MACHAKOS UNIVERSITY

University Examinations 2020/2021 Academic Year

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

FOURTH YEAR FIRST SEMESTER EXAMINATION FOR

BACHELOR OF EDUCATION (SPECIAL NEEDS)

BACHELOR OF EDUCATION (SCIENCE)

SCH 402: CONCEPTS OF ORGANIC SYNTHESIS

DATE: 17/8/2021 **TIME: 11.00-1.00 PM**

INSTRUCTIONS:

- The paper consists of **two** sections.
- Section **A** is **compulsory** (30 marks).
- Answer any **two** questions from section **B** (each 20 marks).

SECTION A

QUESTION ONE (30 MARKS)

a) Explain the following terms as used in organic synthesis. (5 marks)

i. Functional group interconversion

ii. Functional group protection

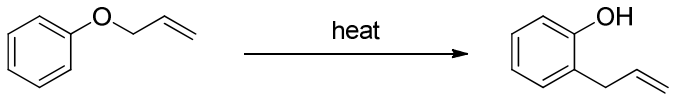
iii. Synthon

iv. Retrosynthetic analysis

v. Retro-Diels-alder reaction

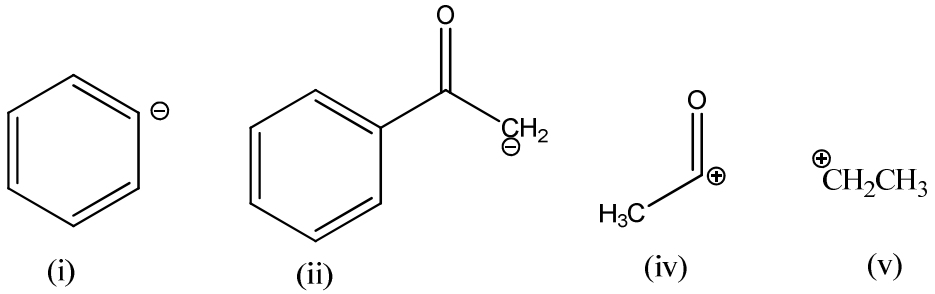
b) 1-Butanol is prepared commercially by a route that begins with an aldol reaction. Show the steps that are likely to be involved. (4 marks)

c) Provide the mechanism for the Claisen rearrangement to form the product shown below. (3 marks)



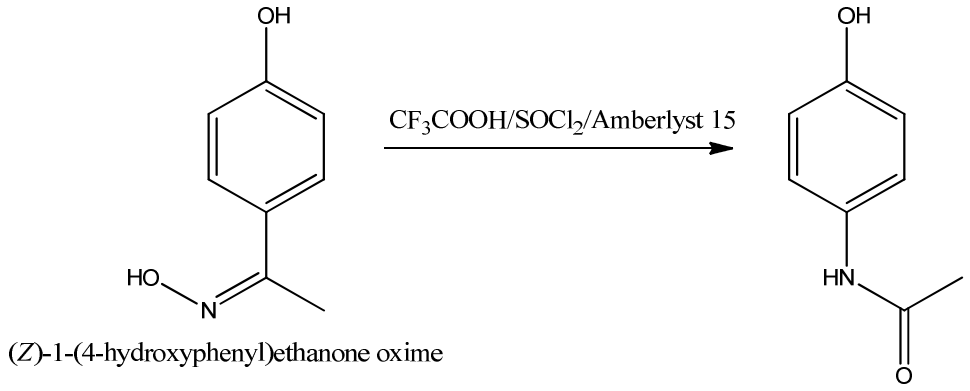
d) Discuss the key differences between aldol reaction and claisen condensation. (4 marks)

e) Provide the possible synthetic equivalents for the following synthons (4 marks)



(i) (ii) (iv) (v)

