FULL NAME: ……..

STUDENT ID #: ……..

SIGNATURE: ……..

COURSE: ……..

University of Canterbury
Mid-Year Examinations, 2008

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

Time Allowed: 120 MINUTES

Number of pages: 14

Before commencing work, read the instructions on this page.

1. This is both your examination paper and your answer book. You may use the blank page opposite for any additional working related to your answer.

2. Please ensure that your name and student ID have been entered in the appropriate spaces above and you have signed off.

3. ANSWER ALL QUESTIONS.

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

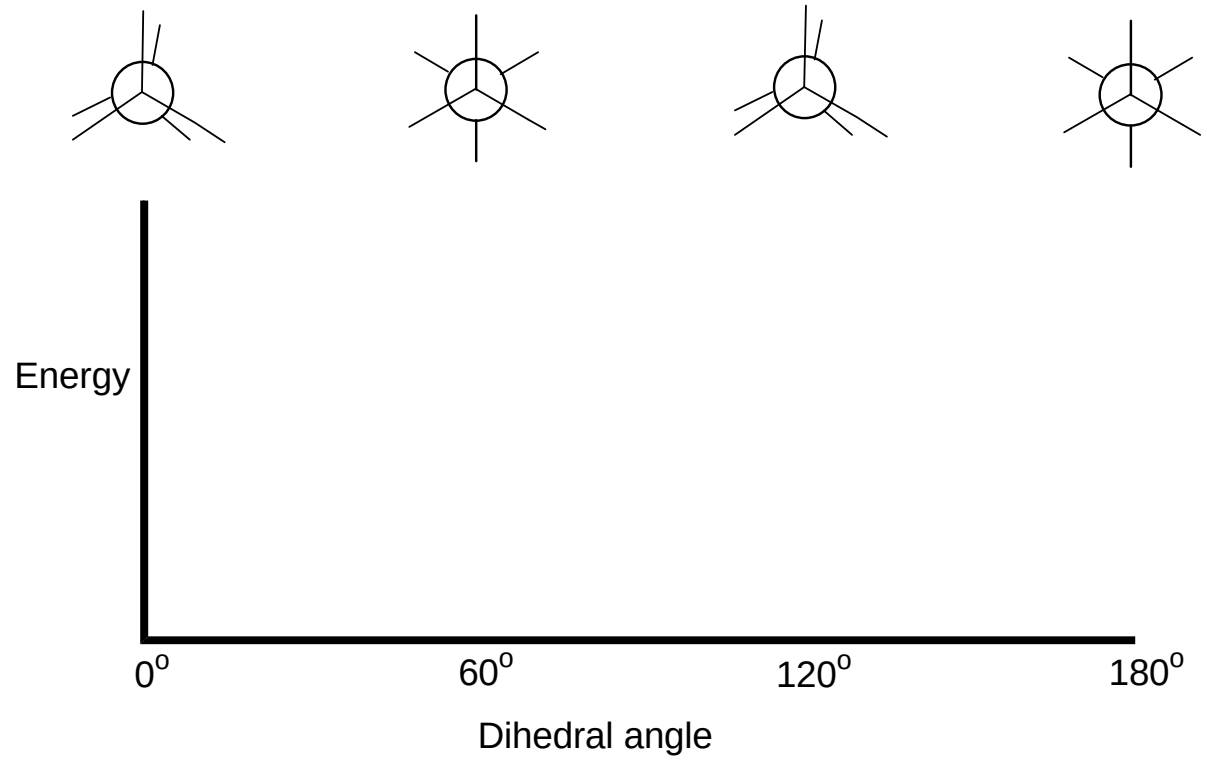
Please write your answers within the spaces provided

For examiners use only

1-4	5-7	8-10	11-15	16-17	18-19	20-23	Total/120

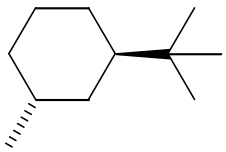
1. (5 marks)

In the diagram below complete the Newman projections and show the plot of the relative energies of the conformers for a **180°** rotation about the **central** bond of **butane**.



2. (4 marks)

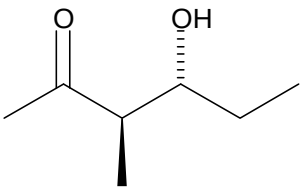
For the molecule shown below show the interconversion between the two chair conformations and circle the conformation that is more stable.



