MACHAKOS UNIVERSITY

University Examinations 2021/2022

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

FOURTH YEAR SUPPLEMENTARY/SPECIAL EXAMINATION FOR

BACHELOR OF EDUCATION SCIENCE (SPECIAL NEEDS)

BACHELOR OF EDUCATION (SCIENCE)

SCH 402: CONCEPTS OF ORGANIC SYNTHESIS

DATE: 15/03/2022 **TIME: 2:00-4:00 PM**

INSTRUCTIONS:

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

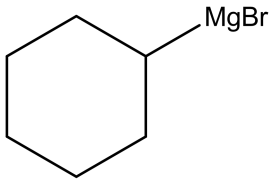
SECTION A

QUESTION ONE (30 MARKS)

a) Explain the following terms as used in organic synthesis (4 marks)
(i) Intramolecular aldol reaction
(ii) Ylide
(iii) Functional group protection
(iv) Enolate

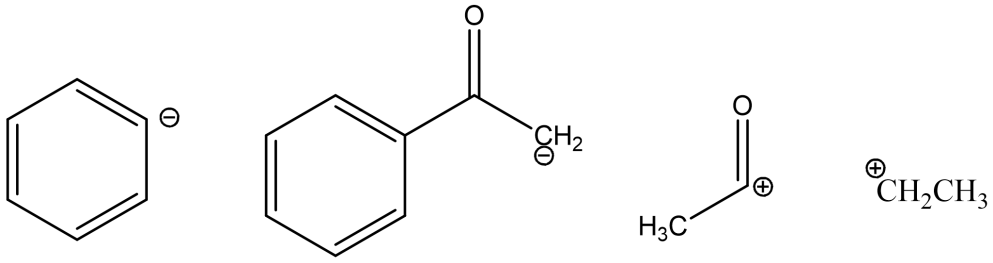
b) 1-Butanol is prepared commercially by a route that begins with an aldol reaction. Show the steps that are likely to be involved. (4 marks)

c) Describe how you would synthesis the Grignard reagent shown below starting with cyclohexane. (4 marks)



d) Using examples, define the following concepts (6 marks)
(i) Carbocation rearrangement
(ii) Keto-enol Tautomerism
(iii) Stereospecific and stereoselective reactions

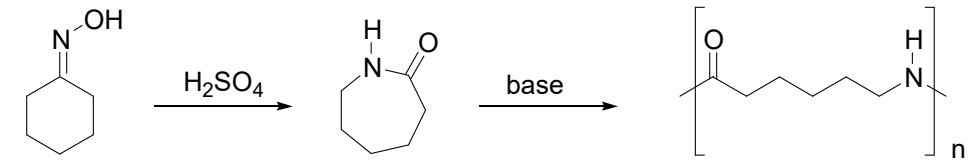
e) Provide the possible synthetic equivalents for the following synthons (4 marks)



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

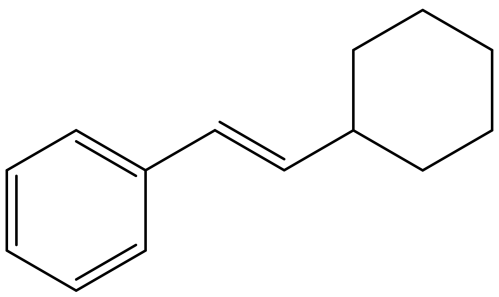
f) Beckmann rearrangement is useful in the conversion of cyclohexanone to caprolactam via oxime. Caprolactam is the feedstock in the production of Nylon 6. Following the appropriate mechanism, show how oxime shown below rearranges to form caplolactam.

(4 marks)



oxime caprolactam nylon

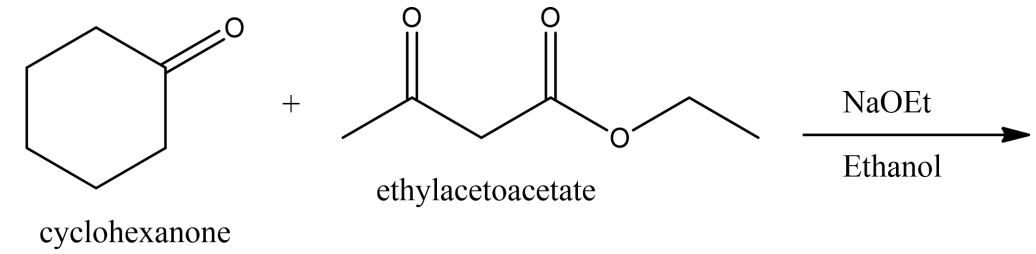
g) Perform a retrosynthetic analysis on the alkene shown below. Then, propose a synthetic route of this alkene from a carbonyl compound and phosphorus ylide. (4 marks)



