MACHAKOS UNIVERSITY

University Examinations 2019/2020Academic year

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

…….. YEAR …….SESSION EXAMINATION FOR

MASTER OF SCIENCE (CHEMISTRY)

SCH 804: MODERN SYNTHETIC ORGANIC CHEMISTRY

DATE: SCHOOL BASED **TIME:**

INSTRUCTIONS TO CANDIDATES

- The paper consists of **two** sections.
- Section **A** is **compulsory** (30 marks).
- Answer any **two** questions from section **B** (each 15 marks).

SECTION A

QUESTION ONE (30 MARKS)

a) Explain the following terms as used in organic synthesis (2 marks)

i. Electrophilic aromatic substitution

ii. Keto-enol Tautomerism

b) Providing examples, differentiate between the following (4 marks)

i. Stereoselective and stereospecific reactions

ii. Stabilized and unstabilized ylides

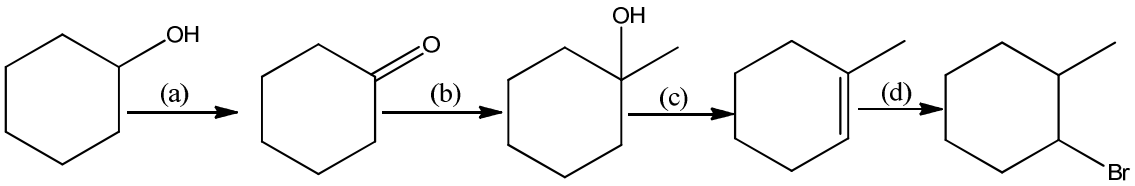
c) Predict the major products of the following reactions (3 marks)

i. Nitration of bromobenzene

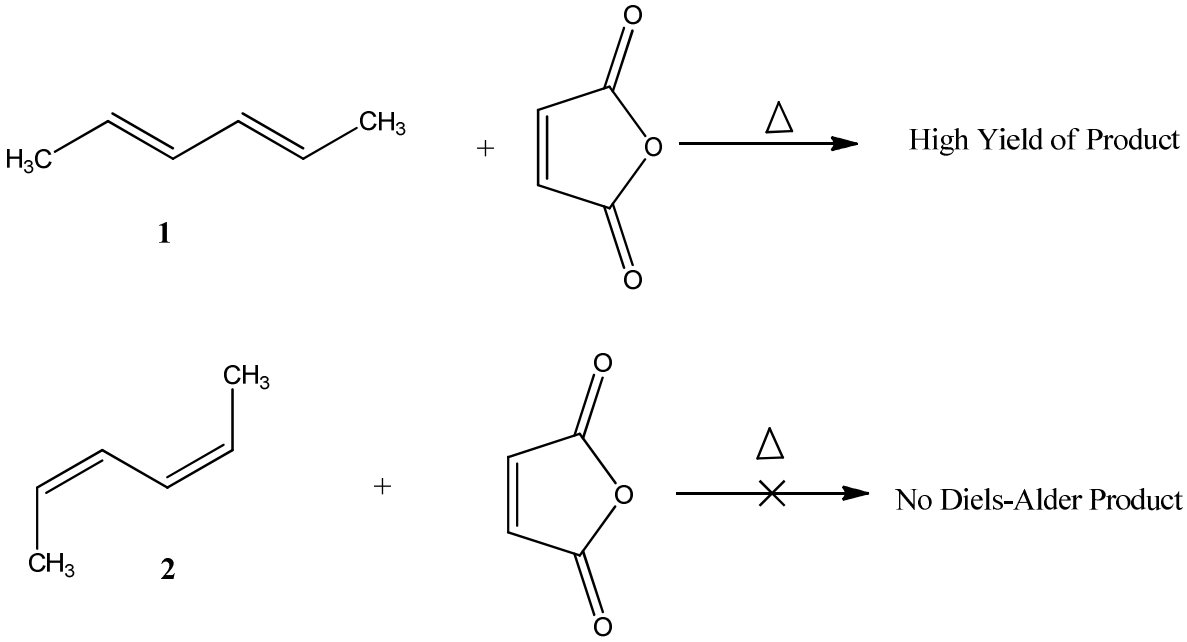
ii. Chlorination of Phenol

iii. Bromination of nitrobenzene

d) Provide the missing reagents in steps (a), (b), (c), and (d) (4 marks)



e) 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)



