



# MURANG'A UNIVERSITY OF TECHNOLOGY

## SCHOOL OF PURE AND APPLIED SCIENCE

DEPARTMENT OF APPLIED SCIENCE

UNIVERSITY ORDINARY EXAMINATION

2017/2018 ACADEMIC YEAR

EXAMINATION FOR MASTER OF SCIENCE IN CHEMISTRY

ACH 602: ADVANCED ORGANIC CHEMISTRY

DURATION: 3 HOURS

DATE:

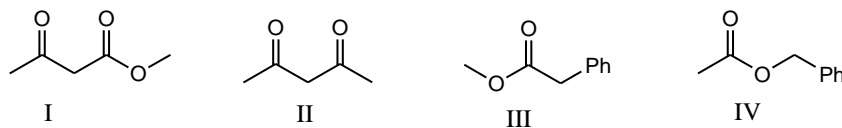
TIME:

### **Instructions to Candidates:**

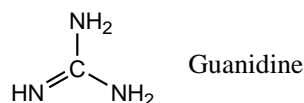
1. Answer **Any Four** questions.
2. Mobile phones are not allowed in the examination room.
3. You are not allowed to write on this examination question paper.

### QUESTION ONE (25 marks)

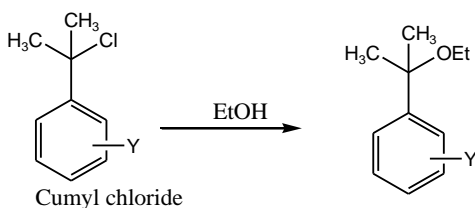
- (a) Arrange the following compounds in order of decreasing acidity and justify your order. (3 marks)



- (b) Account for the fact that guanidine ( $pK_a = 13.6$ ) is one of the strongest nitrogenous bases known. (4 marks)

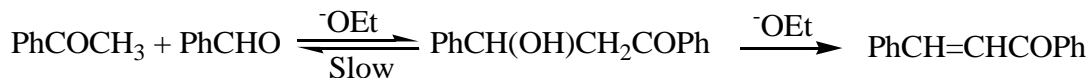


- (c) Substituted cumyl chloride undergoes solvolysis in ethanol at  $25^\circ\text{C}$  and the observed reaction rates are as indicated in the table below. Account for the variations in the reaction rates. (5 marks)

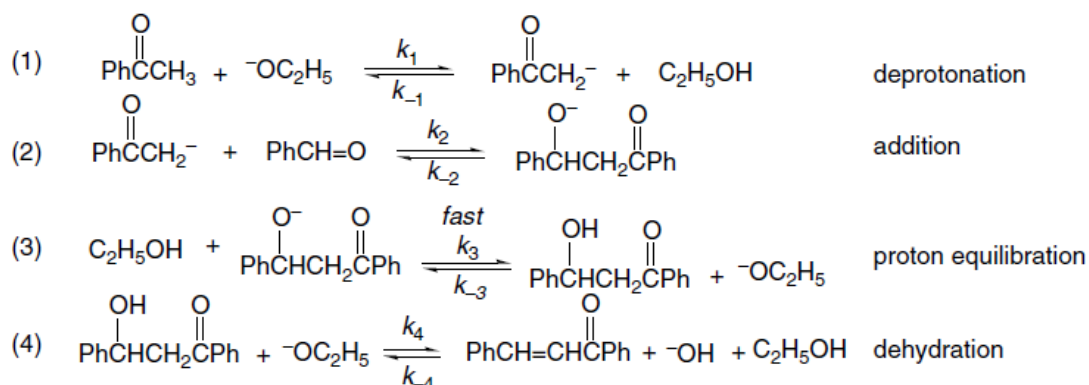


Substituent (Y)	$K_{S\text{-meta}}/k_H$	$K_{S\text{-para}}/k_H$
H	1	1
$\text{CH}_3\text{O}$	0.6	3400
F	0.03	2
Cl	0.02	0.3
Br	0.02	0.21
I	0.02	0.24

- (d) Acetophenone reacts with benzaldehyde in the presence of sodium ethoxide according to the equation below:

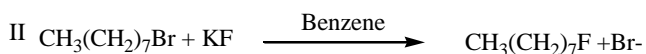
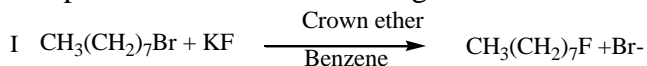


The proposed sequence of steps involved is given below:

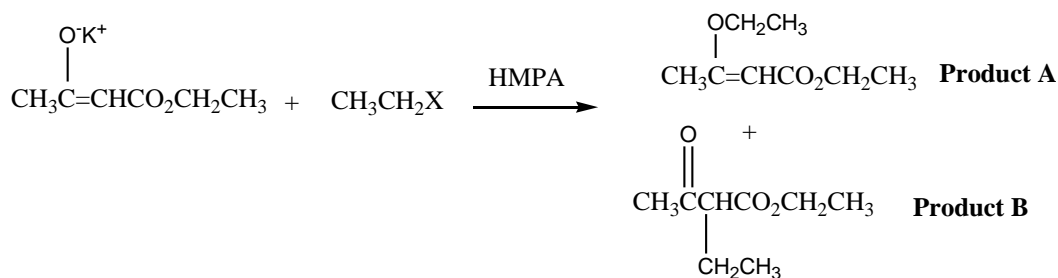


Assuming step 3 to be the rapid step, and  $k_4 \gg k_3$ , determine the rate equation of the reaction. (6 marks)

(e) Explain which of the following reactions would be faster: (3 marks)



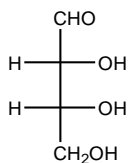
(f) Account for the variation in the proportions of products A and B in the products composition. (4 marks)



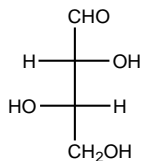
Substituent (X)	Products A%	Products B%
OTs	88	11
Cl	60	32
Br	39	38
I	13	71

### QUESTION TWO (25 marks)

(a) Assign configuration to each stereo-center in the stereoisomers below and convert the Fisher projections to extended and Newman projections. (6 marks)

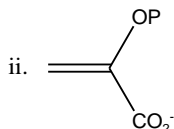
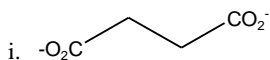


i



ii

(b) In the molecules below, identify all pairs of hydrogen that are homotopic, enantiotopic or diastereotopic and label the prochiral hydrogen as  $\text{H}_R$  or  $\text{H}_S$ : (4 marks)



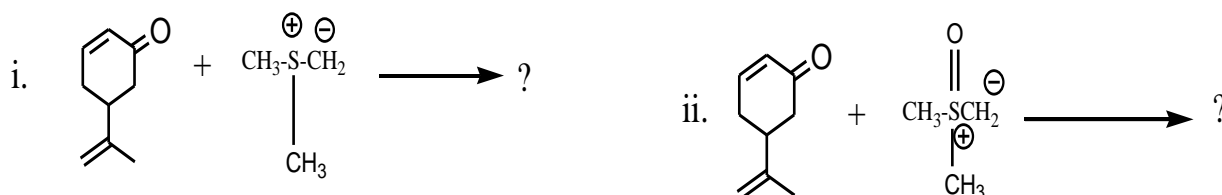
(c) Using suitable Newman projections suggest the energy level profile of 1-butene conformations (dihedral angle 0–180). (5 marks)

(d) Predict the least stable and the most stable conformations of compound A. Explain. (3 marks)



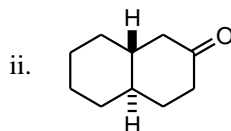
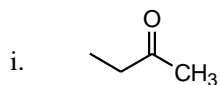
(e) Draw the *cis* and *trans* chair conformations of 1,4-dimethylcyclohexane and arrange them in order of increasing stabilities. Explain the order of their stabilities. (5 marks)

(f) Complete the reactions below by drawing the structures of the products and account for the difference in the products. (2 marks)