SECTION B

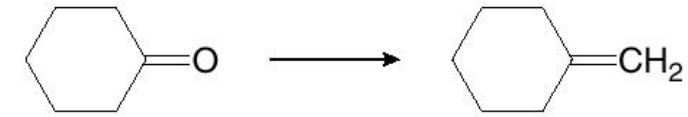
QUESTION TWO (20 MARKS)

a) Following the correct mechanism, provide the product formed in the reaction below. (4 marks)



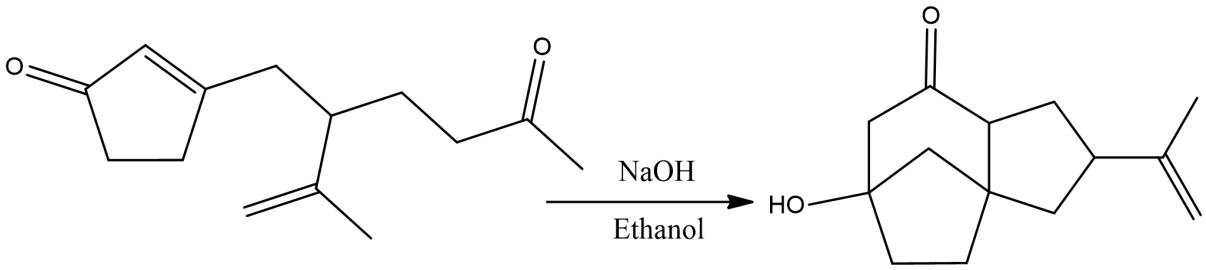
cyclohexanone ethylacetoacetate

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



cyclohexanone **B**

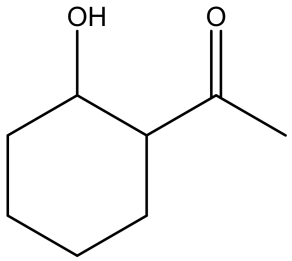
c) The following reaction involves an intramolecular Michael reaction followed by an intramolecular aldol reaction. Write both steps, and show their mechanisms. (6 marks)



d) Mixed aldol reactions are not economically useful because a number of products are likely to be formed. Using examples, describe two ways in which aldol reaction can be made synthetically useful. (4 marks)

QUESTION THREE (20 MARKS)

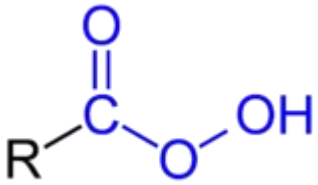
a) Following the appropriate disconnection demonstrate how the molecule below can be synthesized (5 marks)



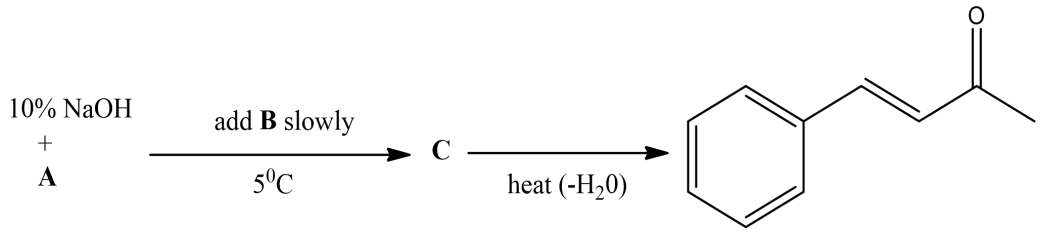
1-(2-hydroxycyclohexyl)ethan-1-one

b) Upon heating the solution, the above compound is likely to be converted into α,β-unsaturated carbonyl. Show the mechanism for the base catalyzed dehydration of the above compound (5 marks)

c) Provide the product formed when cyclohexanone reacts with peroxyacid shown below to produce an ester via Baeyer-Villiger oxidation (5 marks)



d) 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).

