FULL NAME: ……..

STUDENT ID #: ……..

SIGNATURE: ……..

COURSE: ……..

University of Canterbury
Mid-Year Examinations, 2009

Prescription Number(s):	CHEM 232 BCHM 205 ENCH 241
Paper Title:	Bioorganic Chemistry Engineering Chemistry 2

Time Allowed: 120 MINUTES

Number of pages: 9

Before commencing work, read the instructions on this page.

1. This exam is divided into **TWO** sections:

   Section A: Worth 40 marks. Answer this section on the examination paper. You may use the blank page opposite for any additional working related to your answer.

   Section B: Worth 80 marks. Answer this section in the separate answerbook.

2. Please ensure that your name and student ID have been entered in the appropriate spaces above and on the separate answer book and that you have signed both.

3. ANSWER **ALL** QUESTIONS.

Total marks = 120: you should allocate about one minute per mark.

For examiners use only

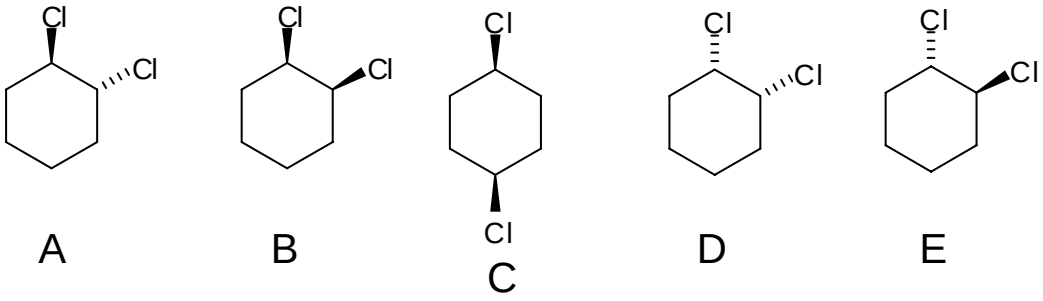
1-2	3-5	6-7	8	9	10	11	12	Total/120

SECTION A:

(Answer **ALL** questions. Answers should be written in the spaces provided.)

1. (8 marks)

Examine the structures shown below.



List two which are constitutional isomers. Ans:

Which pair(s) are enantiomers? Ans:

List two which are diastereoisomers. Ans:

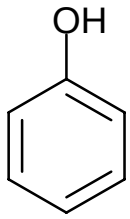
List two which are identical. Ans:

Which structures represent meso compounds? Ans:

Draw compound A in its two chair conformations and circle the one that is more stable.

2. (2 marks)

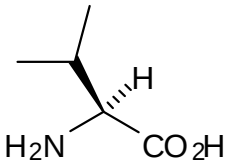
Draw the structures of **TWO** of the resonance contributors of the **conjugate base** of phenol.



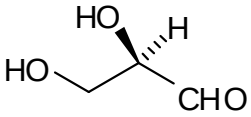
phenol

3. (3 marks)

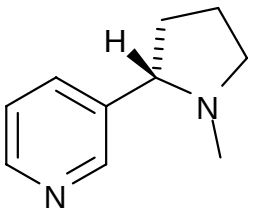
Assign R- or S-descriptors to each of the following naturally-occurring compounds..



valine



glyceraldehyde

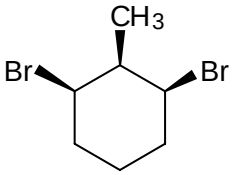


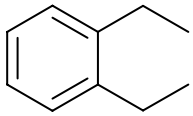
nicotine

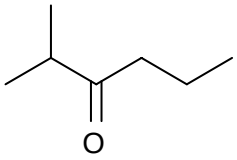
Ans:

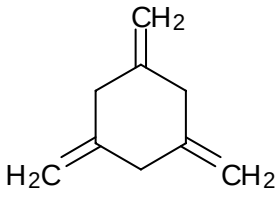
4. (4 marks)

How many signals would there be in the ^{13}C NMR spectrum of each of the following compounds?





