 – ADVANCED ORGANIC CHEMISTRY

Answer all questions. **Time: Three (03) hours**

01.

Consider the base catalyzed hydrolysis of X substituted ethyl benzoate.



a) Write down a suitable mechanism for the above reaction.

Use following data to calculate

b) Reaction constant.

c) Substituent constant for p-CF_3.

d) Base catalyzed rate constant for p-OMe substituted ethyl benzoate.

X	k (s^{-1})	σ
H	$1x10^{-4}$	0
m-NO_2	$6.3x10^{-3}$	0.71
p-CF_3	$9.0x10^{-4}$	?

(100 marks)

02.

a) Explain the following observations.

X	σ
p-NO_2	0.78
m- NO_2	0.71
p-OMe	-0.27
m-OMe	0.12

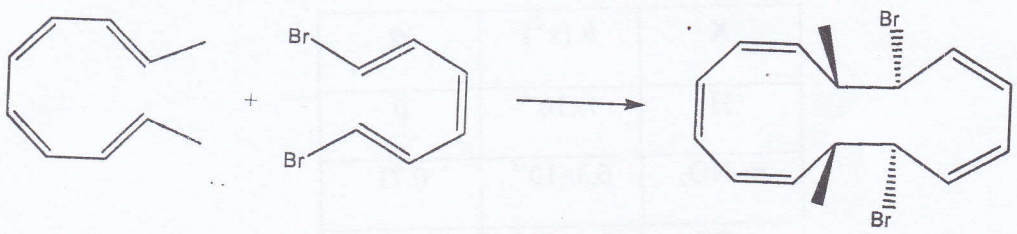
(40 marks)

b) Briefly explain the two types of Kinetic Isotope Effects. Include types of transition states, and use suitable examples to illustrate your answer.

(60 marks)

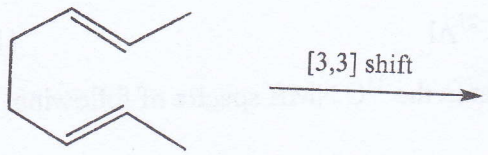
03.

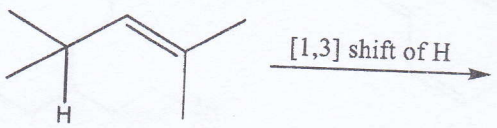
a). Apply Woodward-Hoffmann selection rules to predict whether following reaction is thermally allowed or not.



(60 marks)

b). Predict the products of following sigmatropic rearrangements.





(40 marks)

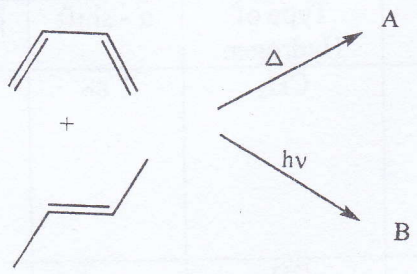
04.

a). How would you explain the conrotatory ring closure of 1,3-butadiene is thermally allowed? Use a **correlation diagram** for your explanation.

(60 marks)

b). Apply the Huckel- Mobius analysis to predict the products of following reactions. Indicate the **stereochemistry**.

(40 marks)



05.

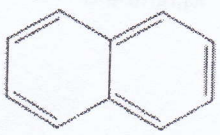
a).

i. What are the nuclei that do not give rise to NMR signals from below compounds?

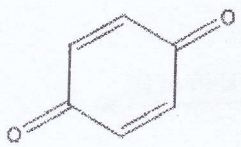
^{12}C, ^{13}C, ^{31}P, ^{19}F, ^{16}O, ^{35}Cl, ^{3}H, ^{10}B, ^{27}Al (10 marks)

ii. How many signals would you expect in the ^{13}C NMR spectra of following compounds?

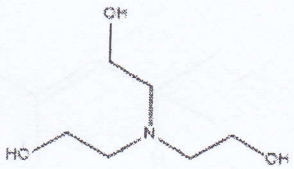
a



b



c



(05 x 3 marks)

(b).

i. Define the terms "upfield" and "downfield" (10 marks)

ii. Express the relevant equation of chemical shift (05 marks)

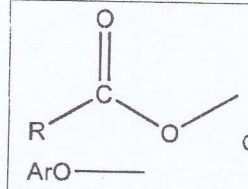
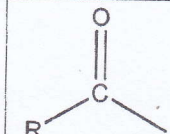
iii. Calculate the chemical shift value of methyl propionate in ^{1}H NMR

Base chemical shifts:

CH_3 - : 0.87

$-CH_2$ - : 1.2

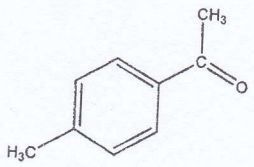
Added chemical shifts:

Substituent	Type of Hydrogen	α - shift	β – shift
 or	CH_3	2.88	-
 Where R is alkyl, aryl, OH, OR', H, CO or N	CH_3	-	0.18
	CH_2	1.05	-

(10 marks)

(c). Determine the number of peaks in proton NMR spectrum of given molecules and draw the relevant NMR spectra

i. 2-methyl-1-propanol
ii. 4-octyne
iii. 3-butylpyridine
iv.

