University of Canterbury

End of Year Examinations 2005

Prescription Number(s):	CHEM 469
Paper Title:	Special Topic

Time Allowed: THREE HOURS

Number of pages: TEN

This paper contains **THREE** sections, **A**, **B** and **C.**

Answer **FOUR** questions in total.

Answer **AT LEAST ONE** from **EACH** section.

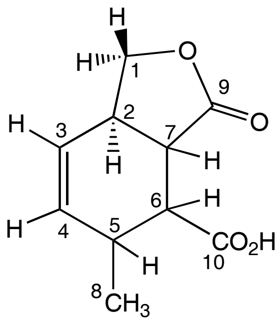
All questions are of equal value.

TURN OVER

SECTION A

Answer **AT LEAST ONE** question from this section.

1.



1

The NMR spectra in the attached two pages (which may be handed in as part of your answer) are provided for compound **1**:

A	^{1}H 1D NMR spectrum with integral data
B	1D NOE spectrum resulting from irradiation of signal at 3.40 ppm
C	2D COSY spectrum
D	^{13}C 1D NMR spectrum
E	2D HSQC-DEPT spectrum
F	2D HMBC (CIGAR) spectrum

(a) Explain, in general terms, what information can be derived from spectra of the types E and F.

(b) Utilising information from spectra A and C, assign as many as possible of the resonances in spectrum A to specific protons in compound **1**. Show your reasoning.

(c) With these assignments made, assign as many as possible of the resonances in spectrum D to a specific carbon in compound **1**.

(d) Assign any remaining carbon resonances from information contained in spectrum F. Explain how you have made these assignments.

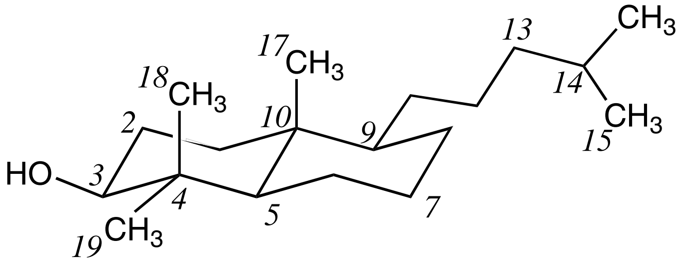
(e) Use information from spectrum B and your assignments made in part (b) to establish the stereochemistry at positions 6 and 7 relative to that for position 2.

(f) Describe how you could determine the relative stereochemistry at position 5.

2. (a) Give a brief description of the mechanism for dipole-dipole spin-lattice relaxation, indicating how environmental and molecular parameters influence the magnitude of this phenomenon.

(b) Describe a pulse sequence for the measurement of the spin-lattice relaxation parameter, T_1, showing the behaviour of the nuclear magnetization vectors in this experiment.

(c) Account for the differences between the ^{13}C T_1 values (sec) for the positions indicated on the following structure.