Is this molecule superimposable on its mirror image? Answer (circle one): **Yes** **No**

3. (5 marks)

The molecule shown below has recently been prepared in the Chemistry Department. Assign stereochemical designators (R- or S-) to the two stereogenic centres and draw (in the boxes) the structures of the enantiomer, a diastereoisomer, and an enol tautomer of this molecule.



enantiomer

diastereoisomer

enol tautomer

4. (4 marks)

Draw the structures of:

(a) a meso compound

(b) two atropisomers

(c) the resonance contributors to the structure of nitromethane (CH_3NO_2)

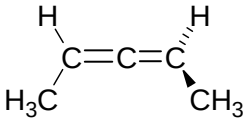
(d) the resonance contributors to the structure of the congugate base of a carboxylic acid (RCO_2H)

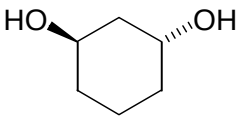
5. (2 marks)

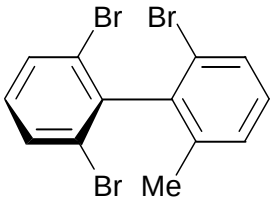
Draw Newman projections (each viewed down two bonds) of the chair and boat conformations of cyclohexane.

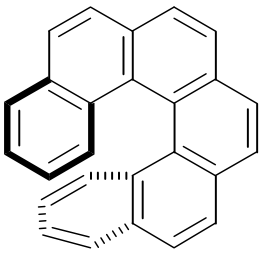
6. (4 marks)

Indicate (Yes/No) whether each of the following compounds could exist as two different enantiomers.



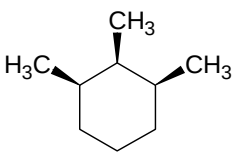


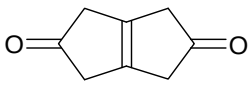


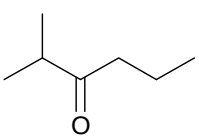


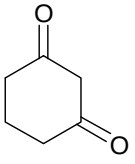
7. (4 marks)

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





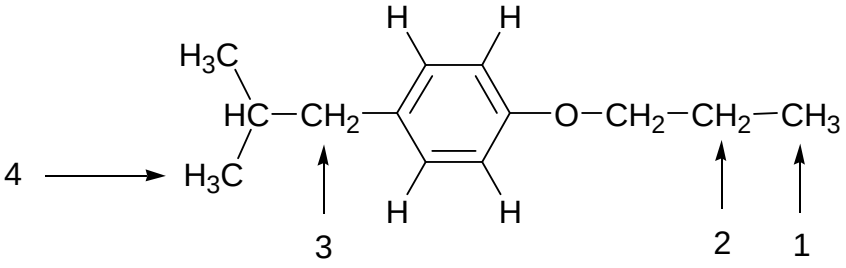




Ans:

8. (4 marks)

Consider the appearance of ^{1}H NMR signals in the spectrum of the molecule shown below. Into how many peaks would the signals for the indicated protons (numbered 1 to 4) be split by spin-spin coupling?



Ans:

H 1

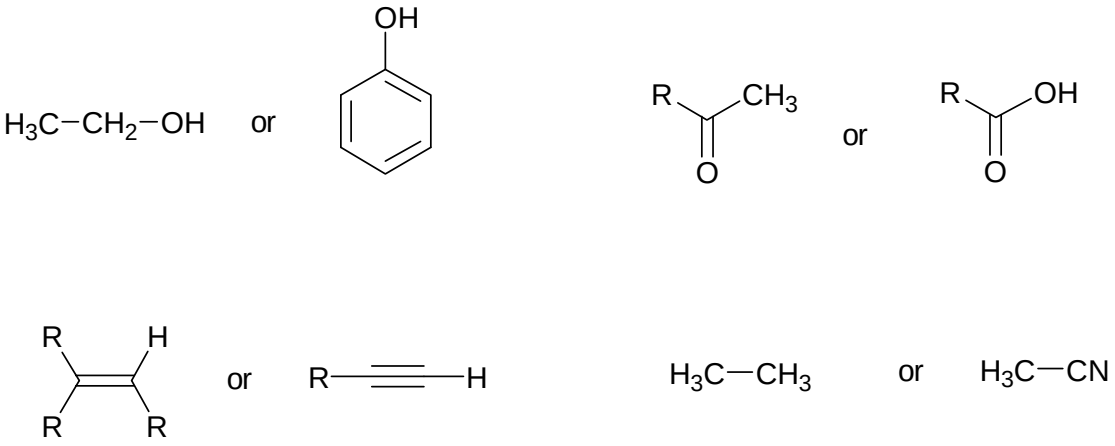
H 2

H 3

H 4

9. (4 marks)

For each of the following pairs of compounds circle the one that is the more acidic.