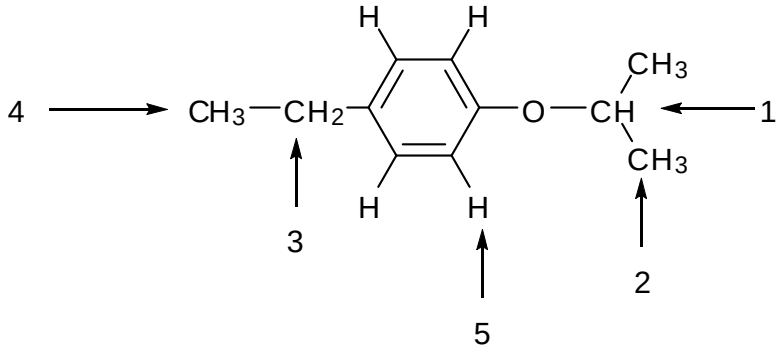




Ans:

5. (5 marks)

Consider the molecule shown below. Into how many peaks would each of the protons (numbered 1 to 5) be split by spin-spin coupling?



Ans:

H 1

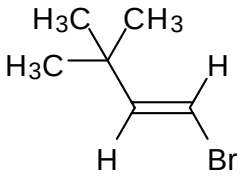
H 2

H 3

H 4

H 5

6. (6 marks)
Predict the appearance of the ^{1}H NMR spectrum of the compound shown below.



Is this the E- or the Z-stereoisomer? Ans:

How would the appearance of the ^{1}H NMR spectrum of the opposite stereoisomer differ?

Ans:

7. (3 marks)
Draw Newman projections showing the anti, gauche and eclipsed conformations of butane, viewed down the central bond. Indicate their relative order of stability.

8. (9 marks)
For each of the following statements indicate whether it is True or False.

(i) Mass spectrometry readily distinguishes between stereoisomers.

(ii) The molecular ion is always the most abundant (tallest) peak in a mass spectrum.

(iii) Elemental analysis readily distinguishes between constitutional isomers.

(iv) ^{1}H NMR spin-spin coupling constants depend on the dihedral angle between the protons.

(v) NMR spectroscopy uses microwave radiation.

(vi) Enantiomers have different ^{1}H NMR spectra.

(vii) All ketones have identical infrared spectra.

(viii) The optical rotation of a racemic mixture is always zero.

(ix) The ^{1}H NMR spectrum of benzene shows only a single peak.

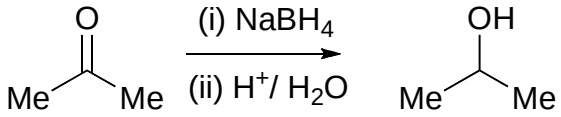
SECTION B:

(Answer **ALL** questions. Answers should be written in the separate answerbook provided. Total marks = 80; allow 80 minutes for this section.)

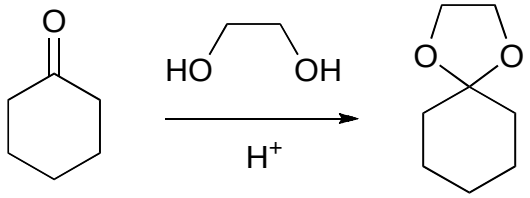
9. (a) (10 marks)

Give mechanisms for **two** of the following synthetic transformations:

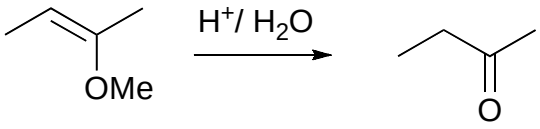
(i)



(ii)

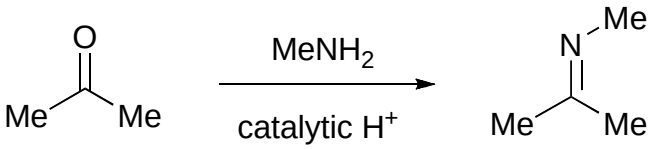


(iii)

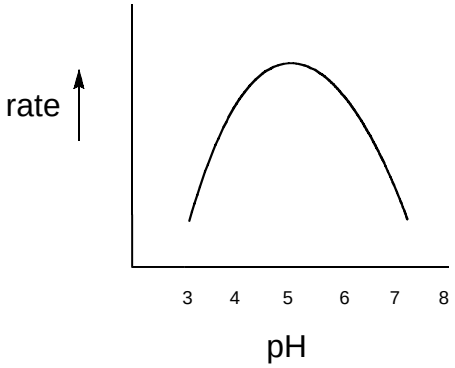


(b) (10 marks)

