



MACHAKOS UNIVERSITY

University Examinations 2020/2021

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

FIRST YEAR FIRST SEMESTER EXAMINATION FOR
MASTER OF SCIENCE (CHEMISTRY)

SCH 804: MODERN SYNTHETIC ORGANIC CHEMISTRY

DATE: 15/5/2021

TIME: 2:00 -5:00 PM

INSTRUCTIONS:

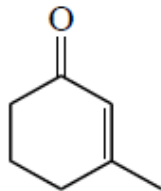
- The paper consists of **two** sections.
- Section **A** is **compulsory** (30 marks).
- Answer any **two** questions from section **B** (each 15 marks).

SECTION A (COMPULSORY)

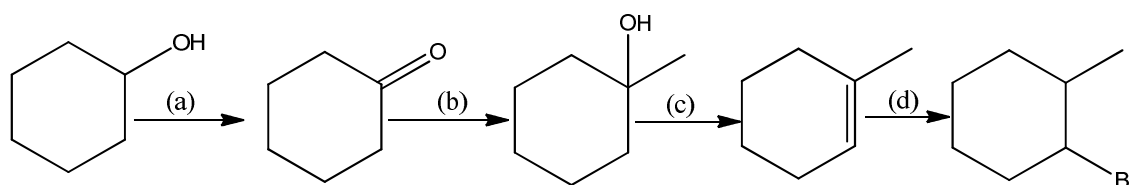
QUESTION ONE (30 MARKS)

- a) Aldehydes are more reactive towards nucleophilic addition reactions than ketones. Justify!
(2 marks)
- b) Providing examples, differentiate between the following: (4 marks)
- (i) Stereoselective and stereospecific reactions
 - (ii) Stabilized and unstabilized ylides
- c) Clearly illustrate the difference between the aldol addition and aldol condensation?
(4 marks)

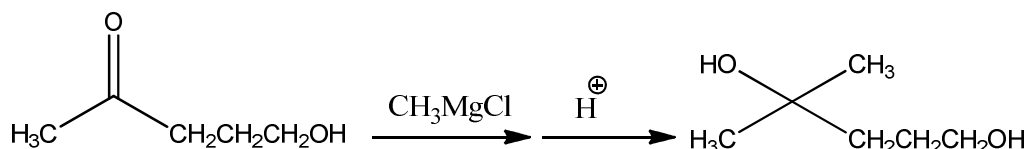
- d) Show how the α , β -unsaturated ketone shown below can be prepared by an aldol condensation. (4 marks)



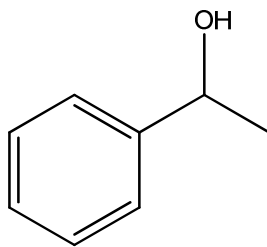
- e) In aldol addition reaction of acetone, the equilibrium favors the ketone reactant rather than the addition product, diacetone alcohol. Discuss how the yield for the product can be increased. (2 marks)
- f) Provide the missing reagents in steps (a), (b), (c), and (d) below (4 marks)



- g) Outline how you would synthesize *p*-bromonitrobenzene from benzene. (2 marks)
- h) 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. (2 marks)



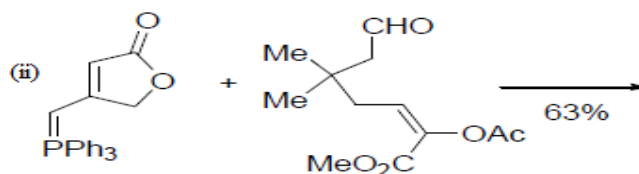
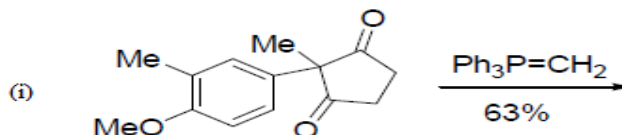
- i) Using lithium diisopropylamide (LDA) and any other unsymmetrical ketone, explain the term regioselectivity. (2 marks)
- j) Describe how you would synthesize the molecule below from cyclohexyl bromide (4 marks)



QUESTION TWO (15 MARKS)

