

University of Canterbury

Mid Year Examination and Test Period 2007

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

Time Allowed: TWO HOURS

Number of pages: EIGHT

This paper is marked out of 120 and is divided into **TWO** sections.

Section A: Answer **ALL** questions (84 marks).

Section B: Answer **THREE** questions out of **SIX** (36 marks).

All questions are of equal value and should take ~12 minutes each to answer.

TURN OVER

SECTION A (84 marks):Answer **ALL** questions

Each question is worth 12 marks (= 12 minutes)

1. Allene is an unusual molecule that has the structure $\text{H}_2\text{C}=\text{C}=\text{CH}_2$.
 - (a) Draw a detailed picture of the bonding orbitals in allene.
 - (b) Assign the hybridisation of each carbon in allene. Explain your answers.
 - (c) What shapes would you predict for allene and $\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}_2$? Explain your answer.
 - (d) Can a substituted allene be chiral? Explain your answer.

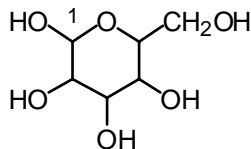
2.
 - (a) Define what is meant by 1,3-diaxial steric strain. Would you expect a *tert*-butyl [$-\text{C}(\text{Me})_3$] or a cyano [$-\text{CN}$] group to cause the most 1,3-diaxial steric strain? Explain your answer in detail.
 - (b) Explain why 1,3-*trans* disubstituted cyclohexanes must have one substituent in an axial orientation and the other in an equatorial orientation while 1,3-*cis* disubstituted cyclohexanes must have both substituents in axial or both substituents in equatorial orientations.
 - (c) Draw the most stable chair conformation of *trans*-1-methyl-3-bromocyclohexane and explain your choice.

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

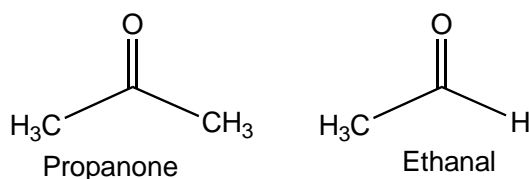
4. Using examples of your choice, discuss the link between the three-dimensional shape of a biomolecule and its biological function.

TURN OVER

5. (a) β -Glucopyranose contains a six-membered ring in which all of the substituents are equatorial. Draw β -glucopyranose in the more stable chair conformation.



- (b) Draw a Newman projection looking along C2-C3 of β -glucopyranose.
- (c) α -Glucopyranose has the opposite configuration at C1. Draw α -glucopyranose in its more stable chair conformation.
- (d) Define the anomeric effect with reference to your structures for α - and β -glucopyranose.
6. Aldehydes and ketones:
- (a) are polar molecules because of the $>C=O$ dipole. Show the dipolar nature of the carbonyl group using propanone as an example.
- (b) are weakly basic and will react with protons, H^+ . Using propanone as an example draw a scheme for this reaction and show the protonated form of propanone.
- (c) undergo nucleophilic addition reactions. There are TWO general ways (mechanisms) by which this occurs. One is under basic conditions and the other is under acidic conditions. Using curly arrows show the schemes for the addition of an **appropriate** nucleophile to ethanal under acid **and** under base conditions.



7. Experimentally it is observed that:

- aldehydes are generally more reactive towards nucleophilic addition than ketones, and
- amides are more resistant to hydrolysis to acids than esters.

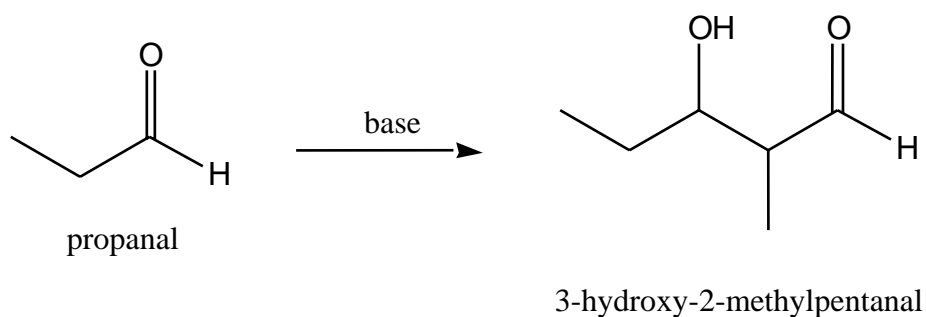
Using steric and electronic arguments, rationalise these experimental observations.

