University of Canterbury

Mid-Year Examinations 2005

Prescription Number(s):	CHEM 222 CHEM 262 BCHM 205
Paper Title:	Organic Chemistry

Time Allowed:	TWO HOURS
Number of pages:	SEVEN

Answer **ALL** questions

Total marks = 120.
You should allocate about
1 minute per mark.

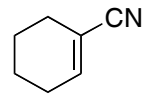
TURN OVER

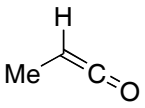
1. (12 mark)

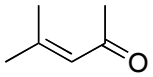
For each of the following **four** structures:

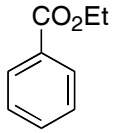
(i) what is the hybridization of each carbon; and

(ii) what is the geometry of the bonds around each carbon?







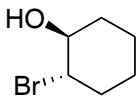


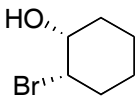
2. (12 marks)

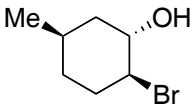
Butane can exist in an infinite number of conformations. Draw Newman projections for the most significant of these and indicate their relationship on a conformational plot of relative energy *vs* dihedral angle.

3. (12 marks)

Draw the two alternative chair conformations for each of the following three molecules. In each case carefully label each substituent as axial or equatorial. For each pair predict, with reasons, which would be the preferred conformation.







4. (12 marks)

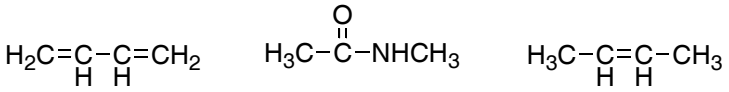
Draw the structure of (*R*)-lactic acid [lactic acid: CH_3-CH(OH)-CO_2H]. Explain the basis of your answer. How, in principle, might you resolve a racemic mixture of (±)-lactic acid?

5. (12 marks)

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

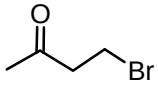
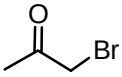
(a) In each case, draw both isomers.

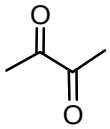
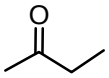
(b) Giving reasons, rank the three molecules in terms of the ease with which the isomeric forms interconvert.

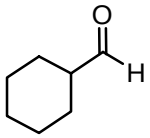
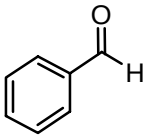


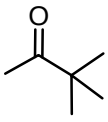
6. (12 marks)

For each of the pairs (a) to (d), select the compound you consider would be more reactive in a nucleophilic carbonyl addition reaction. In each case, briefly explain your choice.

(a)  or 

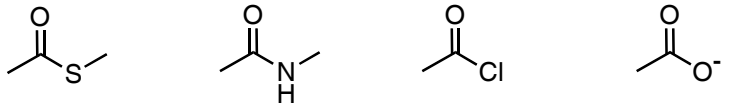
(b)  or 

(c)  or 

(d)  or 

7. (16 marks)

Draw all possible resonance structures for each of the following compounds and then answer the questions that follow.

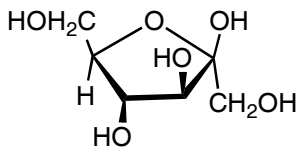


(a) In each case, do your resonance structures contribute equally? If not make an assessment of the relative contributions.

(b) Place the compounds in order of reactivity with respect to nucleophilic substitution reactions. Justify your order of reactivity.

8. (12 marks)

(a) Is β-D-(-)-fructofuranose:



β-(D)-(-)- fructofuranose

(i) a hexose? (Y/N)

(ii) a ketose? (Y/N)

(iii) an aldohexose? (Y/N)

(iv) a glycoside? (Y/N)

(b) When β-D-(-)-fructofuranose is dissolved in water, the optical rotation changes rapidly from -133.5^0 to -91^0. What is this process called? Draw configurational diagrams to explain what is happening in this process.

(c) In solution, fructose can also exist in pyranose forms. Draw a possible structure for β-D-(-)-fructopyranose.

9. (12 marks)

Answer **EITHER** (a) and (b) **OR** (c)

EITHER

(a) Coenzymes play a vital role in many biological cycles. Briefly, what is the role for each of the following?

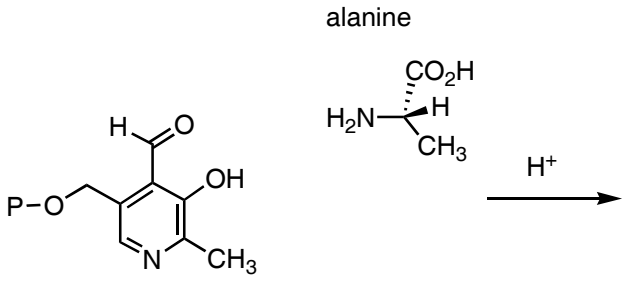
(i) coenzyme A

(ii) NAD^+/NADH

(iii) thiamine pyrophosphate

(iv) pyridoxal phosphate

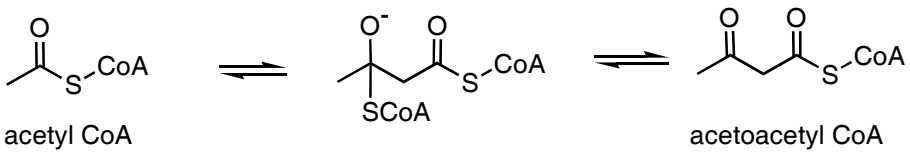
(b) A key step in the biological role of pyridoxal phosphate is its condensation with an amino acid to form an imine. Using alanine as the amino acid, show all the steps in this condensation. Use curly arrows.



pyridoxal phosphate

OR

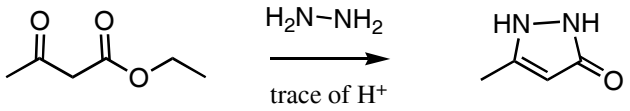
(c) Nature makes extensive use of thiol esters based on coenzyme A. What is so special about thiol esters? Include an analysis of the following Claisen reaction in your explanation.



acetyl CoA acetoacetyl CoA

10. (8 marks)

Based on your understanding of carbonyl group chemistry, suggest the likely steps in the following reaction. Use curly arrows to describe the steps in your mechanism and comment of any selectivity issues.



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