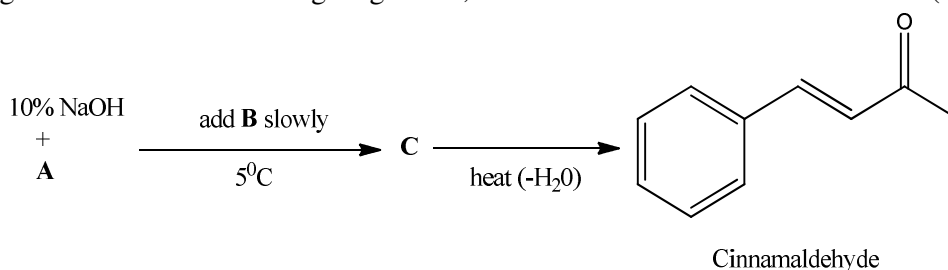
a) Provide the product in the following reactions.

(4 marks)



b) Discuss why the product of aldol addition between two propanals is 3-hydroxy-2-methylpentanal and not 4-hydroxyhexanal. (2 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)

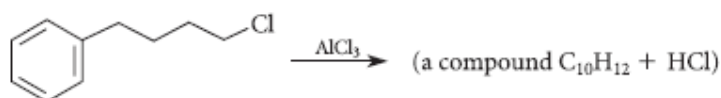


d) Following the appropriate mechanism, show why electrophilic aromatic substitution reaction for methoxybenzene occurs in ortho and para positions. (6 marks)

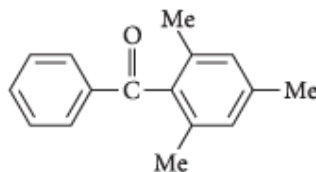
QUESTION THREE (15 MARKS)

a) What electrophilic substitution product is formed when 2-methylpropene is added to a large excess of benzene containing HF and the Lewis acid BF_3 ? By what mechanism is it formed? (4 marks).

b) Predict the product of the following reaction and draw the curved-arrow mechanism for its formation. (5 marks)



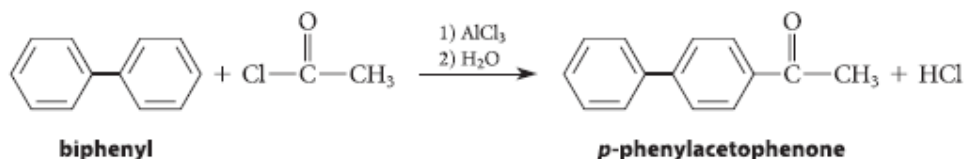
- c) State two different Friedel-Crafts acylation reactions that can be used to prepare the following compound. (4 marks)



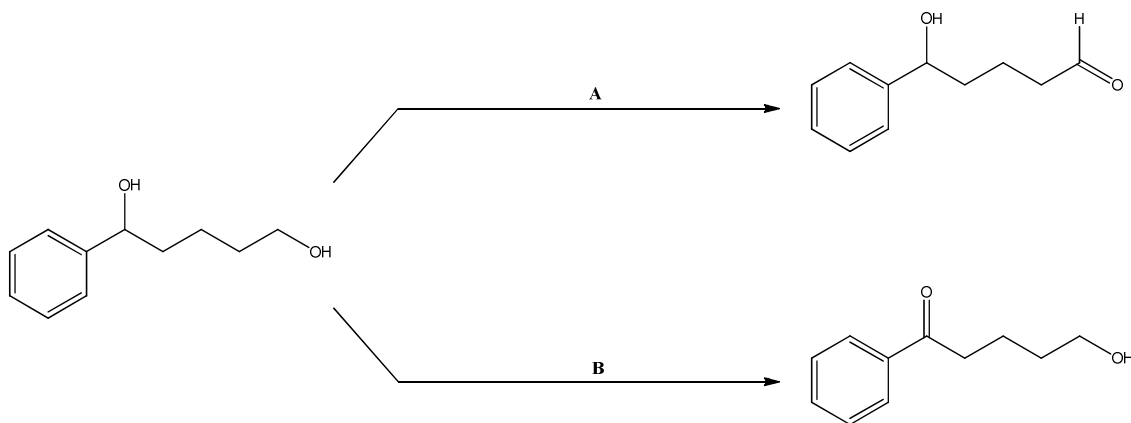
- d) In the spirit of protecting our environment, provide an alternative to chromium based oxidizing agents if given an alcohol to oxidize. (2 marks)