(i) Give a mechanism for the following reaction

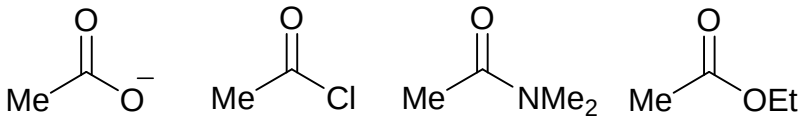


(ii) Explain why the pH rate profile for this reaction has the following form:-



10. (a) (5 marks)

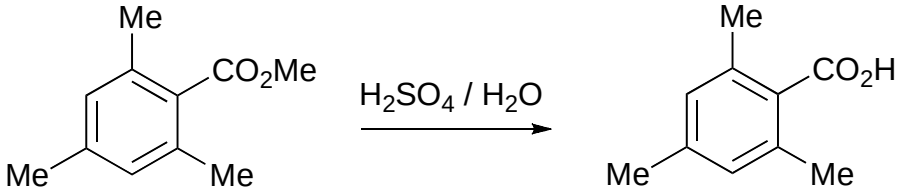
Rank the following carboxylic acid derivatives in order with respect to their reactivity with nucleophiles. Explain your answer.



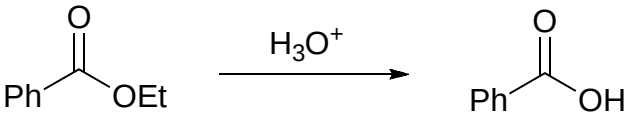
(b) (10 marks)

Give mechanisms for **two** of the following ester hydrolyses:

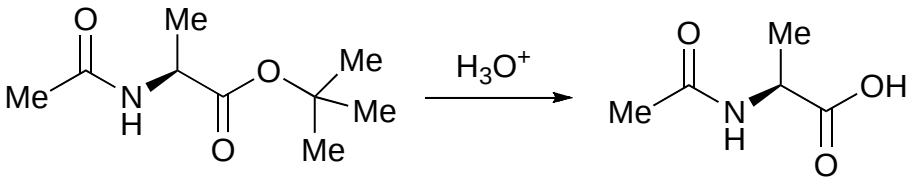
(i)



(ii)



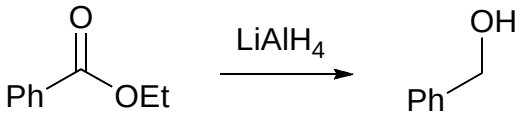
(iii)



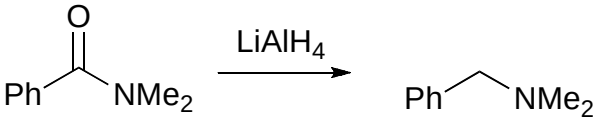
(c) (5 marks)

Give a mechanism for **one** of the following synthetic transformations:

(i)



(ii)



11. (a) (3 marks)

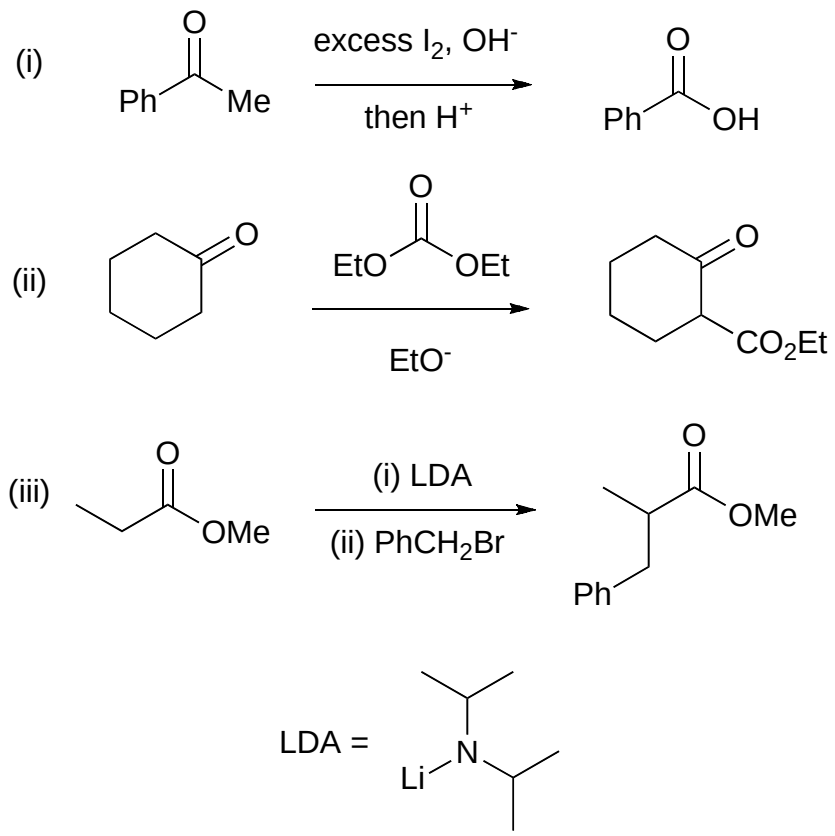
Define what tautomers are.