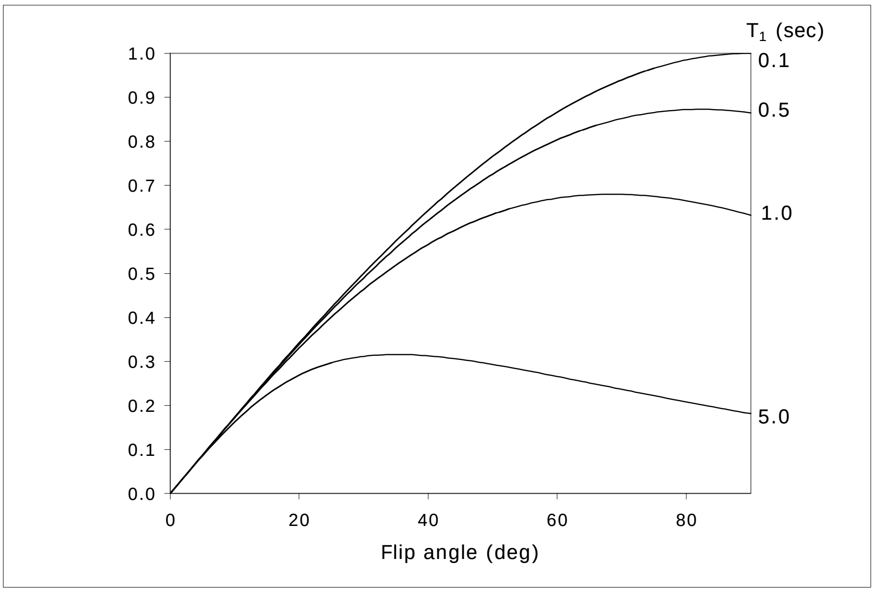


position	T_1 (s)
2	0.4
3	0.8
4	1.8
5	0.8
7	0.4
9	0.8
10	1.9
13	0.8
14	1.2
15	2.5
17	3.1
18	3.1
19	2.0

3. (a) (15 marks)

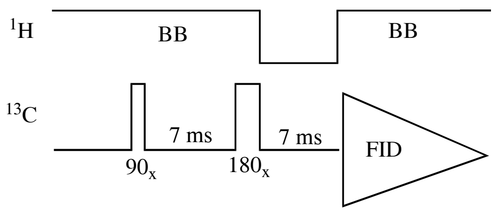
The following graph shows the steady-state magnetization responses (and hence relative signal intensities) in the repetitive-pulse Fourier-transform NMR experiment, for a selection of ^{13}C nuclei with different T_1 relaxation times, and as a function of flip angles 0-90°. The data acquistion time is 1 s, and the pulse delay is 0 s.

Discuss how you could vary the acquisition parameters for this experiment (flip angle, acquisition time, pulse delay) to optimise the intensity response (relative to noise) for all nuclei, given that you would only have a fixed time for running the experiment.



(b) (10 marks)

Explain how the behaviour of the nuclear magnetization varies for each of the carbon types CH_3, CH_2, CH and C during the evolution period of the APT pulse sequence shown below. Describe how the differences in behaviour allow for distinctions to be made between some of these types.



SECTION B

Answer **AT LEAST ONE** question from this section.

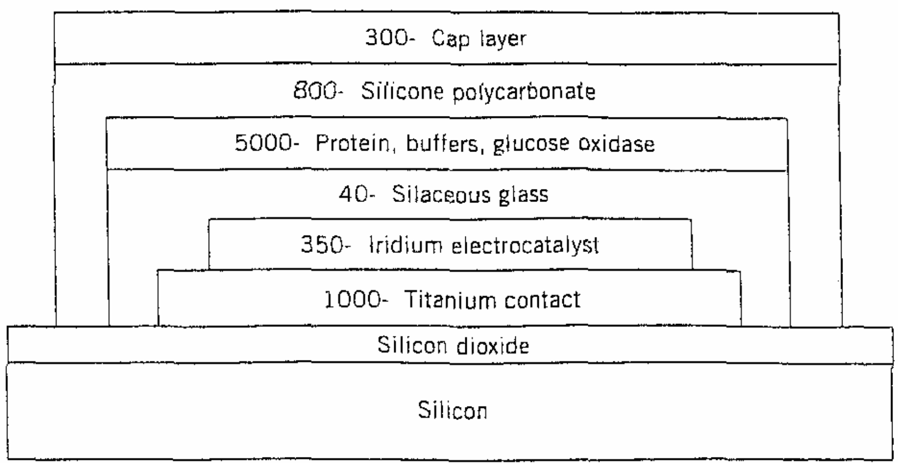
4. (a) (i) Define the term **amperometric biosensor**.

(ii) Briefly explain how an amperometric two-electrode cell functions.

(iii) List the advantages of enzymes for sensing strategies.

(b) Outline the usual components and basic functioning of glucose oxidase-based amperometric biosensors for blood glucose measurement. Describe and discuss the different formats found in two commercially available and one 'under-development' glucose biosenors.

To assist with your answer, a diagram of the i-STAT glucose-sensing electrode is given below.



5. "Nanoparticles (including nanoshells and nanotriangles) play an important role in many sensing strategies. The signal may be based on a change in the optical properties of the nanoparticles, or the nanoparticles may be used to amplify a signal (e.g. for a fluorescence or mass-based detection scheme)."

