



RAJARATA UNIVERSITY OF SRI LANKA

FACULTY OF APPLIED SCIENCES

B.Sc. (Honors) Degree in Chemistry

Fourth Year - Semester I Examination – June / July 2018

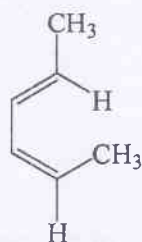
CHE 4309 – ADVANCED ORGANIC CHEMISTRY

Answer all questions.

Time: Three (03) hours

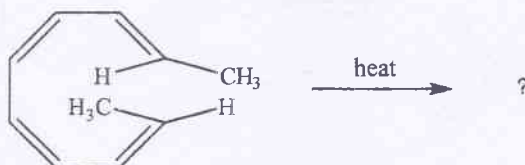
01.

- (a) Predict the product for the concerted photochemical cyclization of *cis,trans*-2,4-hexadiene?

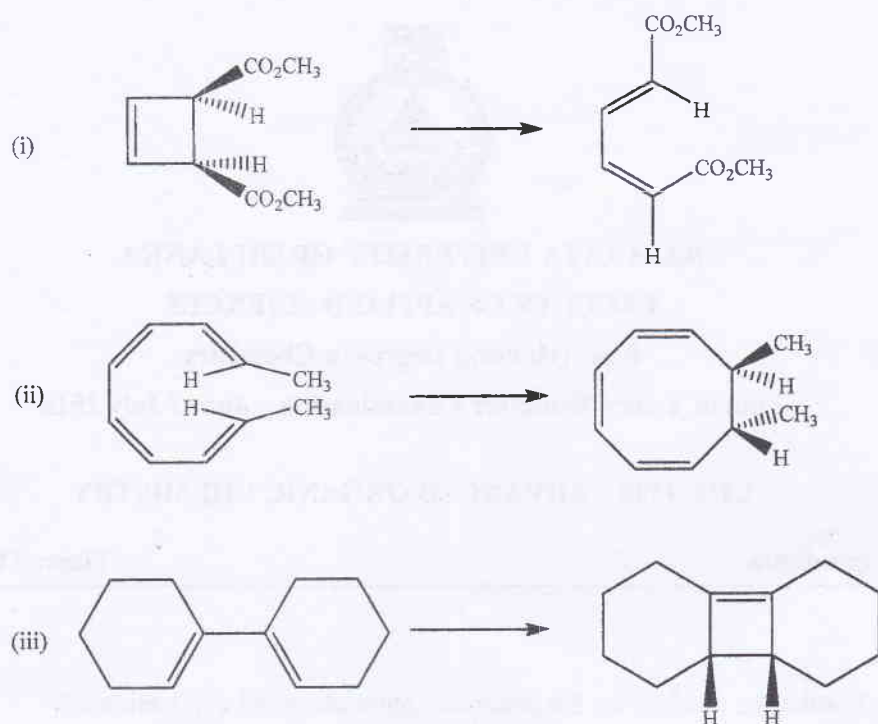


cis,trans-2,4-hexadiene

- (b) The following compound, 2,4,6,8-decatetraene undergoes ring closure to dimethylcyclooctatriene when heated or irradiated. Propose the product under given condition.



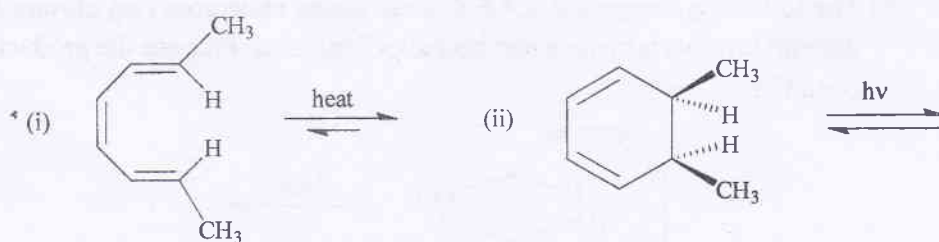
- (c) For each of the following reactions, state whether conrotatory or disrotatory motion of the groups is involved and the condition of the reaction take place (under heat or light).



