



Semester II Examinations 2010 / 2011

Exam Code(s) 4BS
Exam(s) 4th year Chemistry – CH401

Module Code(s) **CH434**
Module(s) **Organic Chemistry II**

Paper No.

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Instructions: Answer one question from Section A, one question from Section B and two questions from Section C

Use a separate answer book for each section

Each section carries 100 marks distributed as shown where appropriate. Leave the first page of the answer book blank and list on it clearly the numbers of the questions attempted.

Duration 2 hours
No. of Pages 12 (incl. this front page)
Discipline(s) Chemistry

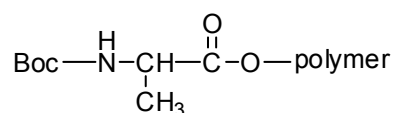
Requirements None

Section A.

Answer either question 1 (100 marks) or question 2 (100 marks)

1. Answer all parts

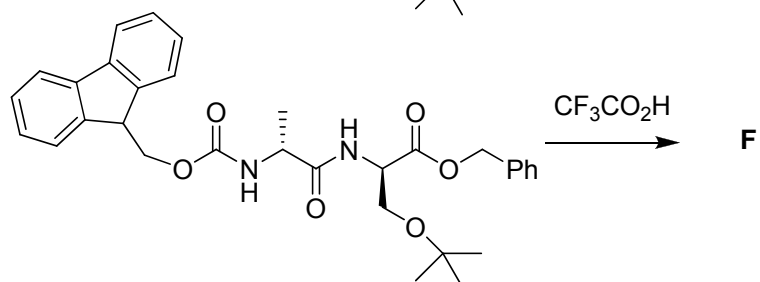
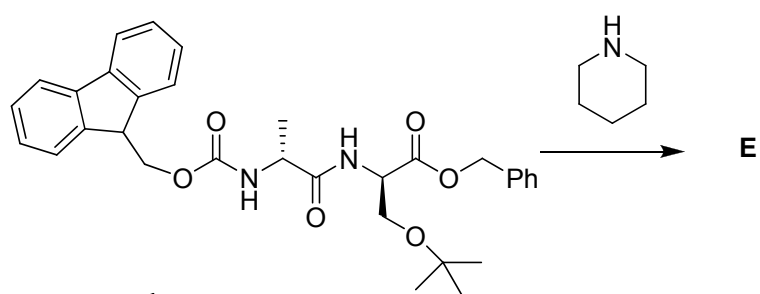
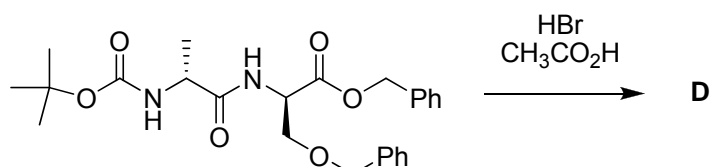
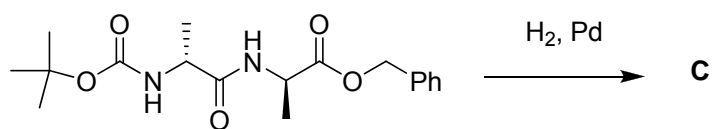
- (a) Using diagrams for each step, describe a three step synthesis of a soluble dipeptide Ala-Ala **B** starting from the polymer-supported alanine derivative **A**. In your answer, include the structure of any reagents that are required and discuss any precautions taken to avoid racemisation. Give a mechanism for racemisation. What structural features in the polymer are important and why?



A

[50 Marks]

- (b) Give the products of each of the following reactions **C-F**. Give brief mechanistic explanations for the formation of **D-F**.



[50 marks]

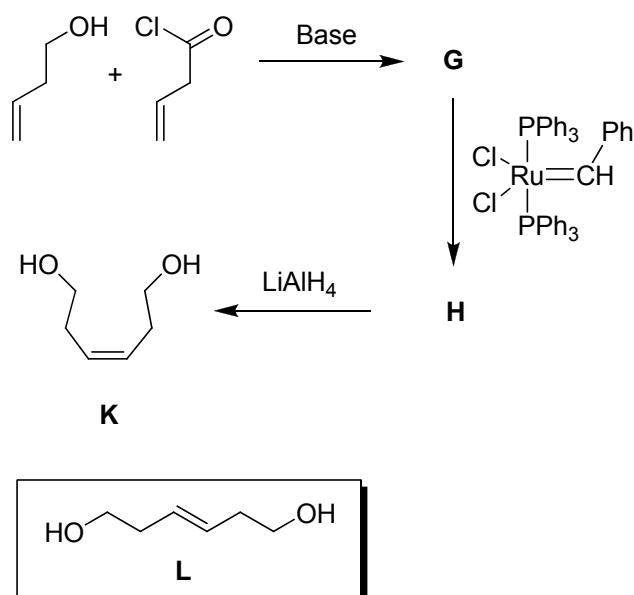
2. Answer all parts

- (a) Discuss the Wittig reaction in the synthesis of alkenes. In your answer refer to the following:

structure of stabilized and unstabilized ylides;
the stereoselectivity observed in formation of alkenes from reactions of aldehydes with both stabilized and unstabilized ylides;
a mechanism for the stereoselectivity in the reaction of an aldehyde with a stabilized ylide, which ultimately gives an alkene. **[40 marks]**

- (b) Draw the structure of a Horner-Wadsworth-Emmons reagent and give an application for this reagent in synthesis. **[10 marks]**

- (c) The synthesis of the *cis*-alkene **K** is shown in the scheme. Give structures for **G** and **H**. Why is the strategy shown suitable for *cis*-alkene synthesis? Suggest a strategy for the preparation of the *trans*-alkene **L**.



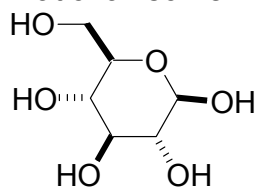
[50 marks]

Section B

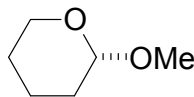
Answer either question 3 (100 Marks) or question 4 (100 marks)

3. Answer all parts

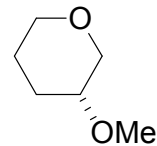
- (a) Draw possible chair conformations for **A-C** and predict the favoured conformational isomer in each case. Explain briefly your choice in each case.



A (β -D-glucopyranose)



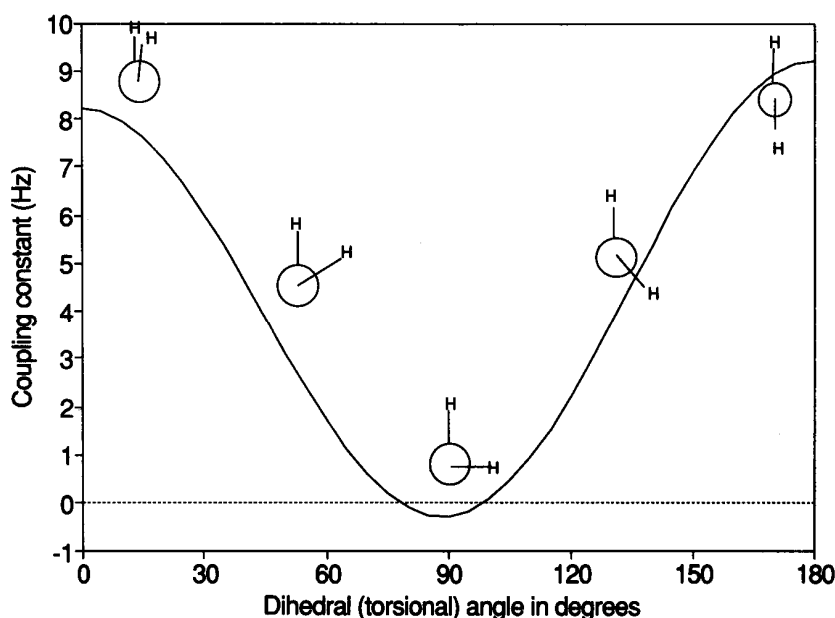
B



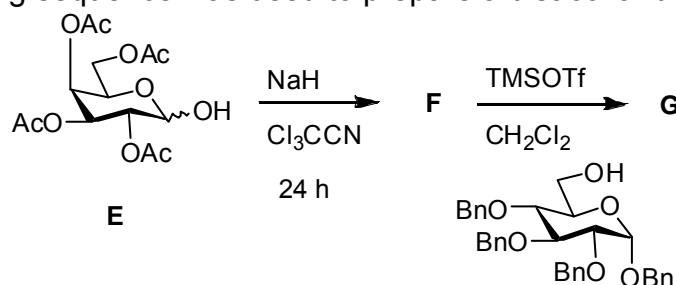
C

[33 Marks]

- (b) Explain how $^1\text{H-NMR}$ spectroscopy could be used to determine the preferred conformation of **A**. Use the Karplus curve provided below. **[7 Marks]**



