DEDAN KIMATHI UNIVERSITY OF TECHNOLOGY

UNIVERSITY EXAMINATIONS 2021/2022

YEAR ONE SEMESTER ONE EXAMINATIONS FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

SCH 6102 ADVANCED ORGANIC SYNTHESIS

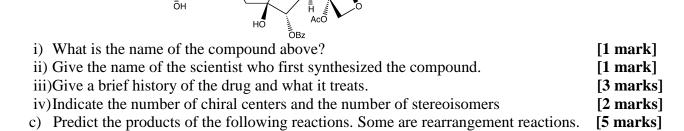
DATE: OCTOBER 2021

TIME: 2 HOURS

INSTRUCTION: Answer ALL questions

QUESTION ONE [15 MARKS]

- a) Define the following terms:
 - i) Sigmatropic rearrangement
 - ii) The Claisen-Schmidt reaction
 - iii) Mannich Reaction
- b) Use the following compound to answer the questions that follow.



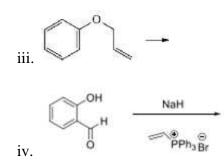
HO

[3 marks]



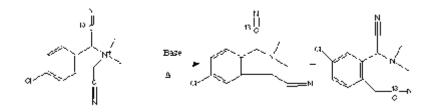
ii.

i.



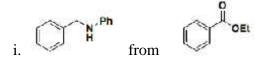
QUESTION TWO: [15 MARKS]

a) When compound 1 is treated with base and heated, it rearranges to give the products shown. The ¹³C isotope is distributed unequally between two products. Explain this result in mechanistic terms, and clearly indicate the type of reactions occurring and their nomenclature. [9 marks]



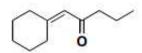
b) Propose how to synthesize the following compounds.

[6 marks]



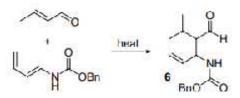
QUESTION THREE: [15 MARKS]

d) Propose a retrosynthetic analysis of the following compound. Your answer should include both the synthons, showing your thinking, and the reagents that would be employed in the actual synthesis.
[5 marks]



one of the starting material is cyclohexanone

e) The synthesis of the alkaloid Pulimiotoxin C may be achieved through the reaction sequence illustrated below, which proceeds via the formation of intermediate 6.



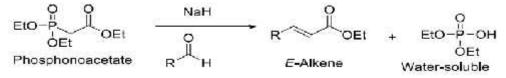
i. What type of cycloaddition reaction is the above

[2 marks]

- ii. Account for the control of the regiochemistry of 6 in the cycloaddition. [3 marks]
- iii. Draw a transition state for the cycloaddition reaction, showing the frontier molecular orbitals and thus predict the relatively configurations of the three chiral centres in 6. [3 marks]
- iv. The above reactions are known to be stereoselective and regioselective. Give the description of each case. [2 marks]

QUESTION FOUR: [15 MARKS]

- a) Use frontier molecular orbital diagram to show whether a [2+2] thermal reaction is forbidden or allowed. [5 marks]
- b) Using dimethyl sulfoxide and oxalyl chloride, illustrate mechanistically how primary alcohol is converted to aldehyde. [5 marks]
- c) Study the reaction given below and answer the following questions.



- i. What is the name reaction of the equation above?
- ii. Propose a plausible mechanism for the reaction in c above

[1 mark] [4 marks]