



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

Answer all questions

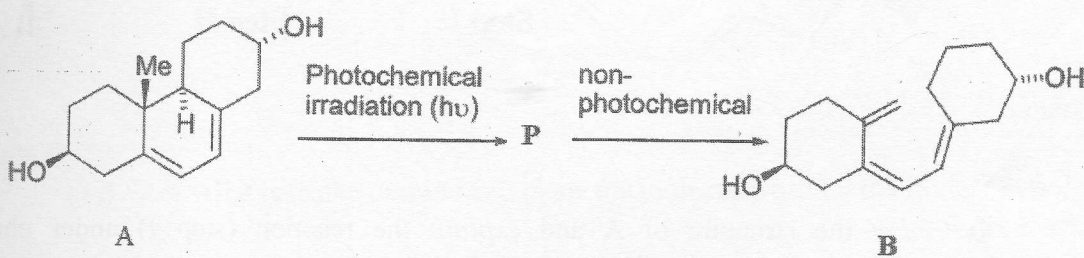
Time Allowed: Two hour

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.

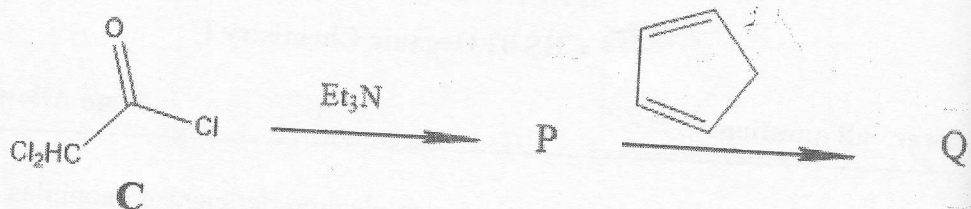


(25 marks)

- 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.

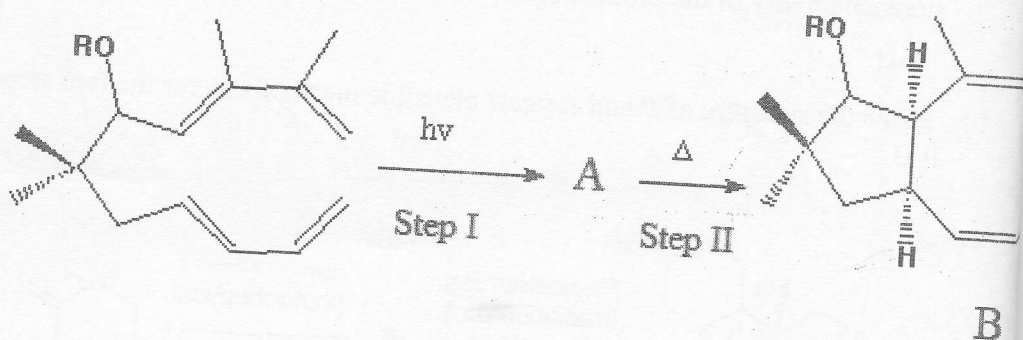
- i. Explain the following reaction and draw the structure of P.
- ii. Explain the formation of the final product Q and draw the structure of the product including the stereochemistry.



(35 marks)

2.

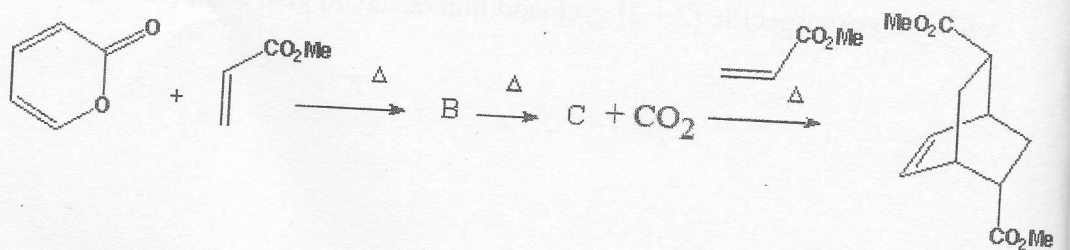
a)



- 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)

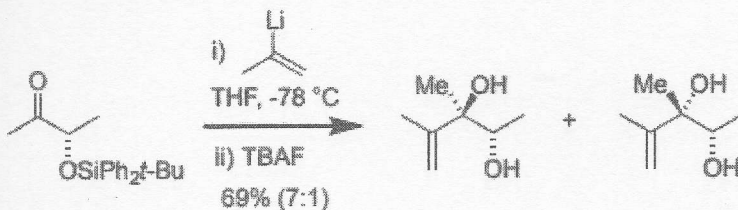
b) Draw the structures of the products B and C of the following reaction and explain.



(30 marks)

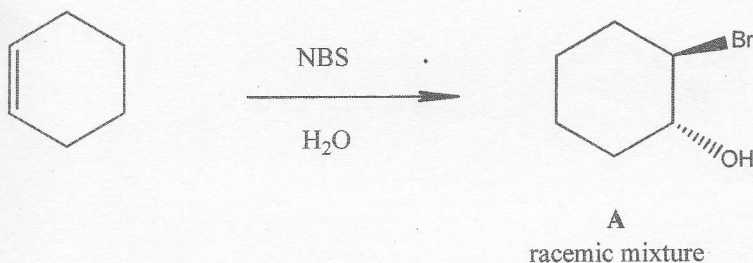
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4. a) The following diastereomeric addition products are formed in a 7:1 ratio. *Assign* the major and minor diastereomers and using the Felkin-Anh model *explain* how the following reactions yields different diastereoisomers as their product (TBAF is a quaternary salt that is used as a source of fluorine. The fluorine anion is typically used for deprotection of silyl ether groups or as a mild base).



(40 marks)

- b) Synthesis of a racemic mixture of compound A involves the following reaction process. *Propose* a plausible radical mechanism for this reaction.

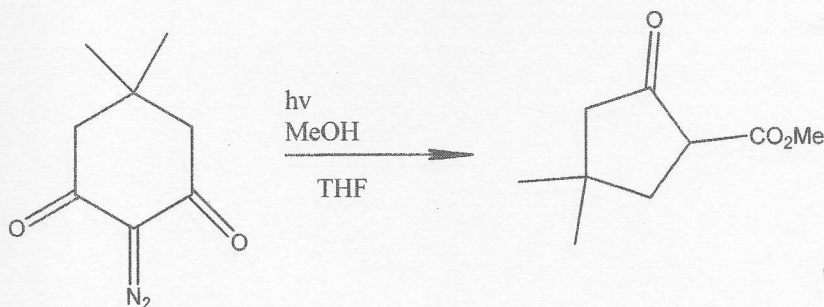


(25 marks)

- c) i) *State* what is triplet carbene and *draw* the molecular orbital diagram.

(10 marks)

- ii) *Propose* a plausible mechanism of the following reaction.



(25 marks)

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