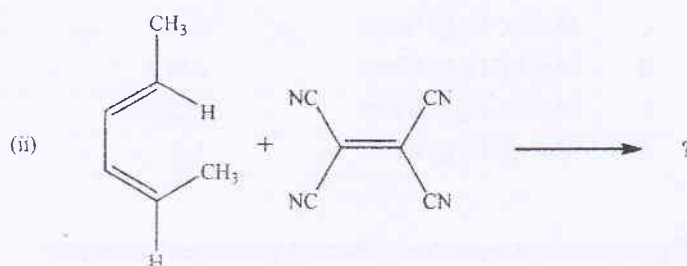
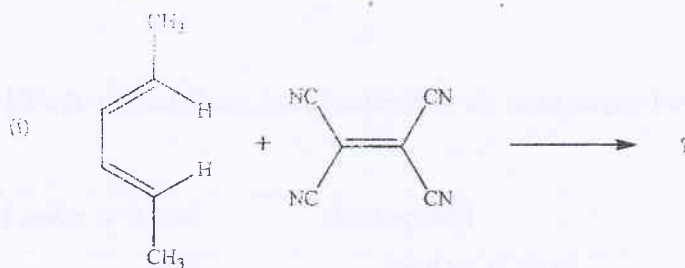
(100 marks)

02.

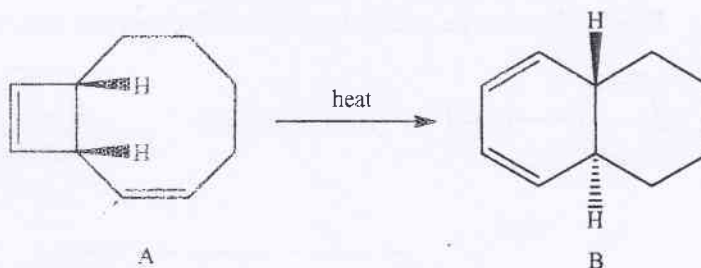
- (a). Give the stereochemistry of the product that you would expect from each of the following electrocyclic reactions.



- (b). Illustrate the products of the following reactions.



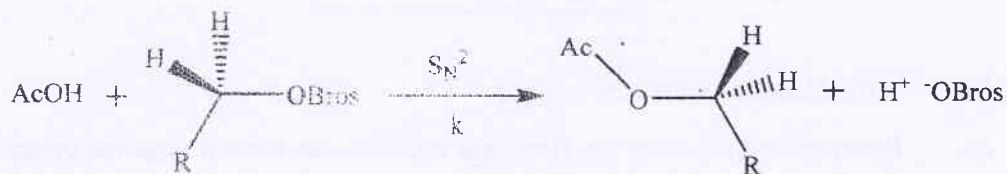
- (c). When compound A is heated, compound B can be isolated from the reaction mixture. During the process two electrocyclic reactions occur; first involves a 4 π -electron system, and the second involves a 6 π -electron system. Outline both electrocyclic reactions and give the structure of the intermediate that involves.



(100 marks)

03.

The solvolysis of a primary sulfonate in a protic solvent can be given as,



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Relative solvolytic rates for ω -methoxyalkyl sulfonates in AcOH are

	Compound	Relative rates, k
a	$\text{Me}(\text{CH}_2)_3\text{OBros}$	1.00
b	$\text{MeO}(\text{CH}_2)_2\text{OBros}$	0.25
c	$\text{MeO}(\text{CH}_2)_3\text{OBros}$	0.67
d	$\text{MeO}(\text{CH}_2)_4\text{OBros}$	657.0
e	$\text{MeO}(\text{CH}_2)_5\text{OBros}$	123.0
f	$\text{MeO}(\text{CH}_2)_6\text{OBros}$	1.2

- (a). Briefly explain the term “neighboring group participation”
 (b). Explain the relative rate for each compound using a suitable mechanism.

(100 marks)

04.

- (a). Substituent constants for ortho and para substituted benzoic acid are given below. Briefly discuss the values by means of resonance structures.