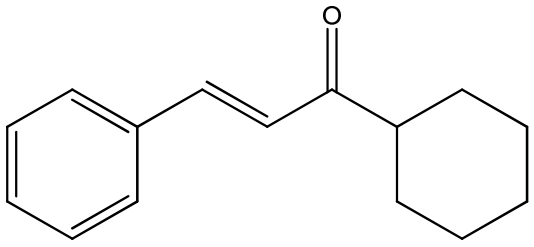
f) Beckmann rearrangement is useful in the synthesis of paracetamol (N-(4-hydroxyphenyl) acetamide). Starting from the oxime shown, provide the mechanism for the rearrangement. (4 marks)



(*Z*)-1-(4-hydroxyphenyl)ethanone oxime

N-(4-hydroxyphenyl)acetamide

g) Perform a retrosynthetic analysis on the target molecule shown below showing clearing the synthons and synthetic equivalents (SEs). Using the identified SEs, perform a forward reaction to form the target molecule following the correct mechanism. (6 marks)

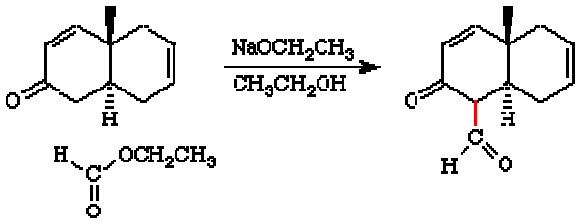


SECTION B

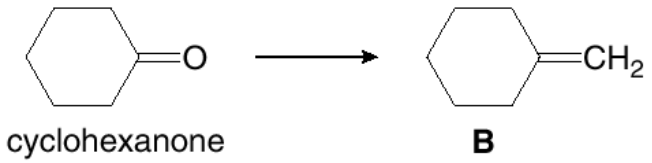
QUESTION TWO (20 MARKS)

a) Explain one factor to consider with regards to the base used when carrying out claisen condensation. (2 marks)

b) Devise a mechanism to show how the product in the reaction below is formed by using curly arrows to indicate the movement of electrons. Your mechanism must account for the role of the base. (6 marks)

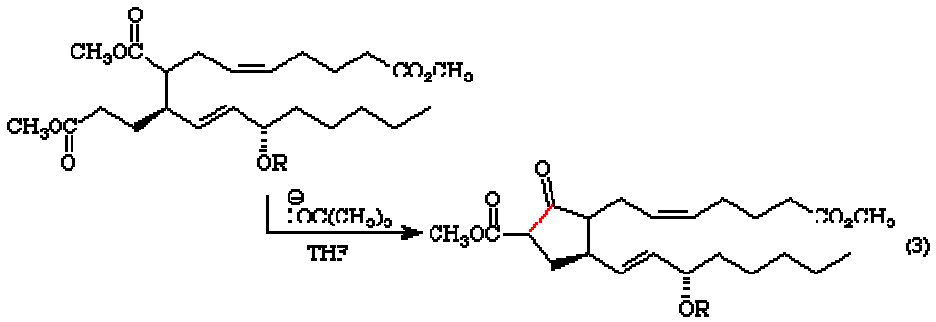


c) Describe two ways of synthesizing cycloalkane (B) from cyclohexanone and indicate the preferred route. (6 marks)



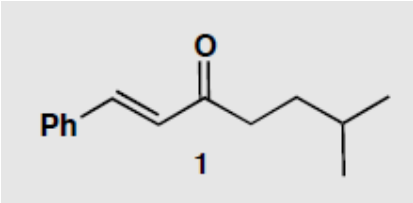
d) The reaction below shows a pathway that can be put to good use as part of the total synthesis of the prostaglandin PGA_2. Show the mechanism for the synthesis of PGA_2.

