

University of Canterbury

Mid Year Examination and Test Period 2006

Prescription Number(s):	CHEM 222 CHEM 262 BCHM 205
-------------------------	----------------------------------

Paper Title:	Organic Chemistry
--------------	-------------------

Time Allowed: TWO HOURS

Number of pages: TEN

This paper contains **TWO** sections, **A** and **B**. Each section is worth half of the total marks

Answer **ALL** questions

Total marks: 120

TURN OVER

SECTION A

1. (12 marks)

For each of the following **three** structures:

- Assign the hybridization of each carbon;
- Assign the geometry of the bonds around each carbon;
- Identify a stereogenic centre and draw it in its R configuration. Explain your answer.

2. (12 marks)

- Draw the all-*anti* conformation of *n*-hexane and explain why this is the thermodynamically preferred conformation;
- Draw Newman projections for all eclipsed and staggered conformations of *n*-hexane generated on rotation about the C3-C4 bond. Indicate with reasons the relative stabilities of each.

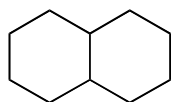
TURN OVER

3. (12 marks)

Discuss ways in which enantiomers can be distinguished and separated. Illustrate your answer with examples.

4. (12 marks)

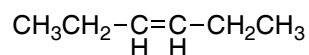
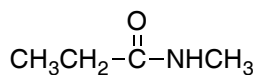
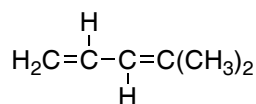
- (a) Draw chair conformations for the two diastereoisomers of decalin (below).
- (b) Is ring inversion (flipping) possible in each case? Draw any ring inverted conformations and refer to any inversion of axial and equatorial groups in your answer.



Decalin

5. (12 marks)

The following molecules exist as *cis* and *trans* isomers.



- (a) In each case, draw both isomers
- (b) Giving reasons, rank the three molecules above in terms of the ease with which their isomeric forms interconvert.

SECTION B

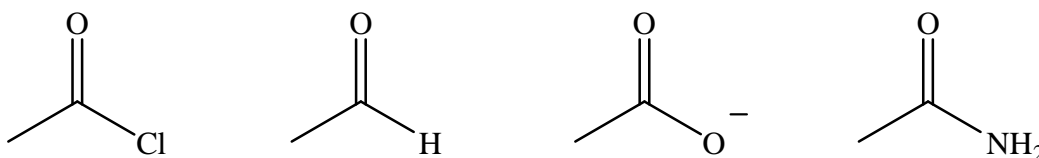
Acidity (pK_a) data that might be useful for this section:

Acid	pK_a	Acid	pK_a
HCl	-7	CH ₃ CH ₂ OH	16.0
H ₃ O ⁺	-1.7	CH ₃ CHO	17
CH ₃ COOH	4.75	CH ₃ COCH ₃	19
CH ₃ COCH ₂ COCH ₃	9	CH ₃ COSCoA	21.0
HCN	9.2	CH ₃ COOCH ₂ CH ₃	25.0
H ₄ N ⁺	9.3	HC≡CH	25
CH ₃ CH ₂ SH	10.3	CH ₃ CONH ₂	30
H ₂ O	15.7	H ₃ N	35
		CH ₃ CH ₃	60

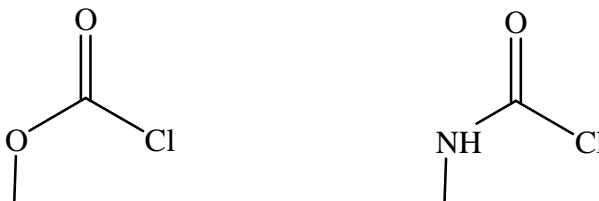
6. (15 marks)

Resonance structures are drawn for compounds that cannot be adequately described by a single Lewis structure.

(a) draw out resonance structures for each of the following compounds:



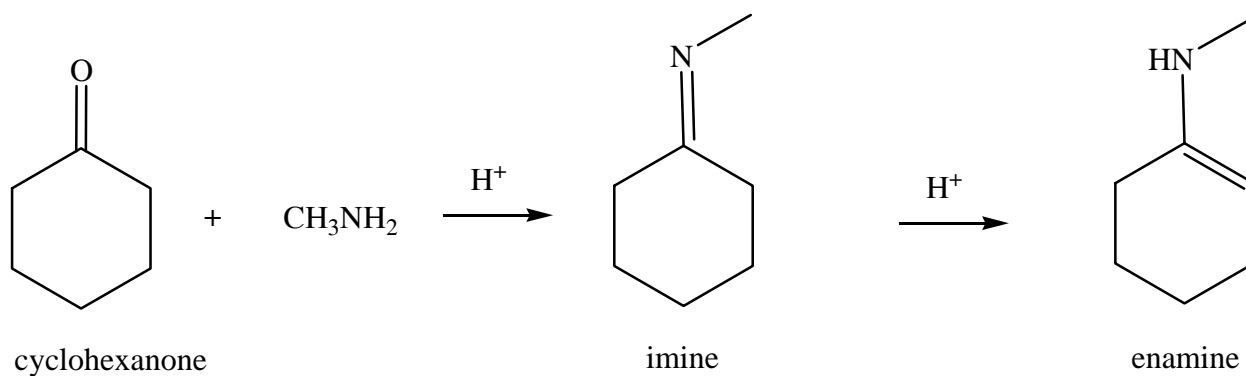
- (b) Place the compounds in order of decreasing reactivity towards nucleophiles. Give reasons for the order you have selected.
- (c) Which of the following two compounds would you expect to react faster with a nucleophile? Explain your answer.