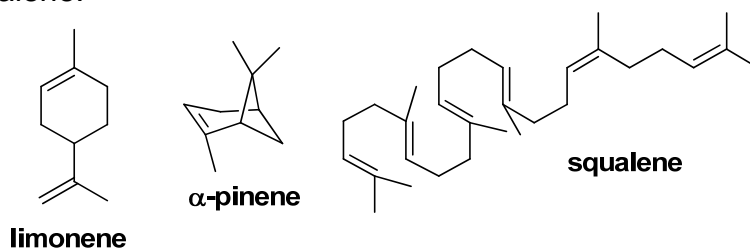
- (c) Describe a synthesis of any thioglycoside donor and show how it can be used in the synthesis of an *O*-glycoside. Give the structure of a glycosyl acceptor, an activating agent and the *O*-glycoside product in your answer. Is there any stereochemical preference in the reaction you have chosen? **[25 Marks]**
- (d) The following sequence was used to prepare a disaccharide **G** from **E**.



Write structures for **F** and **G**. Write a mechanism for the glycosidation reaction and explain the stereoselectivity. Write the structure for an orthoester by-product that might be obtained. **[35 Marks]**

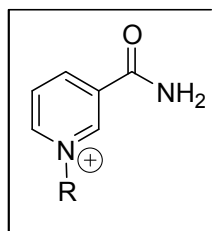
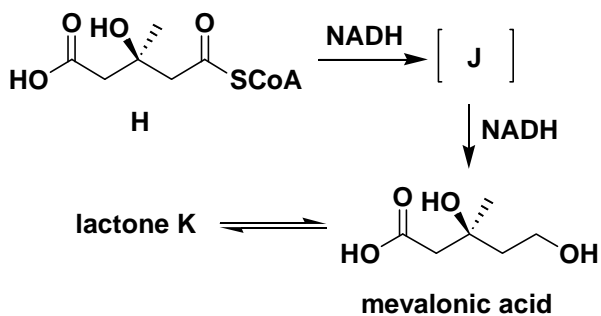
4. Answer all parts

- (a) Explain the isoprene rule. Identify the isoprene units in limonene, α -pinene and squalene.



[15 marks]

- (b) Draw the structure of biosynthetic intermediate **J**, and provide a curly arrow mechanism for the formation of mevalonic acid from thioester **H** using NADH. The structure of NAD^+ is provided.



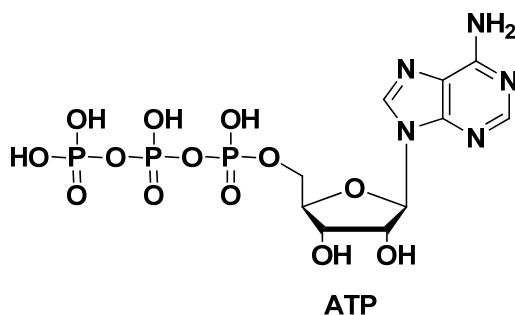
NAD^+ , where R = Ribose + ADP (adenosine diphosphate)

[25 marks]

- (c) Draw the structure of the lactone **K**.

[5 marks]

- (d) ATP is used to convert mevalonic acid into the biosynthetic building block isopentenyl pyrophosphate. Draw the structure of isopentenyl pyrophosphate, and draw a curly arrow mechanism for its formation from mevalonic acid. The structure of ATP is provided below.



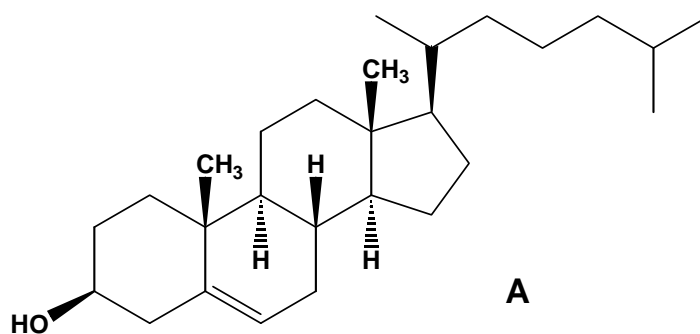
[25 marks]

- (e) Draw a curly arrow mechanism for the biosynthetic conversion of isopentenyl pyrophosphate into limonene. **[30 marks]**

Section C

Answer two questions from questions 5, 6 and 7
(NB: each question in this section is 50 marks)

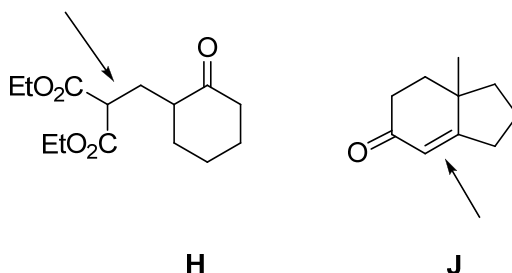
- 5 Structure **A** represents cholesterol. When cholesterol was treated with peroxybenzoic acid (C_6H_5COOOH) it gave only one epoxide **B** in quantitative yield. The epoxide **B** was treated with hydrochloric acid solution to give cholestan-3 β -ol derivative chloride **C** in quantitative yield. Draw structures accounting for the correct stereochemistry for epoxide **B** and chloride **C**. Outline a mechanism for the formation of product **C** from **B**, and draw the energy minimum conformation of **C**.