(6 marks)



QUESTION THREE (20 MARKS)

a) A reaction was planned so as to give compound 1 shown below. Instead the reaction proceeded as shown in scheme 1. Explain what went wrong and suggest a synthetic route that would give the target molecule 1. (5 marks)



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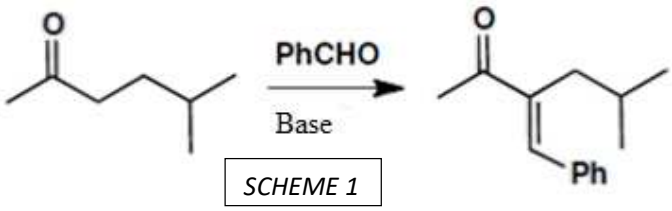
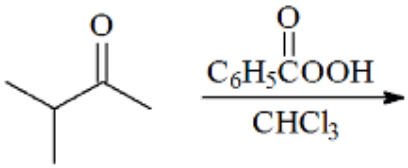
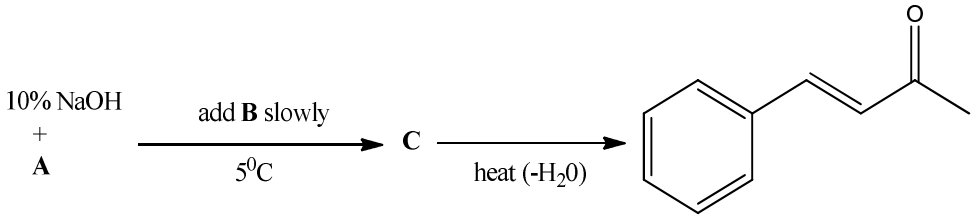


SCHEME 1

b) One of the ways known to convert ketones into esters is a reaction known as a Baeyer-Villiger oxidation. Show the mechanism for the Baeyer-Villiger oxidation shown below. Discuss one factor to consider for unsymmetrical ketones. (6 marks)



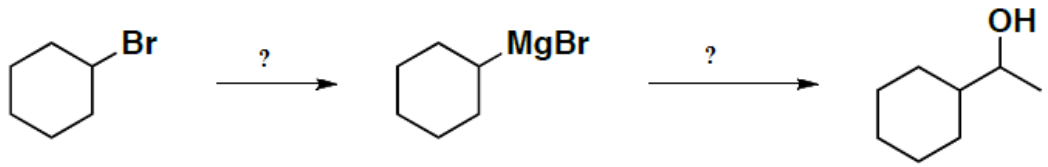
c) Crossed aldol reaction can be used for synthesis of cinnamaldehyde, which is used as a fungicide. Provide the missing reagents **A**, **B** and **C.** (3 marks)



Cinnamaldehyde

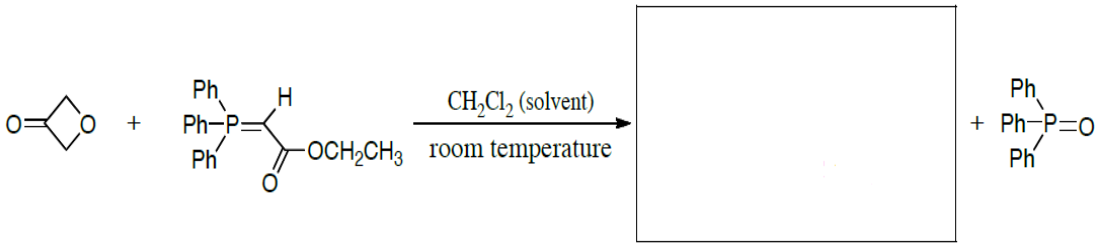
d) Ethanol [CH_3CH_2OH] is often present in technical-grade diethyl ether. If this grade of diethyl ether were used, what effect, if any, would the acetaldehyde have on a Grignard reagent used? Explain through the use of a chemical equation using C_6H_5–MgBr as an example. (4 marks)

e) Provide the missing reagents in the reaction below. (2 marks)