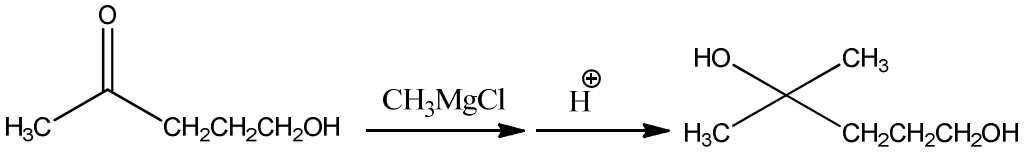
f) Provide the main product in the ozonolysis of 1,4-dimethylcyclohexene followed by a reductive workup with dimethylsulfide (2 marks)

g) Describe how you would go about to synthesis propylbenzene (2 marks)

h) Explain two ways in which aldol reaction can be synthetically useful, providing examples in each case (4 marks)

i) One of the methods used to synthesis carboxylic acid is Grignard reaction. Following the appropriate mechanism, show how the carboxylic acid is synthesized (3 marks)

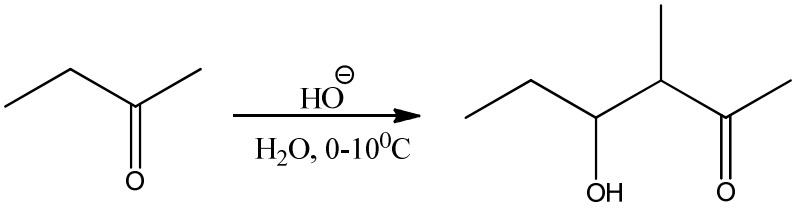
j) The compound below requires to undergo Grignard reaction to form an alcohol. Before the Grignard reagent can be added, the alcohol functional group must be protected. Provide the appropriate steps that must be followed until the desired product is formed (4 marks)



SECTION B

QUESTION TWO (20 MARKS)

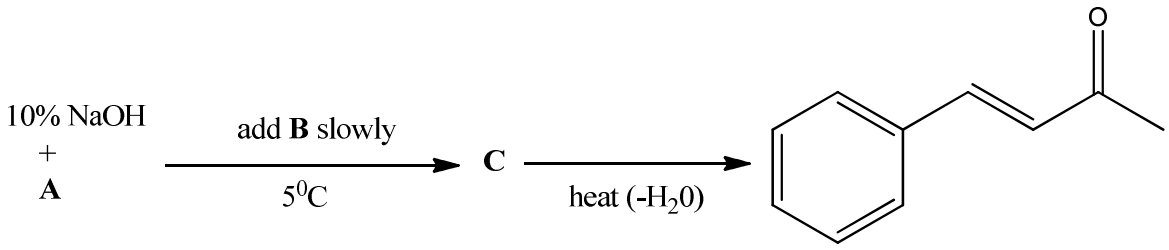
a) i Provide a mechanism for the aldol addition of propanal shown below (3 marks)



ii Provide a mechanism for the reaction above if it was acid catalysed (3 marks)

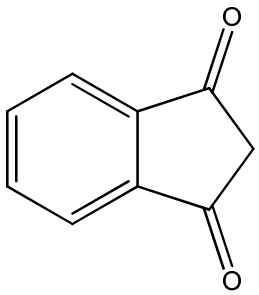
iii Provide a reason why the product of aldol addition is 3-hydroxy-2-methylpentanal and not 4-hydroxyhexanal (2 marks)

b) 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

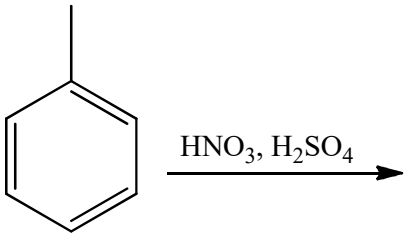
c) Show how the diketone shown below could be prepared by condensation reaction (4 marks)

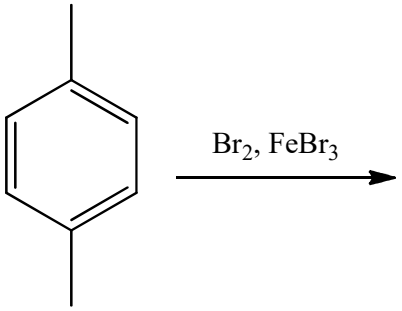


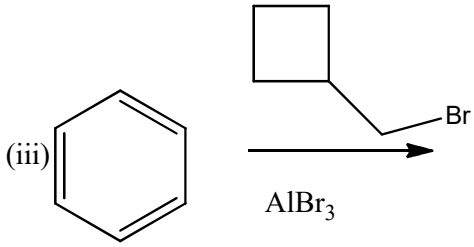
QUESTION THREE (20 MARKS)

a) When benzene reacts with 1-chloro-2,2-dimethylpropane in the presence of aluminium chloride, the major product is 2-methyl-2-phenyl butane not 2,2-dimethyl-1-phenyl propane. Following the correct mechanism explain this observation (4 marks)