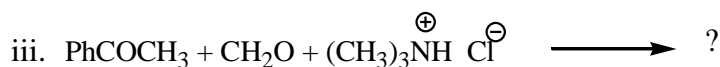
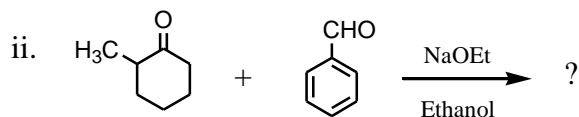
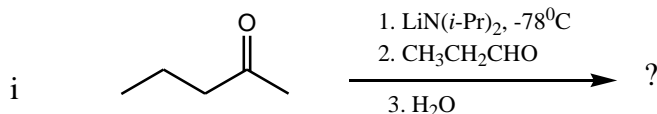


### QUESTION THREE (25 marks)

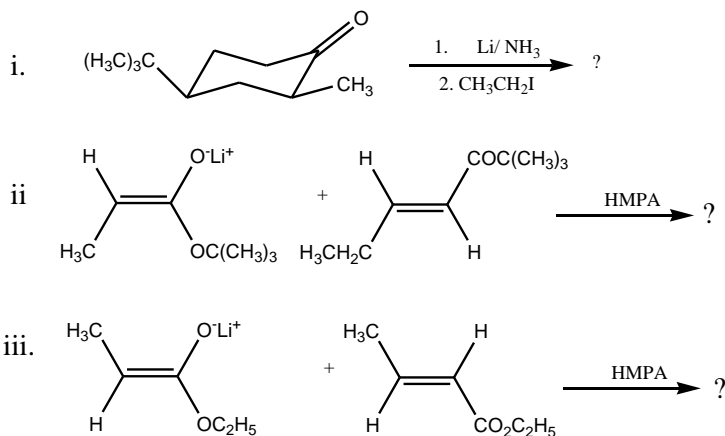
(a) Suggest the structures of all possible enolates for each of the molecules below. Indicate which structure would be favored in a kinetically controlled deprotonation: (4 marks)



(b) Predict the products formed in each of the following reactions. (3 marks)



(c) Draw the structure of the major product(s) in each of the following reaction. Clearly indicate the stereochemistry of the products. (6 marks)

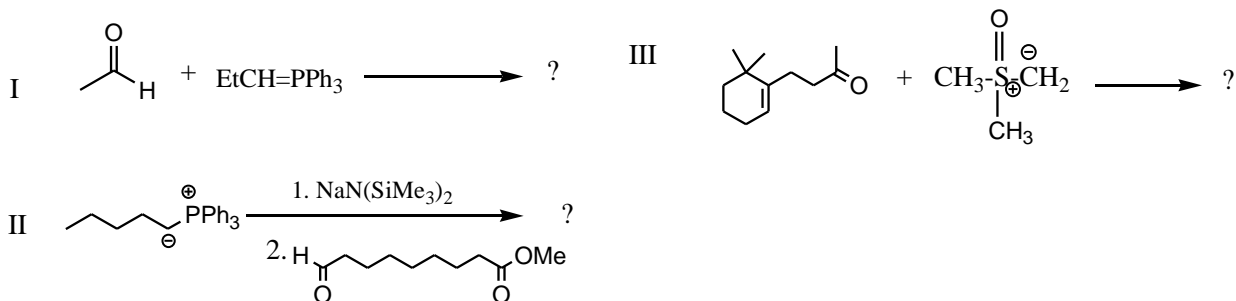


(d) Mixed Aldol reaction can result into a mixture of undesired products. Using suitable examples suggest three ways by which this drawback can be overcome. (6 marks)

(e) Use the reaction equations below to answer the questions that follow:

i. Predict the structures of the products for the reaction I-III (specify the stereochemistry where applicable). (3 marks)

ii. Suggest a transition state that would account for the observed stereochemistry in (I). (3 marks)

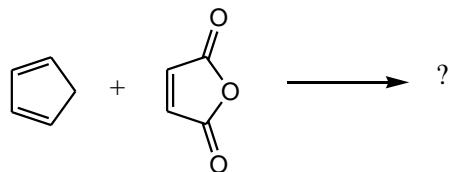


#### QUESTION FOUR (25 marks)

- (a) Draw the energy level diagrams of the frontier molecular orbitals of ethylene and 1,3-butadiene. (4 marks)
- (b) Using the frontier molecular orbitals, predict the structure and stereochemistry you would expect from (2*E*, 4*E*)-2,4-hexadiene and ethylene cycloaddition reaction. (4 marks)
- (c) Using the frontier molecular orbitals predict the structures and stereochemistry obtained from photochemical ring closure of the following: (6 marks)
- (2*E*, 4*Z*, 6*E*)- 2,4,6-octatriene
  - (2*E*, 4*Z*, 6*Z*)-2,4,6- octatriene