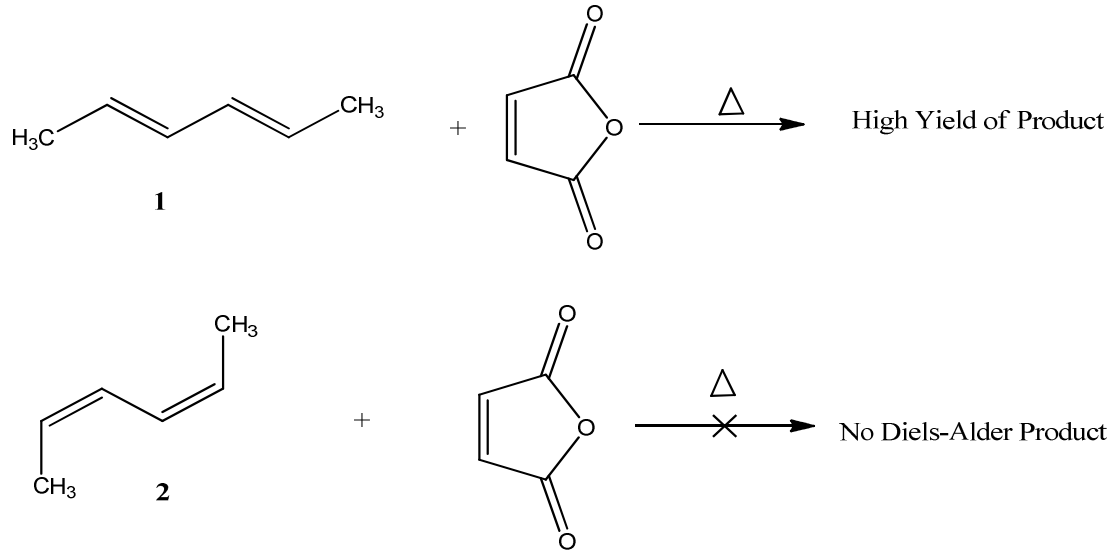


QUESTION FOUR (20 MARKS)

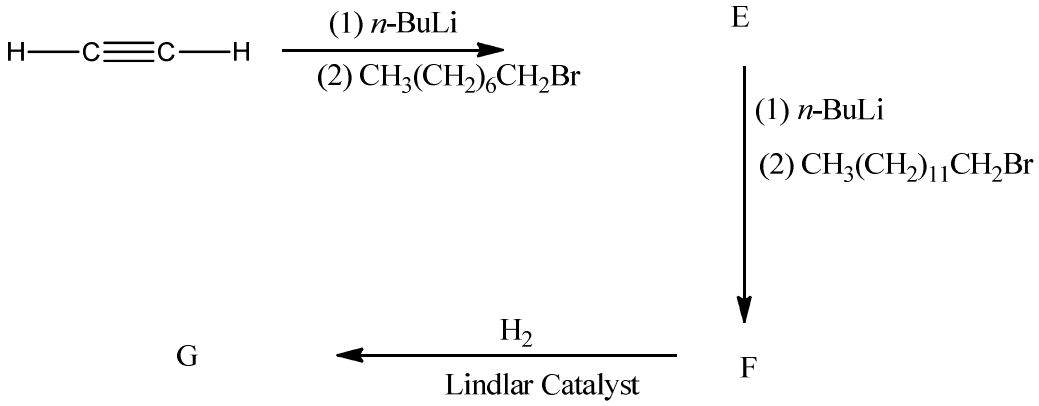
a) For the following reaction, draw in the box the structure of the expected product from the reaction shown and provide a reasonable step-by-step mechanism using the curved-arrow convention that accounts for its formation and explain the driving force for this reaction. (4 marks)



b) The stereoisomeric dienes 1 and 2, shown below, undergo Diels-Alder reactions with maleic anhydride at very different rates. While the reaction using diene 1 proceeds quickly, diene 2 fails to easily undergo a Diels-Alder reaction even at very high temperatures. Provide a clear explanation for this difference in reactivity between dienes 1 and 2. (2 marks)



c) Muscalure, the pheromone of the female housefly Musca domestica, can be synthesized based on the pathway highlighted below.



i. Deduce the structures of the missing intermediate compounds (**E** and **F**) in this synthesis and of the pheromone **G**. (6 marks)