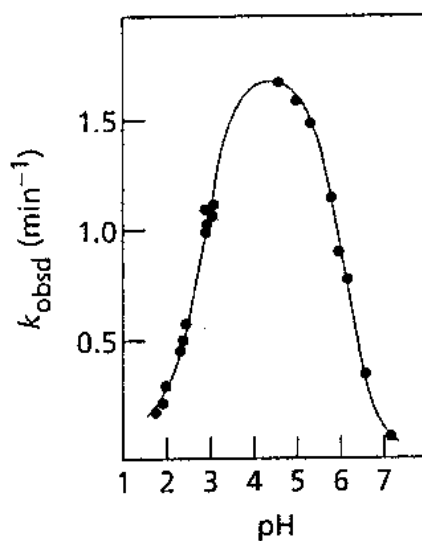
TURN OVER

7. (12 marks)

- (a) Using curly arrows to show the mechanism, draw out the steps involved in the reaction of cyclohexanone with methylamine in the presence of a trace of H^+ to form an imine.



- (b) The pH-rate profile diagram for this reaction is shown below.



- Why is the rate dependent on the pH?
 - Why is the maximum rate observed at pH 4.5?
- (c) Using curly arrows show how the imine can be converted into the enamine.

8. (12 marks)

Answer **EITHER**:

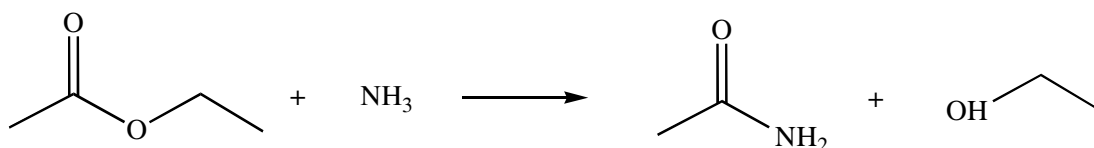
- (a) Place each of the following in order of **decreasing** nucleophilicity and explain your choice of order.



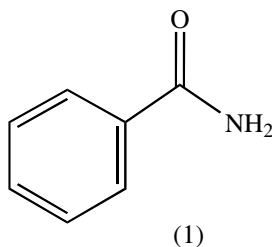
- (b) Place each of the following in order of **decreasing** leaving group ability and explain your choice of order.



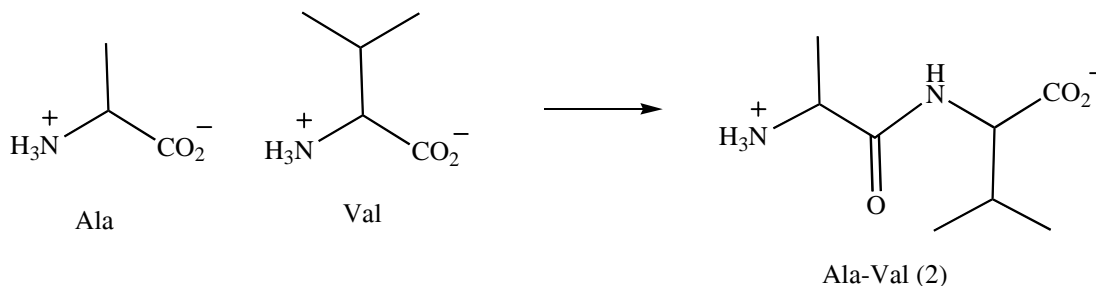
- (c) Explain why the following reaction proceeds as shown.

**OR:**

- (a) For a laboratory or industrial setting, suggest **TWO** methods that could be used for making benzamide (1).

**TURN OVER**

- (b) What approach, or approaches, would nature take to making the dipeptide Ala-Val (2) from the amino acids Ala and Val?