   Discuss this statement giving specific examples of sensing strategies that incorporate nanoparticles. Include in your answer, as appropriate, brief explanations of localised surface plasma resonance, fluorescence, and mass measurements using the quartz-crystal microbalance.

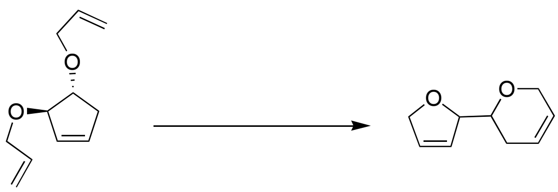
SECTION C

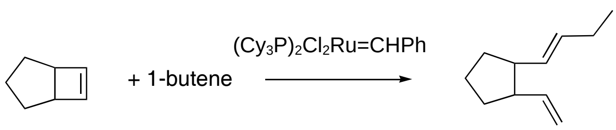
Answer **AT LEAST ONE** question from this section.

6. Olefin metathesis has found numerous applications in organic and polymer synthesis.

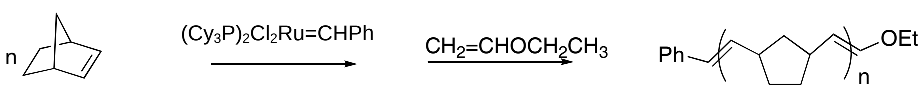
(a) Using appropriate examples, outline the versatility of this reaction.

(b) Draw mechanisms for the following transformations:

(i) 

(ii) 

major product, why?

(iii) 

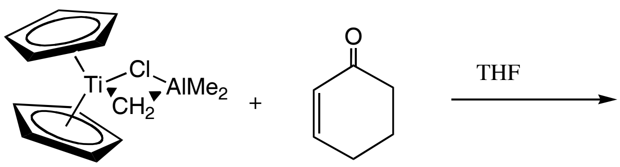
7. Transition-metal carbene (alkylidene) complexes are finding uses in a variety of organometallic and catalytic processes. Key to their applications is the relative reactivity that is controlled both by the metal centre and the ligands.

(a) Draw the three resonance structures that describe the potential polarization of a metal-carbon double bond. The names Schrock and Fischer are associated with two of these structures - label the structures with the correct names. Briefly comment on the reactivity of different metal carbene complexes.

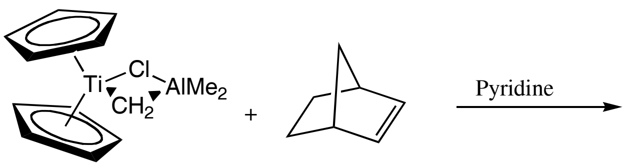
$\longleftrightarrow$ $M{=}CH_2$ $\longleftrightarrow$

(b) Draw structures for the major products of the following reactions and briefly discuss the chemistry involved.

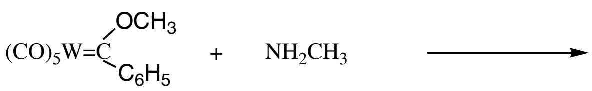
(i)



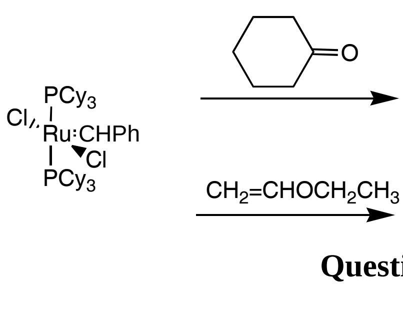
(ii)



(iii)



(iv)



Question 7 continued on following page

Question 7 continued

(c) Although there are a variety of structures of catalysts that fit the general structure of the family of ruthenium olefin metathesis catalysts, two major structures are referred to as the first- and second-generation catalysts.

(i) Draw structures for the two types of catalysts and briefly compare their properties and uses.

(ii) Outline one of the synthetic routes that can be used to prepare members of the first-generation catalysts.

END OF PAPER