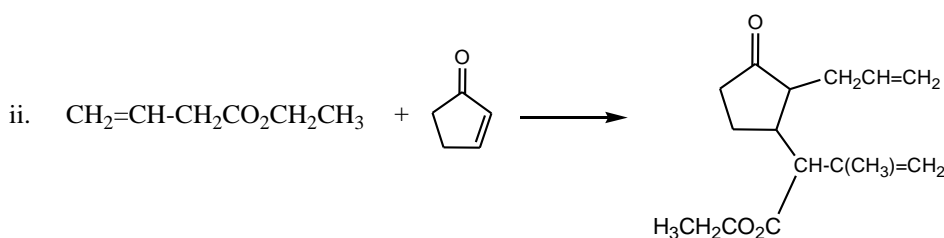
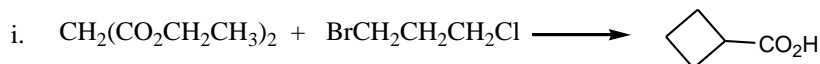
- (d) Draw the structures of the products that would be obtained from the following (indicate the stereochemistry of the products). Which of the products is more stable? Explain.

(4 marks)



- (e) Suggest the major steps for the reactions below. Indicate any required reagents and reaction conditions.

(7 marks)



### QUESTION FIVE (25 marks)

- (a) What is a protecting group? Suggest any three characteristics of a good protecting group.

(4 marks)

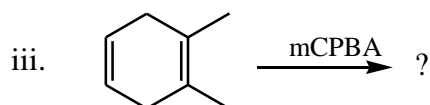
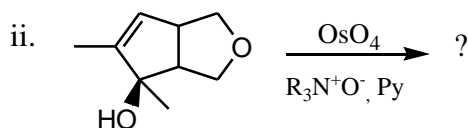
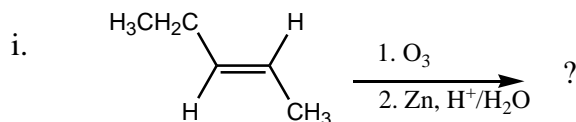
- (b) Identify two protecting groups for each of the following functional groups. (6 marks)

i. Alcohol

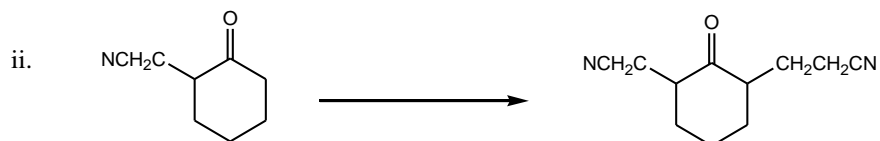
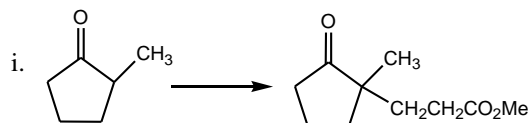
ii. Carboxylic acid

iii. Amine

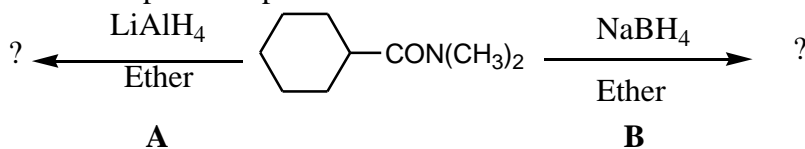
- (c) Predict the structures of the products and account for the stereochemistry where applicable for the following reactions. (6 marks)



- (d) Suggest reagents and reaction conditions suitable for obtaining each of the following compounds by a procedure involving Michael reaction: (4 marks)



- (e) Predict and explain the products for reactions A and B below. (3 marks)



- (f) Suggest a mechanism for the following reaction. (2 marks)