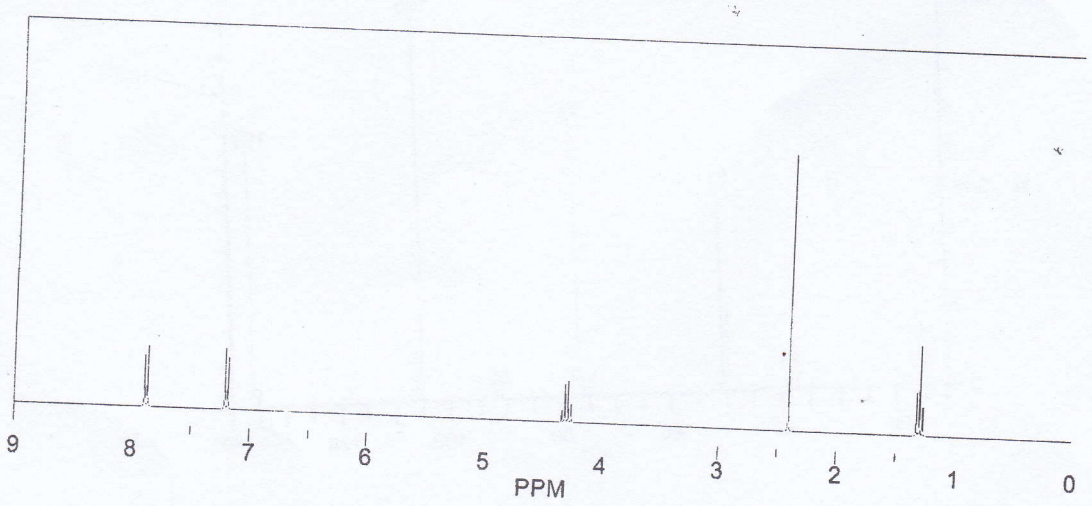


(05 x 4 marks)

(d). Show the structure of the compound with the following data and spectra.

Molecular formula $C_{10}H_{12}O_2$ (IR absorption at 1718 cm^{-1})

Chemical shift (ppm)	Splitting
1.4	triplet
2.4	singlet
4.3	quartet
7.2	doublet
7.9	doublet



(30 marks)

06.

(a).

i. What are the commonly used GC detectors ?
ii. Give 3 applications of Gas chromatography
iii. Sketch a block diagram of mass spectroscopy
iv. Briefly describe "Ion trap mass Analyzer"

(10 x 4 marks)

(b)

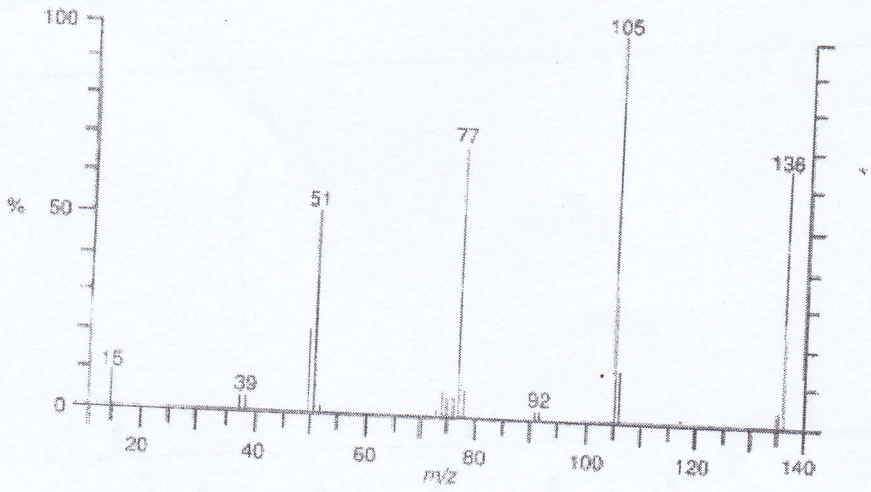
i. Assuming that the molecular ion is the base peak (100% abundance) what peaks would appear in the mass spectrum of each of these molecules
   a. C_2H_5BrO
   b. C_6H_4BrCl

(20 marks)

ii. Suggest possible structure/(s) of C_2H_5BrO and C_6H_4BrCl

(20 marks)

(c). Mass spectrum of methyl benzoate is given below. Identify the ions responsible for the major peaks at m/z = 136, 105, 77 and 51



(20 marks)

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