10. (4 marks)

For each of the following statements indicate whether it is True or False.

(a) Mass spectrometry readily distinguishes between diastereoisomers.

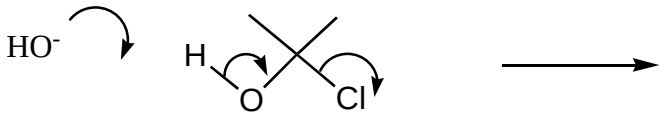
(b) Elemental analysis readily distinguishes between constitutional isomers.

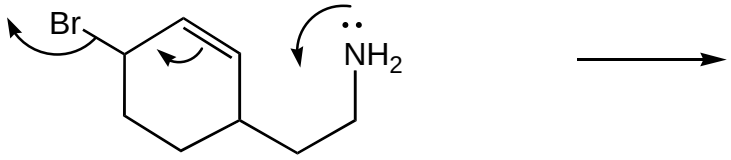
(c) ^{1}H NMR spin-spin coupling constants depend on the dihedral angle between the protons.

(d) ^{1}H NMR chemical shifts (in ppm) are independent of the magnetic field strength.

11. (4 marks)

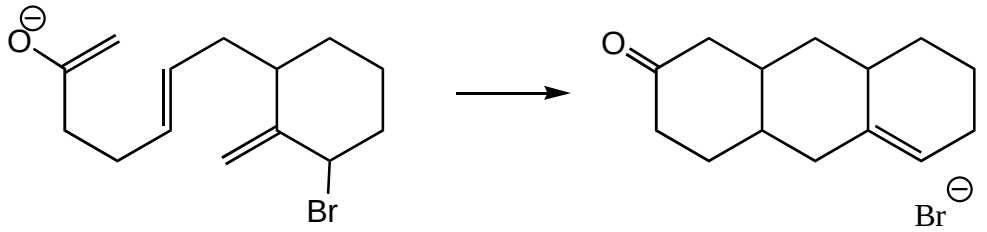
What are the structures of the products of the following two reactions?

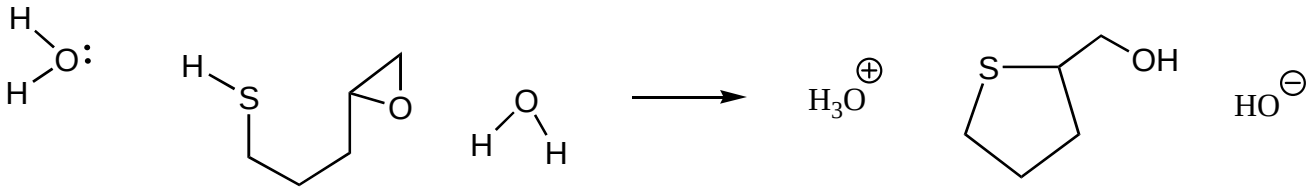




12. (5 marks)

Draw in the arrows on the starting materials that would give the products shown.





Acidity (pK_a) data that might be useful:

Acid	pK_a	Acid	pK_a
HCl	-7	CH_3CH_2O**H**	16.0
H$_3$O+	-1.7	C**H**$_3$CHO	17
CH_3COO**H**	4.75	C**H**$_3$COCH3	19
CH_3COC**H**$_2COCH_3$	9	C**H**$_3$COSCoA	21.0
HCN	9.2	C**H**$_3COOCH_2CH_3$	25.0
H$_4$N$^+$	9.3	HC≡C**H**	25
CH_3CH_2S**H**	10.3	C**H**$_3CONH_2$	30
H$_2$O	15.7	**H**$_3$N	35
		C**H**$_3CH_3$	60

13. (3 marks)

List the following in order of increasing nucleophilicity:

CH_3CH_2OH, Cl^-, H_2O, CN^-, CH_3NH_2, $H_3C–C\equiv C^-$

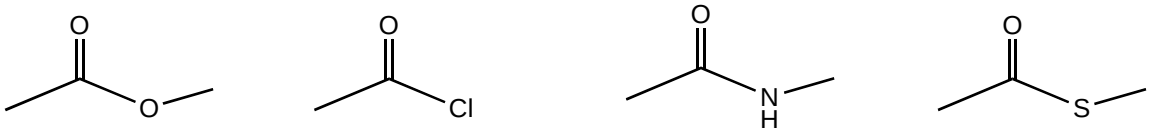
14. (3 marks)