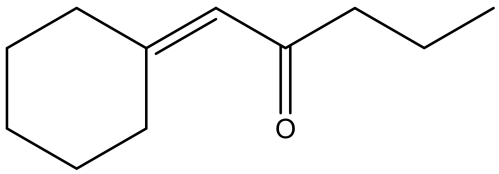


Cinnamaldehyde

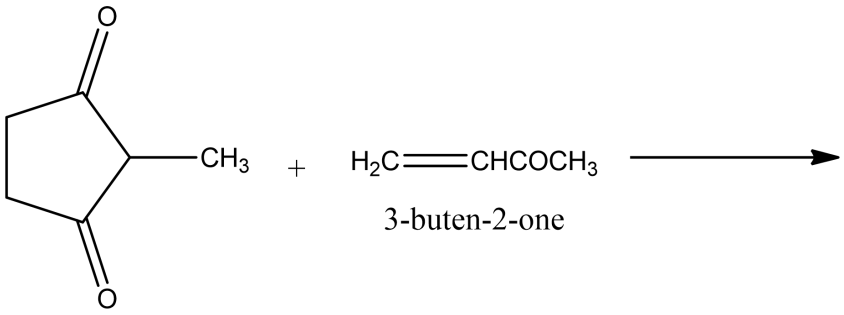
e) One of the methods used to synthesis carboxylic acid is Grignard reaction. Following the appropriate mechanism, show how the carboxylic acid is synthesized (2 marks)

QUESTION FOUR (20 MARKS)

a) Propose a retrosynthetic analysis of the compound shown below (3 marks)



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

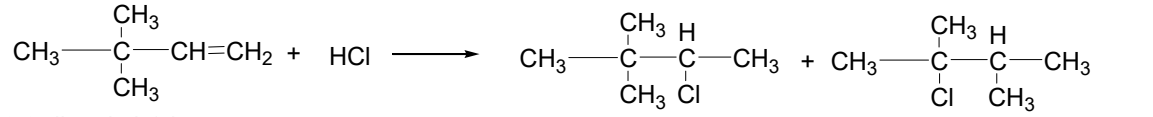


3-buten-2-one

2-methyl- 1,3-cyclopentanedione

c) It is expected that addition of HCl to 3,3-dimethyl-1-butene should give 3-chloro-2,2-dimethylbutane as the major product. However, this in never the case and 2-chloro-2,3-dimethylbutane is isolated as the major product. Explain this observation and show the mechanism resulting in the formation of the major product

(5 marks)



3,3-dimethyl-1-butene

3-chloro-2,2-dimethylbutane
minor product

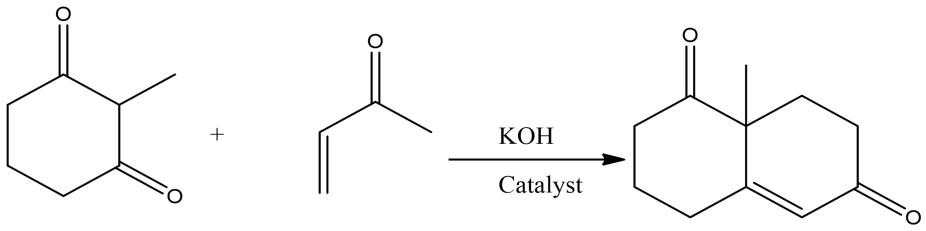
2-chloro-2,3-dimethylbutane
major product

d) 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. (7 marks)

QUESTION FIVE (20 MARKS)

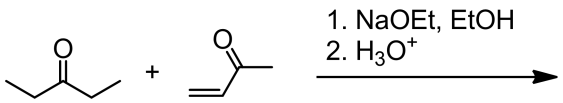
a) Propose a reasonable and stepwise reaction mechanism for the reaction shown below

(5 marks)

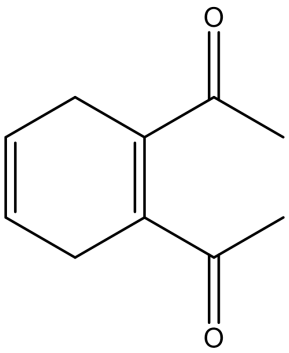


b) Show the product formed in the reactions below following the correct mechanism

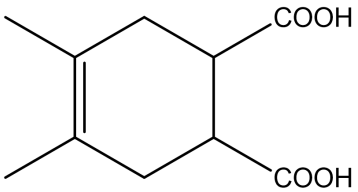
(6 marks)



c) Identify the reactants formed when the molecules shown below undergo retro-Diels -alder reaction. (4 marks)



(i)



(ii)

f) In the aldol reaction between (i) propanal and acetaldehyde, and (ii) acetaldehyde and benzaldehyde, only one is synthetically useful. With reasons, identify the one which is useful and give the mechanism for the resulting product . (5 marks)