SECTION B (36 marks):Answer **THREE** questions out of SIX

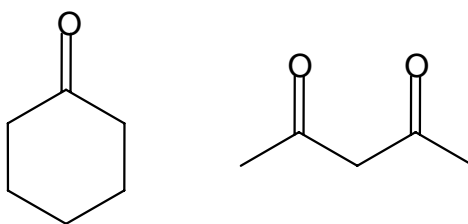
Each question is worth 12 marks (= 12 minutes)

8. (a) By formation of an enolate, carbonyl compounds can act as nucleophiles. Using propanal as an example show, using curly arrows, the scheme for formation of the enolate.

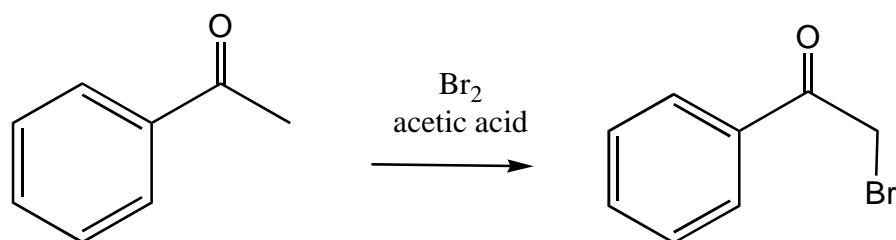
- (b) The aldol reaction is an acid- or base-catalysed dimerisation reaction. Show all the steps in the formation of 3-hydroxy-2-methylpentanal under basic conditions.



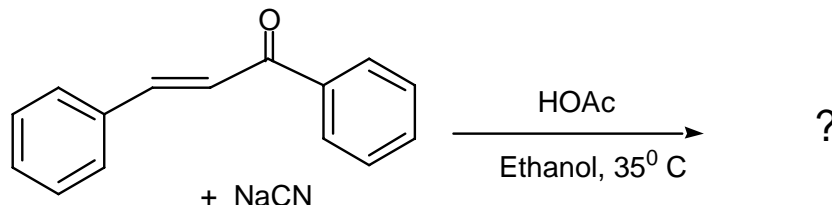
9. (a) Define tautomerism. Draw out the tautomers, for each of following. In each case suggest, with reasons, a likely percentage for each tautomer (keto/enol).



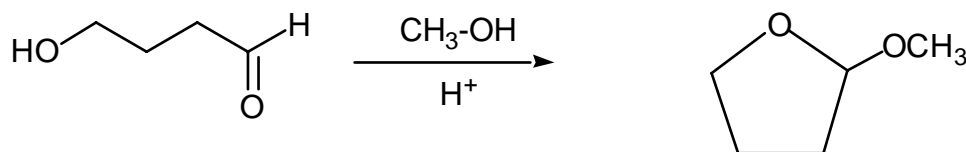
- (b) Using the following example, explain why mono-halogenation of ketones is best carried out in acidic solution and not in basic solution.