List the following in order of increasing nucleofugicity (leaving group ability):

Cl^-, H_2O, H_2N^-, $HCOO^-$, OH^-, CH_3^-

15. (6 marks)

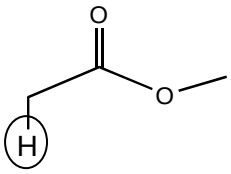
(a) Draw out all resonance structures for the following:



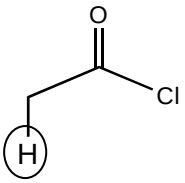
(b) Place the above structures in order of DECREASING reactivity.

16. (10 marks)

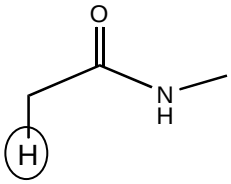
Explain the differing acidities of the circled H atoms:



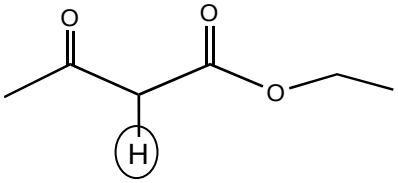
pK_a ~25



pK_a ~19



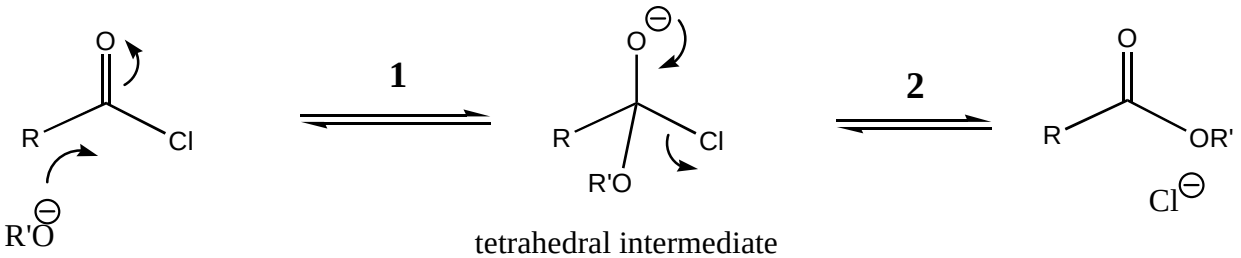
pK_a ~30



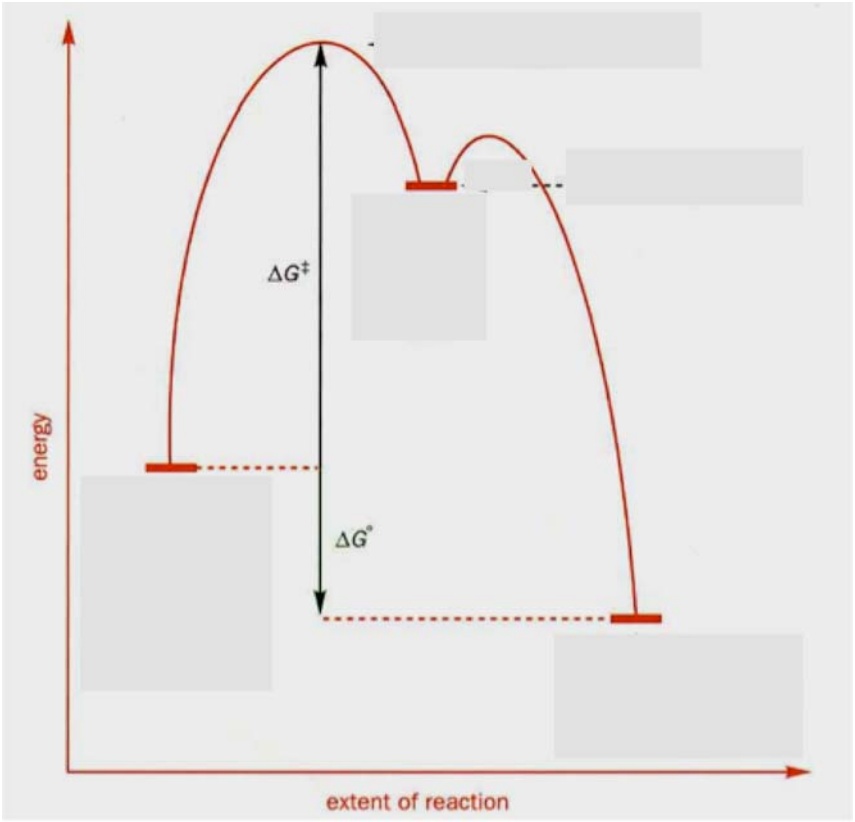
pK_a ~ 9

17. (6 marks)