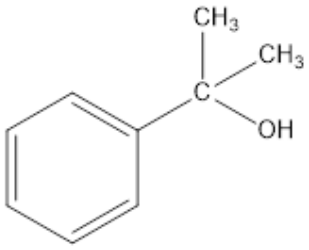
b) Provide the products formed in each of the following reactions following the appropriate mechanism (9 marks)

(i) 

(ii) 

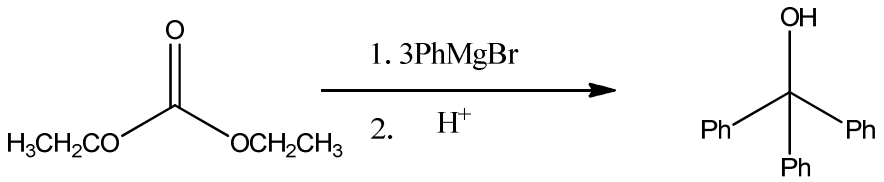
(iii) 

c) Provide the ester and Grignard reagent that are required to prepare the alcohol shown below (2 marks)

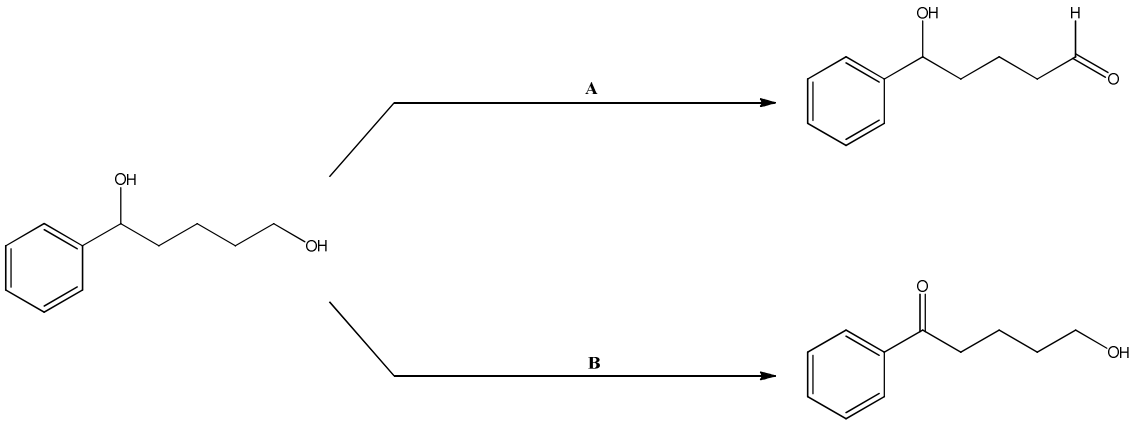


QUESTION FOUR (20 MARKS)

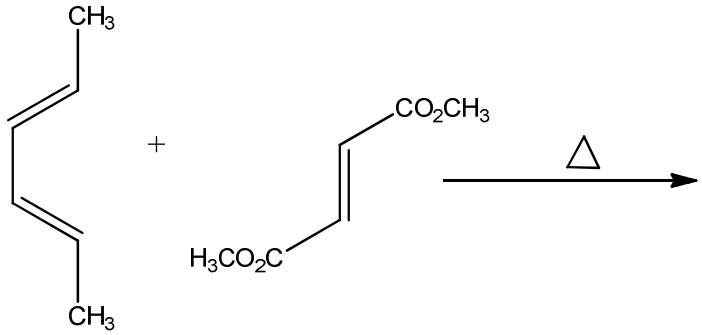
a) Triphenylmethanol can also be prepared by the reaction of PhMgBr with diethylcarbonate $(CH_3CH_2O)_2C=O$, followed by H+ workup. Draw a detailed, step-by-step mechanism for the following reaction (5 marks)