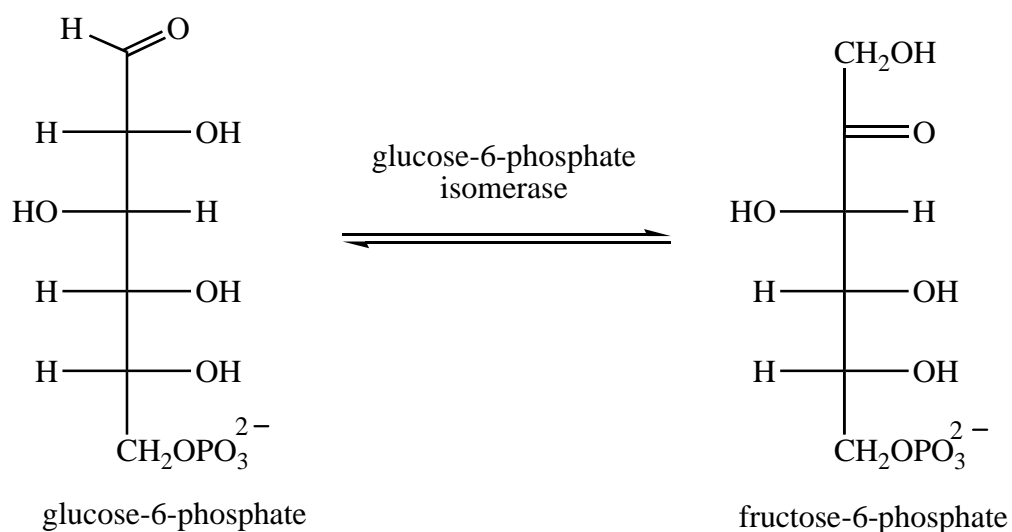
10. (a) Nucleophiles such as CN^- can react with α,β -unsaturated aldehydes or ketones by conjugate addition (1,4-addition). Using the example below, outline what you consider to be the key features of conjugate addition reactions.



- (b) Conjugate addition *competes* with nucleophilic addition to the carbonyl group (1,2-addition), but conjugate addition usually occurs. Why?
11. (a) When 4-hydroxybutanal is treated with acidified methanol the product is 2-methoxytetrahydrofuran. Explain.



- (b) The enzyme glucose-6-phosphate isomerase converts glucose-6-phosphate to fructose-6-phosphate. Suggest a mechanism for this isomerisation.



12. Thiol esters, such as acetyl CoA, play key roles in many metabolic cycles. Explain why:

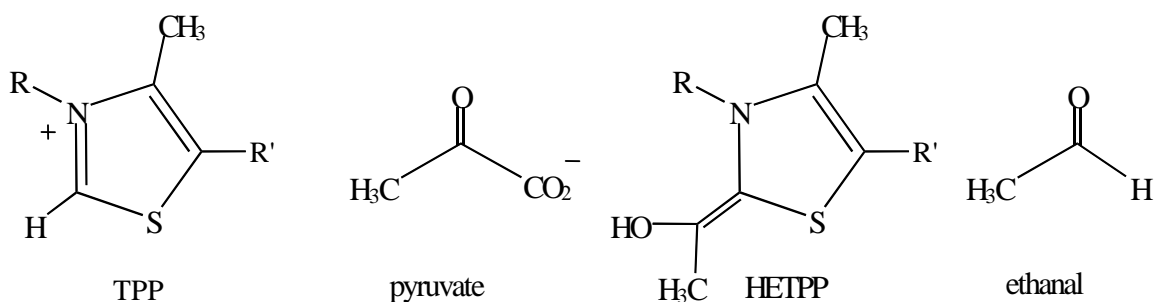
- acetyl CoA is more reactive than ethyl acetate;
- the α -methylene hydrogens of acetyl CoA are more acidic than those of ethyl acetate.

The following data may be of use.

	pK_a
$\text{H}-\text{CH}_2-\text{COSCoA}$	21.0
$\text{H}-\text{CH}_2-\text{COOCH}_2\text{CH}_3$	25.0
$\text{CH}_3\text{CH}_2-\text{S}-\text{H}$	10.3
$\text{CH}_3\text{CH}_2-\text{O}-\text{H}$	16.0

13. Thiamine pyrophosphate (TPP) is a co-factor in *acyl transfer* reactions in biological cycles.

- The key reactive form of TPP is the ylid. Draw out the TPP ylid.
- Show how the ylid reacts with pyruvate to give hydroxyethylTPP (HETPP).
- Indicate how HETPP is converted into ethanal.



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