[50 marks]

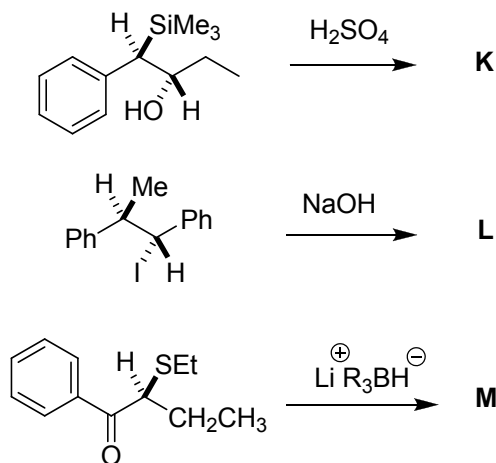
6 Answer each part

- (a) Use retrosynthetic analysis to suggest a synthesis for either **H** or **J**. The bond where the disconnection should be made is indicated with an arrow. Draw synthons and synthetic equivalents.



[20 marks]

- (b) Draw the products of the following reactions **K-M**. Consider the stereoselectivity in each case.



[30 marks]

7 Correlation Tables are provided at the end of the examination paper

A substance **Q** has the molecular formula $C_{11}H_{14}O_2$ and its IR spectrum contains strong absorption bands at 1730, 1205, 750 and 705 cm^{-1} . Its 1H -NMR spectrum is shown in **Fig. 1**, a section of which is expanded in **Fig. 2**. The integration values for each signal appear below the baseline (an integral trace is also included) and the exact chemical shifts appear above each signal.

Decoupling experiments show that the signals at δ 1.22 and 4.11, and at δ 2.60 and 2.94, are coupled. The ^{13}C -NMR spectrum for **Q** is shown in **Fig 3**. The signal at 0.0 ppm is due to TMS and those at 76-78 ppm to the solvent used, $CDCl_3$. An analysis of the DEPT spectrum of **Q** produced the information given in the following table:

Signal (ppm)	172.81	140.54	128.43	128.25	126.18	60.37	35.94	30.98	14.20
Number of hydrogens attached to C-atom responsible for signal	0	0	1	1	1	2	2	2	3