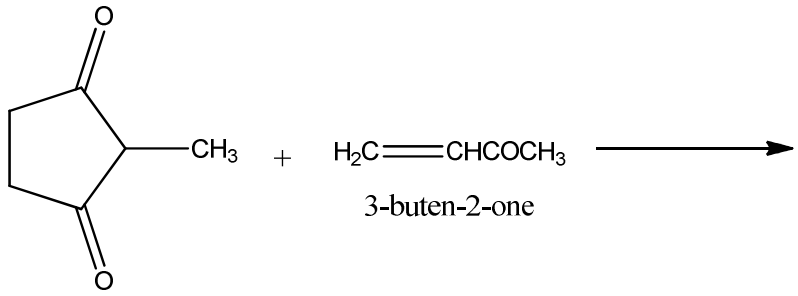
ii. Propose a retrosynthetic pathway for muscalure that is consistent with the synthetic scheme above. (4 marks)

iii. Is the above synthesis a linear or convergent synthesis? (2 marks)

iv. What are the two main advantages of a convergent synthesis over a linear synthesis? (2 marks)

QUESTION FIVE (20 MARKS)

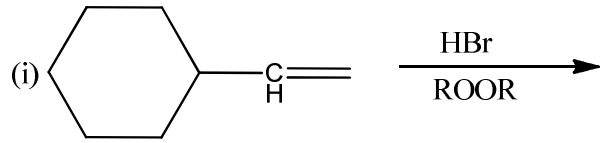
a) What product would you expect from a Robinson annulation reaction of 2-methyl- 1,3-cyclopentanedione with 3-buten-2-one? (5 marks)

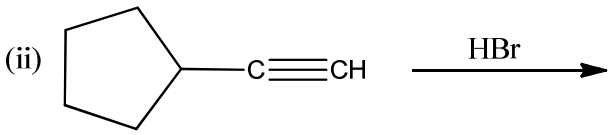


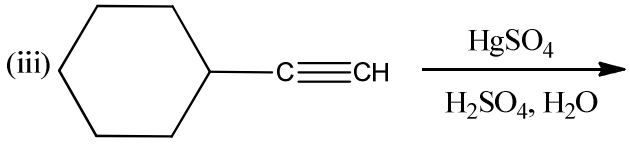
2-methyl- 1,3-cyclopentanedione

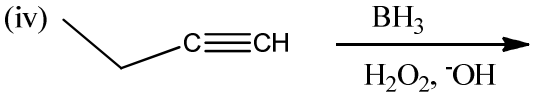
b) Intramolecular aldol cyclization of 2,5-heptanedione with aqueous NaOH yields a mixture of two enone products in the approximate ratio 9:1. Write their structures, and show how each is formed. Identify the major and minor product. (6 marks)

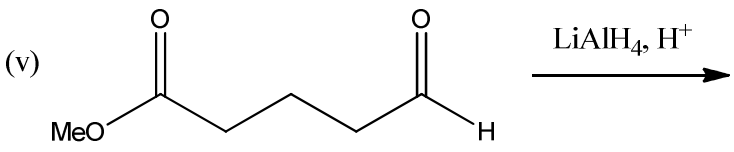
c) Provide the product in the following reactions. (5 marks)



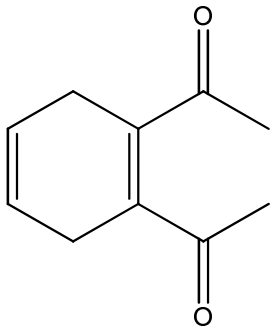




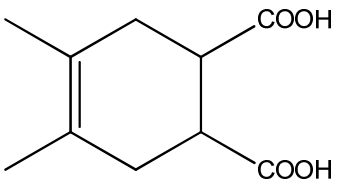




d) By carrying out a retrosynthetic analysis, identify the reactants required to form the Diels-alder products shown below. (4 marks)



(i)



(ii)