



EASTERN UNIVERSITY, SRI LANKA
THIRD EXAMINATION IN SCIENCE-2013/2014 (2019)
SPECIAL DEGREE IN CHEMISTRY
CHS 02 Organic Chemistry I

Answer all questions

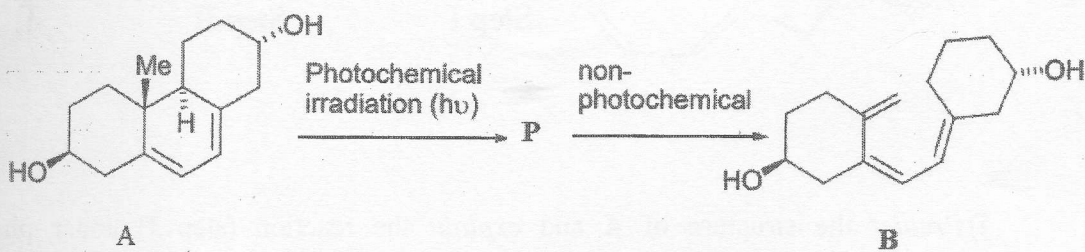
Time Allowed: Two hour

1.

- a) Most of the Diels–Alder reactions use electron-deficient dienophiles and electron-rich dienes. The electron-deficient dienophile has a low-energy LUMO and the electron-rich diene has a high-energy HOMO so that this combination gives a better overlap in the transition state. *Apply* frontier molecular Orbital theory to determine the preferred mode (suprafacial or antarafacial) of cycloaddition reaction of (3E)-2-Methyl-1,3-pentadiene and ethylene under thermal and photochemical condition and hence *predict* the stereochemistry of the product formed in each case.

(40 marks)

- b) Draw the structure of **P** and suggest plausible mechanisms for the two steps A-P and P-B.

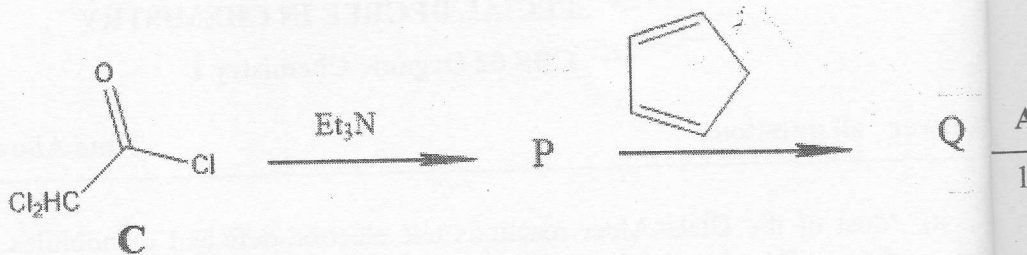


(25 marks)

- c) The very acidic proton on acetylchloride compounds can be removed even with a tertiary amine with loss of chloride ion to obtain ketene. The compound **P** is obtained by reacting the compound **C** with triethylamine. When **P** is treated with cyclopentadiene, a very efficient stereospecific [2 + 2] cycloaddition occurs to give compound **Q**.

Contd.

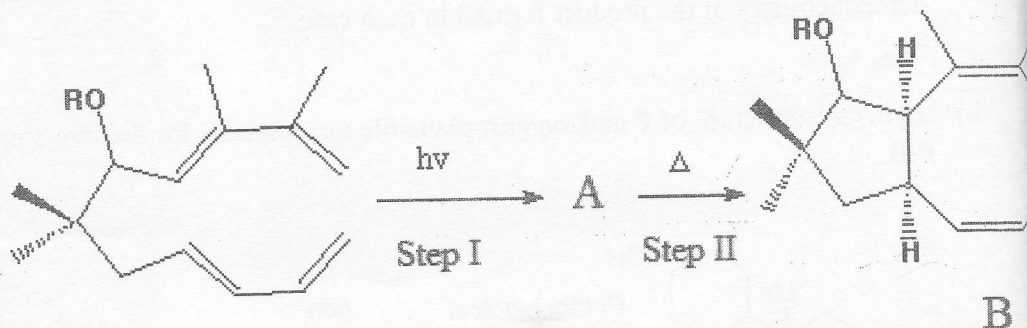
- i. Explain the following reaction and draw the structure of P.
 ii. Explain the formation of the final product Q and draw the structure of the product including the stereochemistry.



(35 marks)

2.

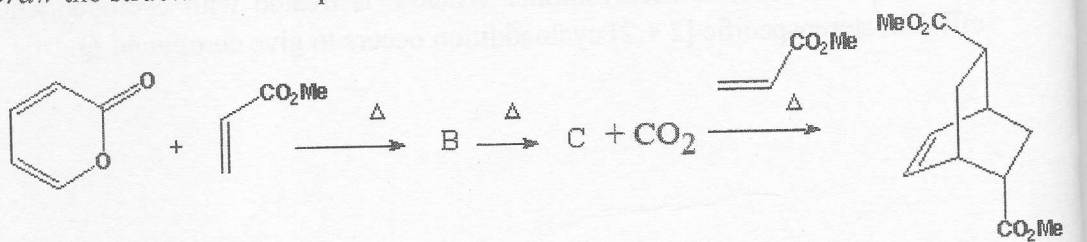
a)



- i) Predict the structure of A and explain the reaction (step I) under photochemical condition.
 ii) Explain the reaction (A to B) under thermal condition (step II).

(30 marks)

b) Draw the structures of the products B and C of the following reaction and explain.



(30 marks)

Contd.