An energy profile diagram is shown below for this reaction that proceeds **spontaneously**:



tetrahedral intermediate



(a) **Circle** and **label** (TS) the energy level(s) corresponding to the transition state(s).

(b) **Circle** and **label** (I) the energy level(s) corresponding to the intermediate(s)

(c) **Circle** and **label** (SM and P) the energy levels corresponding to the starting material and to the product

(d) Are the products of HIGHER energy than the starting materials?

(Circle one only)

Y **N**

(e) Can the transition state(s) be isolated?

Y **N**

(f) Can the intermediate(s) be isolated?

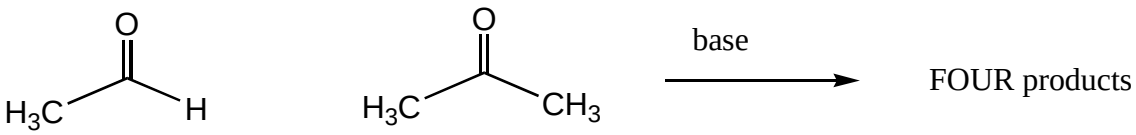
Y **N**

18. (6 marks)

Explain why the reaction in **Question 17** proceeds spontaneously.

19. (12 marks)

In a “mixed” or” crossed” aldol reaction between acetaldehyde and acetone FOUR products are possible.



acetaldehyde acetone

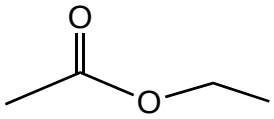
(a) Draw structures of the four products.

(b) Which product will be formed in the greatest yield? Give a brief explanation.

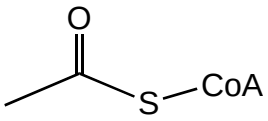
(c) Which product will be formed in the lowest yield? Give a brief explanation.

20. (10 marks)

Thiol esters, such as acetyl CoA, play key roles in many metabolic cycles. Explain why acetyl CoA is more reactive than ethyl acetate.



ethyl acetate



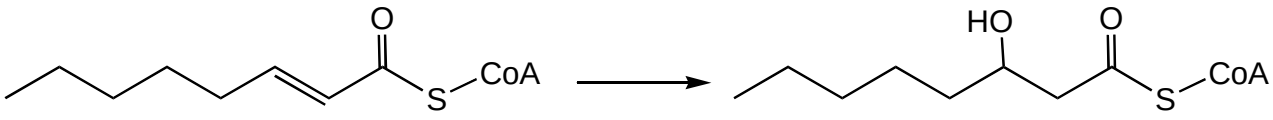
acetyl CoA

The following data may be of use.

	pK_a
H–CH_2–COSCoA	21.0
H–CH_2–$COOCH_2CH_3$	25.0
CH_3CH_2–S–**H**	10.3
CH_3CH_2–O–**H**	16.0

21. (4 marks)

Conjugate or 1,4 addition of water to an αβ-unsaturated CoA ester is an essential step to the β-oxidation of fatty acids in biological cycles.



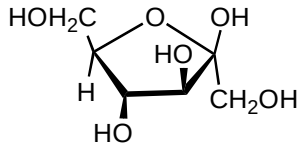
Outline the steps in this reaction.

22. (3 marks)

Why is conjugate (1,4-) and not carbonyl (1,2-) addition usually observed in nucleophilic additions to αβ-unsaturated compounds such as that shown in **Question 21** above?

23. (8 marks)

(a) Is β-D-(-)-fructofuranose:



β-(D)-(-)- fructofuranose

(i) a hexose? **Y** **N** (circle one only)

(ii) a ketose? **Y** **N** (circle one only)

(iii) an aldohexose? **Y** **N** (circle one only)

(iv) a glycoside? **Y** **N** (circle one only)

(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?

(c) Draw diagrams to explain what is happening in **(b)**

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

END OF PAPER