(b) (3 marks)

Using a ketone of your choice, give a mechanism for the inter-conversion of the ketone and enol forms under **acidic** conditions.

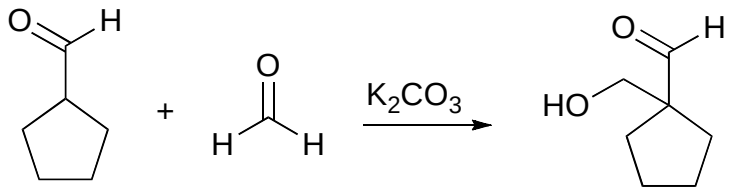
(c) (14 marks)

Give mechanistic explanations for **two** of the following reactions:



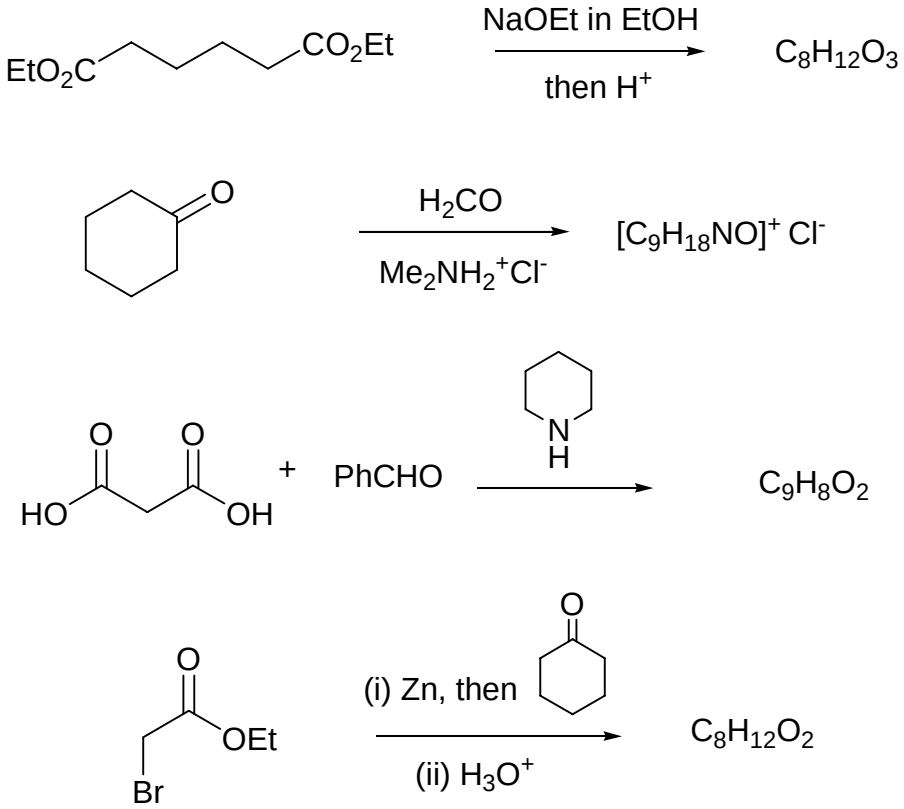
12. (a) (6 marks)

Give a mechanism for the following crossed aldol reaction. Explain why no other products are formed in this particular case.



(b) (14 marks)

Deduce the structure of the products formed, and give mechanisms for **two** of the following reactions.



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