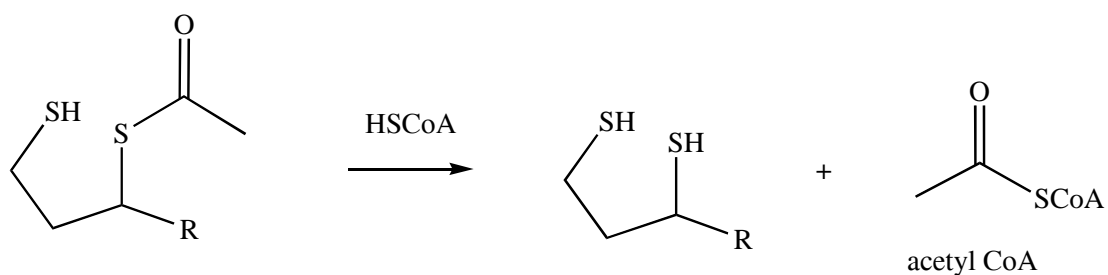


9. (12 marks)

Answer **EITHER**:

Thiol esters such as acetyl CoA play key roles in many metabolic cycles.

- (a) Explain why:
- (i) acetyl CoA is more reactive towards nucleophilic substitution; and
 - (ii) the α -methylene hydrogens of acetyl CoA are more acidic than those of ethyl acetate.
- (b) The final step in acetyl CoA production is shown below. Using curly arrows, describe a mechanism for this reaction.

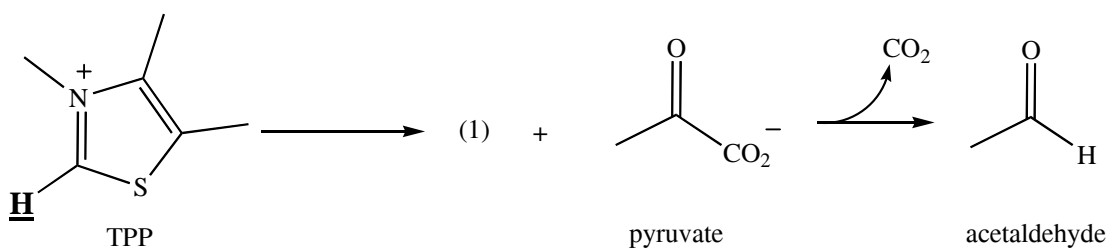


OR:

(a) What reaction is mediated by each of the following coenzymes in association with the appropriate apoenzyme (ie the holoenzyme):

- (i) pyridoxal phosphate;
- (ii) lipoic acid;
- (iii) nicotinamide;
- (iv) biocytin.

(b) Thiamine diphosphate (TPP) is a coenzyme that mediates the oxidative decarboxylation of α -keto acids. The “business” part of TPP is shown below.

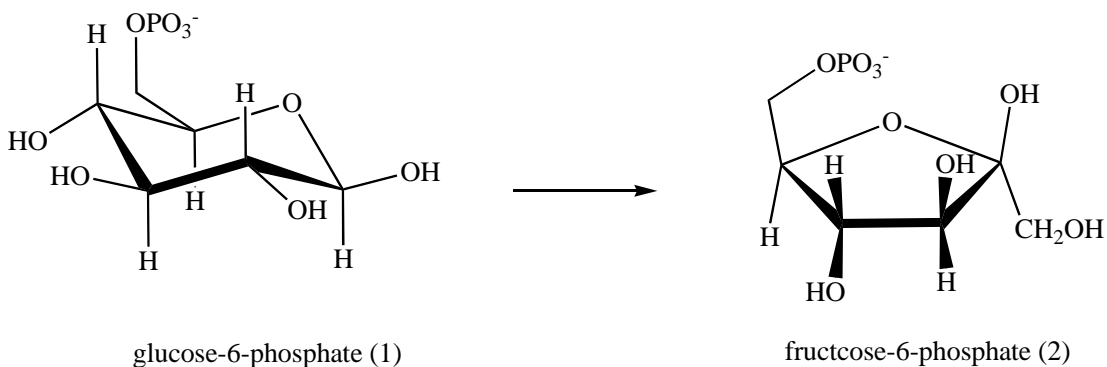


- (i) The highlighted hydrogen is acidic ($pK_a = 18$). Explain why.
 - (ii) If that acidic hydrogen is removed, (1) is formed. What is the structure of (1) and what is the name of this class of compound?
- (c) (1) is the reactive form of TPP. Using curly arrows show how (1) reacts with pyruvate and how the intermediate formed is then converted through to acetaldehyde.

TURN OVER

10. (9 marks)

In the glycolysis pathway glucose-6-phosphate (1) is converted into fructose-6-phosphate (2).



- (a) The trivial names for (1) and (2) are glucose-6-phosphate and fructose-6-phosphate. Suggest more formal names that correctly describe each structure. *[Note: the optical rotations of both glucose-6-phosphate (1) and fructose-6-phosphate (2) are positive]*
- (b) Using curly arrows suggest a mechanism for this isomerisation.

[Hint: Consider using the open chain form of the sugars in your mechanism.]

END OF PAPER