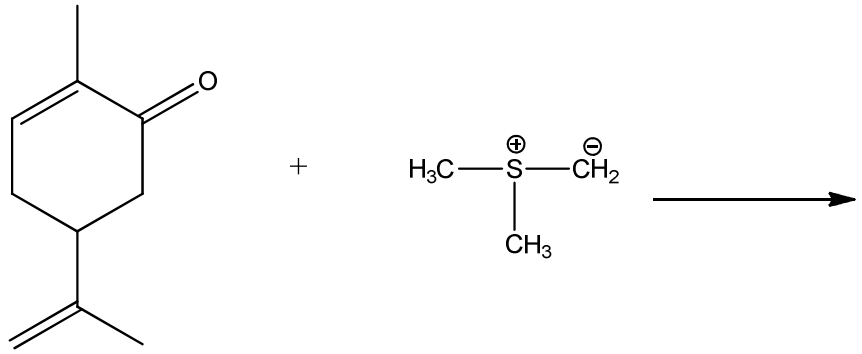
b) Provide the missing reagents A and B in the reactions below (2 marks)

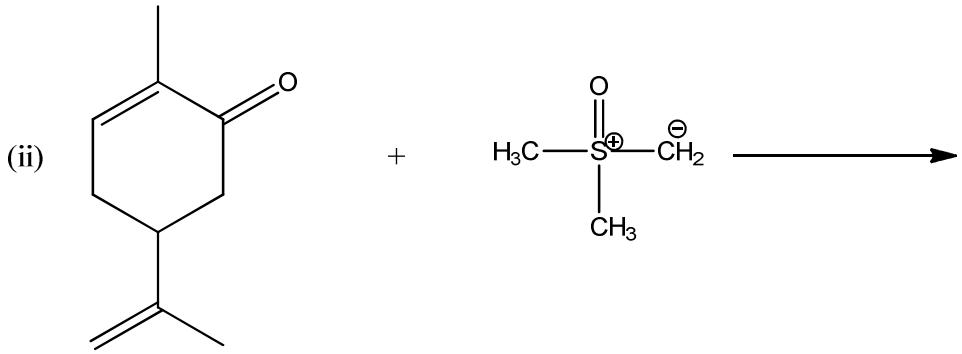


c) Provide Diels-Alder product in the reaction below showing the stereochemistry of the product (3 marks)

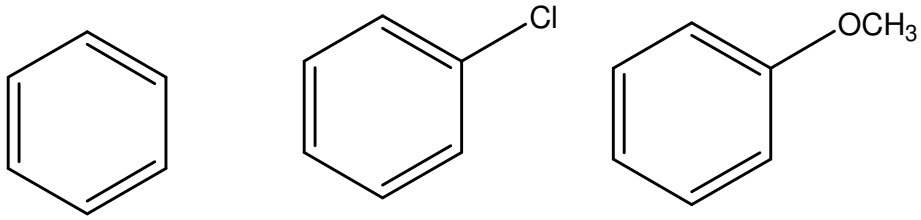


d) Complete the reactions below (2 marks)

(i) 

(ii) 

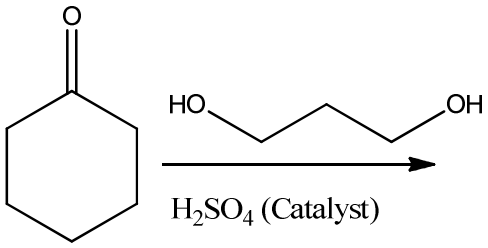
e) Rank the following groups in order of increasing reactivity (3 marks)



QUESTION FIVE (20 MARKS)

a) Show the product formed in the reactions below following the correct mechanism (8 marks)

(i)



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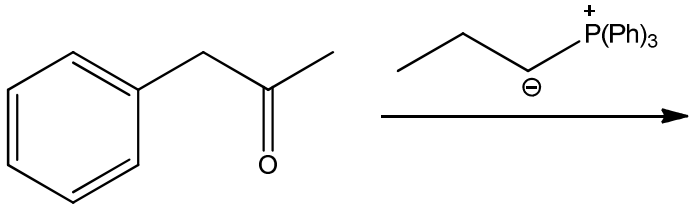

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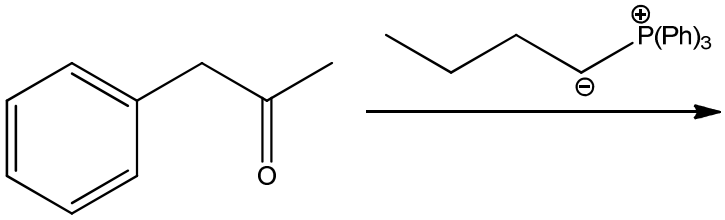

b) Protecting groups are a common feature in multi-step organic synthesis.

(i) Explain, why protecting groups are considered "a necessary evil" in multi-step organic synthesis? (2 marks)

(ii) What are the qualities of a good protecting group in multi-step organic synthesis (3 marks)

(iii) Provide four functional groups that commonly require protection (2 marks)