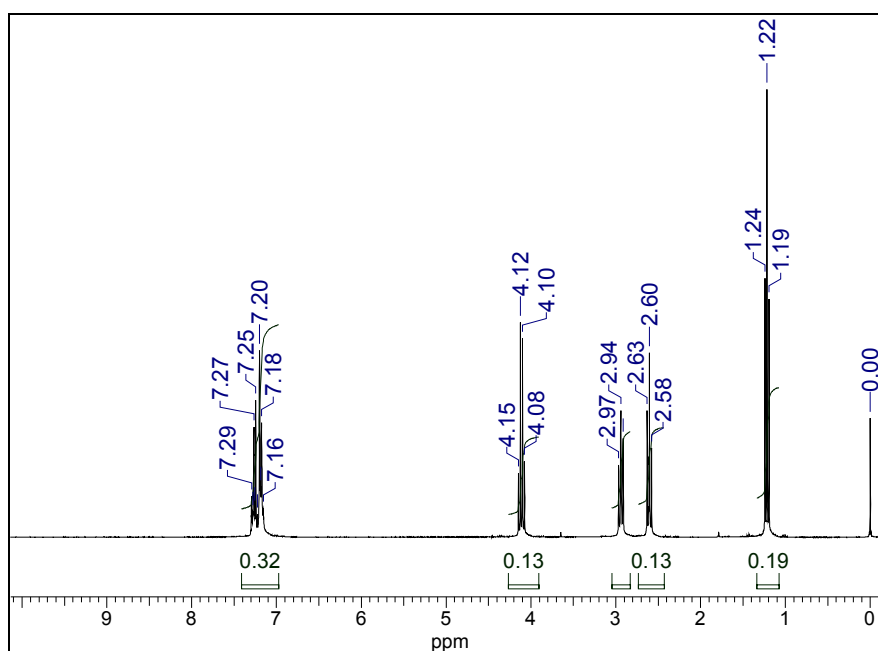


Fig.1

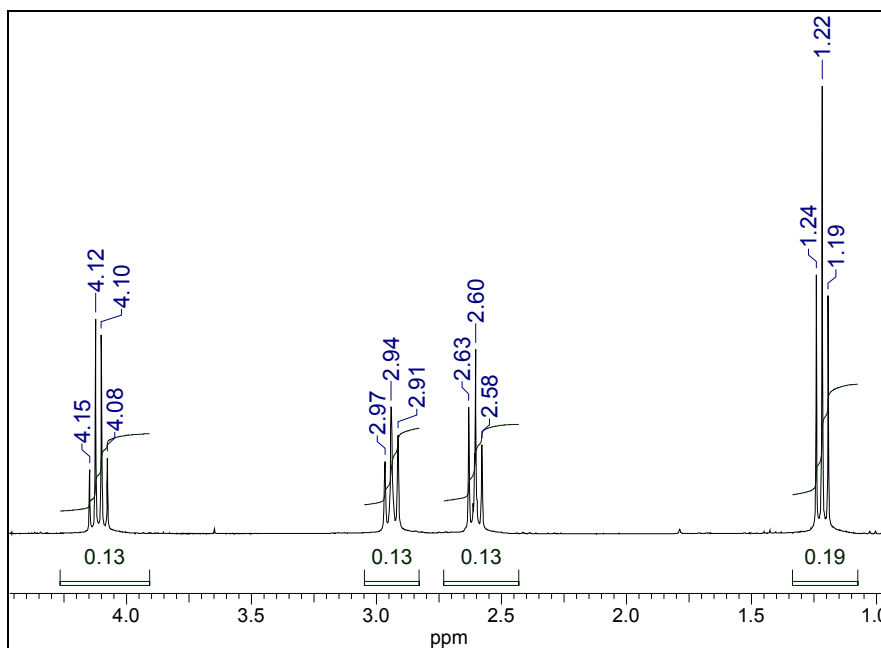


Fig 2

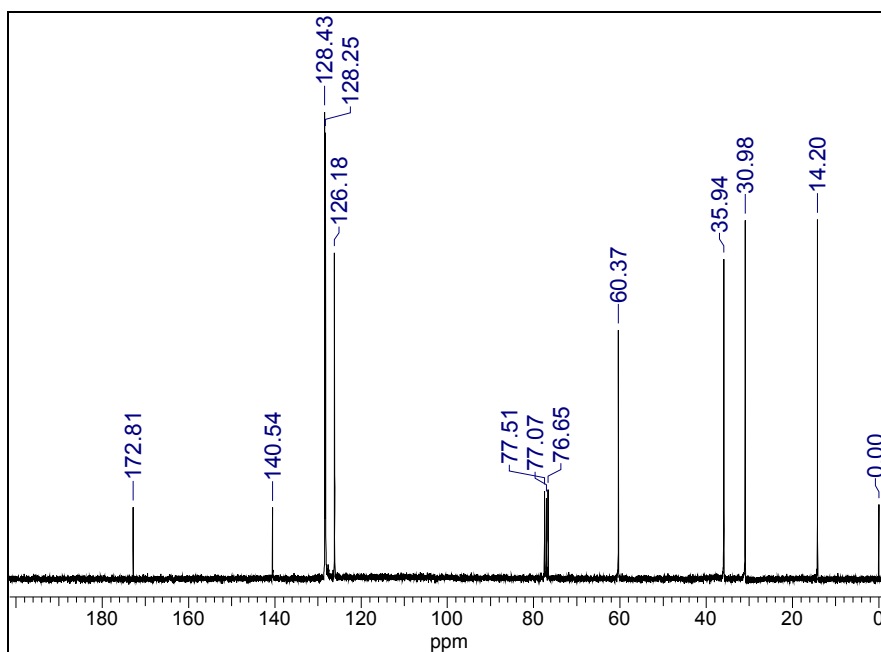


Fig. 3

- (i) Use this information to determine the structure of **Q**. **[25 marks]**
- (ii) Assign the IR bands listed above. **[5 marks]**
- (iii) Assign all the signals in the $^1\text{H-NMR}$ spectrum to the appropriate hydrogen atoms in the structure and account for the coupling patterns of the signals. **[10 marks]**
- (iv) Assign the signals in the $^{13}\text{C-NMR}$ spectrum to the appropriate carbon atoms in the structure. You are not required to distinguish between the signals at 35.94 and 30.98 ppm, nor between those at 128.43, 128.25 and 126.18 ppm. **[10 marks]**