QUESTION FOUR (15 MARKS)

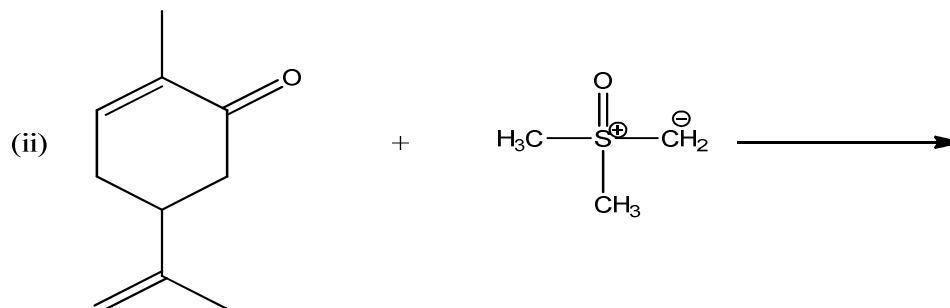
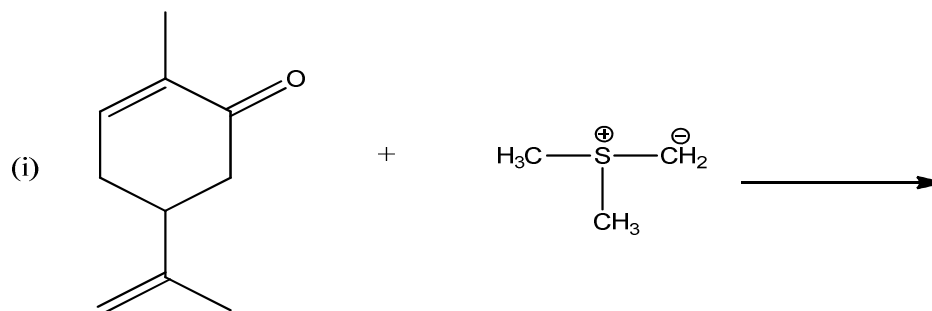
- a) Biphenyl (Phenyl benzene) undergoes the Friedel-Crafts acylation reaction, as shown by the following example



- i) On the basis of this result, what is the directing effect of the phenyl group? (2 marks)
 - ii) Using resonance arguments, explain the directing effect of the phenyl group. (5 marks)
- b) Provide the missing reagents A and B in the reactions below. (2 marks)

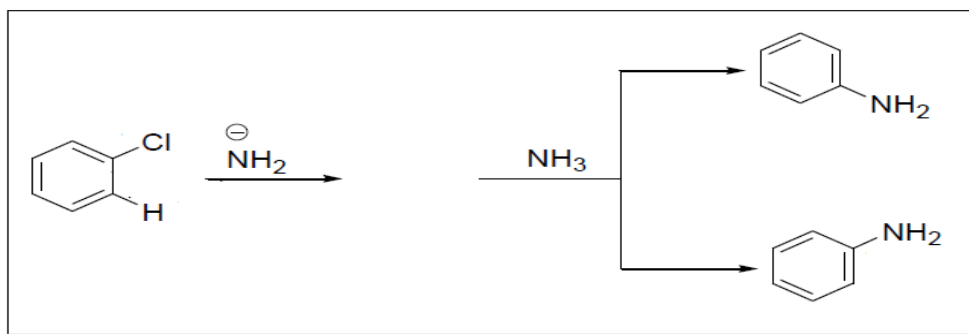


- c) Complete the reactions below and discuss why the two sulphur ylides result into a different product. (6 marks)



QUESTION FIVE (15 MARKS)

- a) Discuss why nucleophilic substitution on aryl halides occurs so slowly that forcing conditions are required. (6 marks)
- b) With appropriate mechanism, discuss why the following nucleophilic aromatic substitution reaction leads to two products. (5 marks)



- c) Explain why each of the following substrates do not undergo Friedel-Crafts reactions. (4 marks)