X	σ
p-OH	-0.37
m-OH	0.12
p-F	0.062
m-F	0.337

- (b). Write Hammett equation.
 (c). Reactions which obey the Hammett equation can have a negative or positive value for the reaction constant. What information you can obtain from the sign and the magnitude of the reaction constant. Explain using suitable examples.

(100 marks)

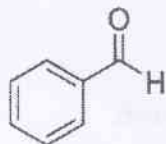
05.

(a).

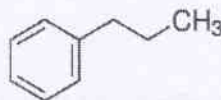
- Name four different features of a ^1H NMR spectrum that provide information about a compound's structure
- Determine the number of peaks in ^1H NMR spectrum of given molecule and draw the relevant NMR spectra



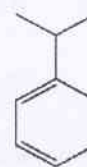
- How many signals would you expect in the ^{13}C NMR spectra of following compounds?. Draw the NMR spectra.



a. Benzaldehyde



b. propylbenzene



c. isopropylbenzene

(50 marks)

(b).

- What are “shielded nucleus” and “deshielded nucleus”
- Define Chemical Shift. At what frequency would the chemical shift of chloroform (CHCl_3 , $\delta = 7.28$ ppm) occur relative to TMS on a spectrum recorded on a 300 MHz spectrometer?

(20 marks)

(c).

Determine the structure of the compound of molecular formula $\text{C}_{15}\text{H}_{14}\text{O}$ using provided data of spectra

MS: Molecular ion at $m/z = 210$, base peak at $m/z = 167$.

^1H -NMR:

- 7.5-7.0 ppm (10H)
- 5.10 ppm (1H)
- 2.22 ppm (3H)

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¹³C-NMR:

- 206.2 (C) 128.7 (CH) 30.0 (CH₃)
- 138.4 (C) 127.2 (CH)
- 129.0 (CH) 65.0 (CH)

IR: strong absorbance near 1720 cm⁻¹

(30 marks)

06.

(a).

- i. List the detectors commonly used with HPLC
- ii. Write a short note on application of HPLC
- iii. Describe the Electron Ionization Process of mass spectrometry
- iv. Briefly describe "Quadrapole Mass Analyzer"

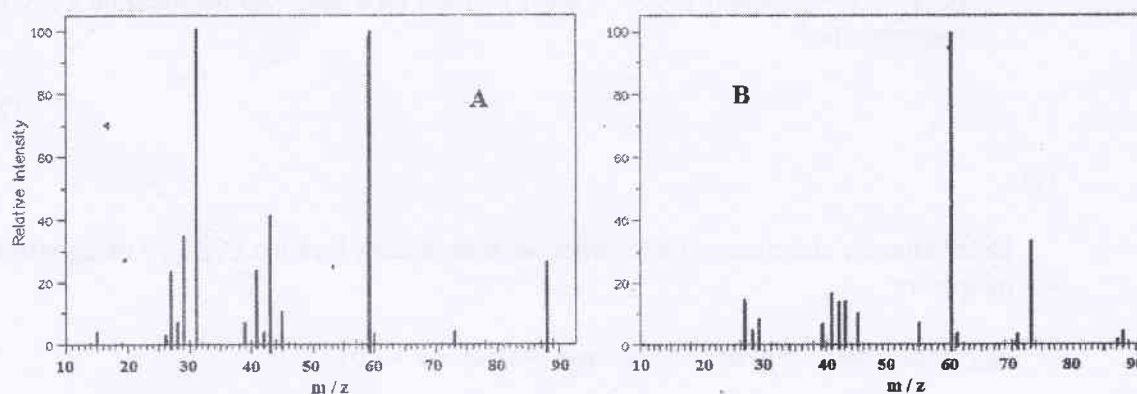
(40 marks)

(b). Suggest possible mass spectrums of the following compounds

- i. 2-Bromopropane
- ii. Nitrobenzene

(10 marks)

(c). Mass spectrums of ethyl propyl ether and butyric acid are given below. Discuss the ionizations and identify the spectrums.



(40 marks)

— END —