

University of Canterbury

End of Year Examinations 2007

Prescription Number(s):	CHEM 222 CHEM 262 BCHM 206
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Paper Title:	Organic Chemistry
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Time Allowed: TWO HOURS

Number of pages: SEVEN

Disassembled molecular model kits are allowed.

This paper is divided into **TWO** sections:

Section A: Answer **TWO** questions out of **THREE**.

Section B: Answer **BOTH** questions;

All questions are of equal value and you should allow approximately 30 minutes to answer each question.

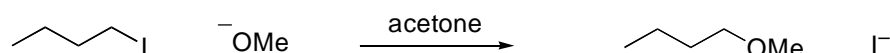
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SECTION A

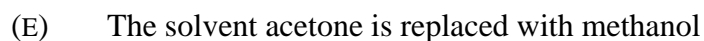
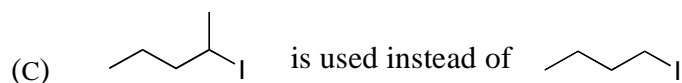
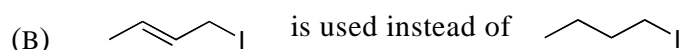
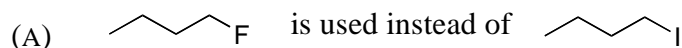
(Answer **TWO** questions out of **THREE**.)

1. (a) By means of structural diagrams illustrate the S_N1 and S_N2 mechanisms for substitution reactions.

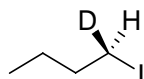
- (b) For the following substitution reaction:



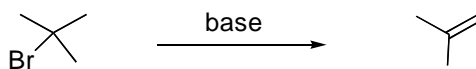
- (i) Would you expect this reaction to proceed via an S_N1 or an S_N2 mechanism? Explain your answer.
- (ii) Draw a reaction energy profile diagram for this reaction. Label the key structures and energy differences.
- (iii) Use the energy profile diagram in (ii) to predict how the rate of the substitution reaction will alter with the following changes. Explain your answers.



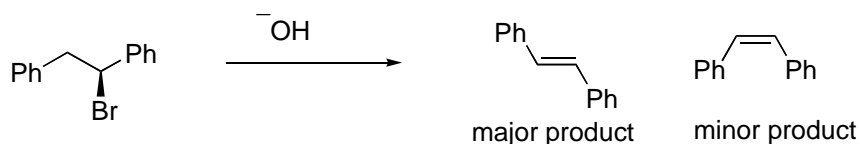
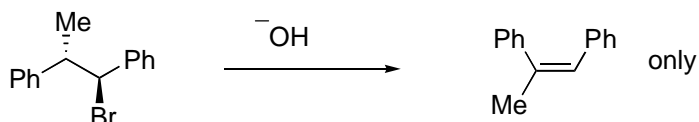
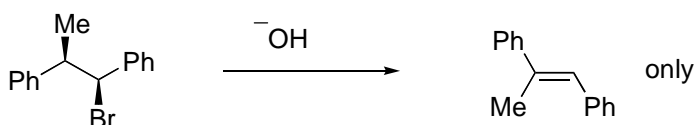
- (iv) Predict the stereochemical outcome of the substitution reaction when the starting material is deuterium labelled as shown below.

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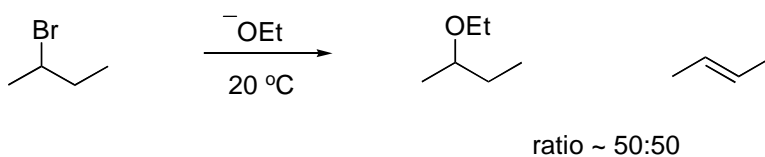
2. (a) The following compound is capable of eliminating by both E1 and E2 mechanisms. Use structural diagrams to illustrate these two mechanisms.



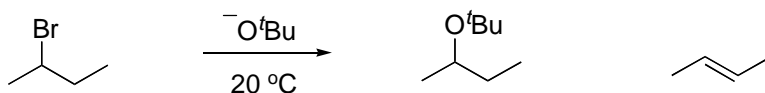
- (b) Explain how the choice of base will affect whether the reaction proceeds via an E2 or an E1 mechanism.
- (c) Explain the stereochemical outcome of the following elimination reactions.



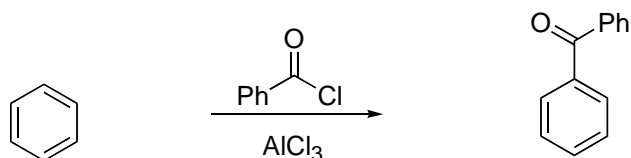
- (d) When 2-bromobutane reacts with ethoxide, both substitution and elimination products are formed, as shown below.



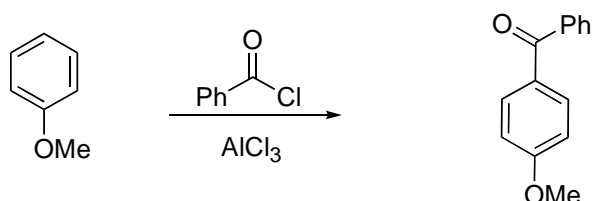
Predict how the ratio of products will alter when the following changes are made to the reaction conditions.



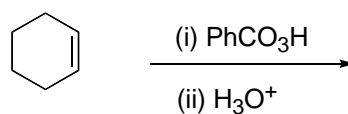
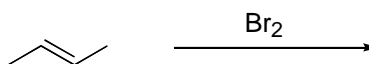
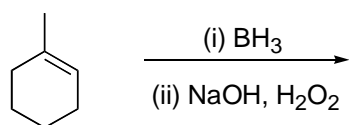
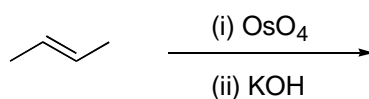
3. (a) (i) Give the mechanism of the following Friedel-Crafts acylation reaction. Explain why it is necessary to have AlCl_3 present for this reaction to take place.



- (ii) Explain why Friedel-Crafts alkylation reactions are less useful than Friedel-Crafts acylation reactions.
- (iii) When OMe-substituted benzene is used instead of benzene, as the starting material the reaction is *faster* and gives rise to only the *para* isomer of the product. Explain these observations.



- (b) For **THREE** of the following transformations below, predict the *structure* and *stereochemistry* of the product, and give mechanisms for the reaction sequences.



SECTION B

(Answer **BOTH** questions in this section.)

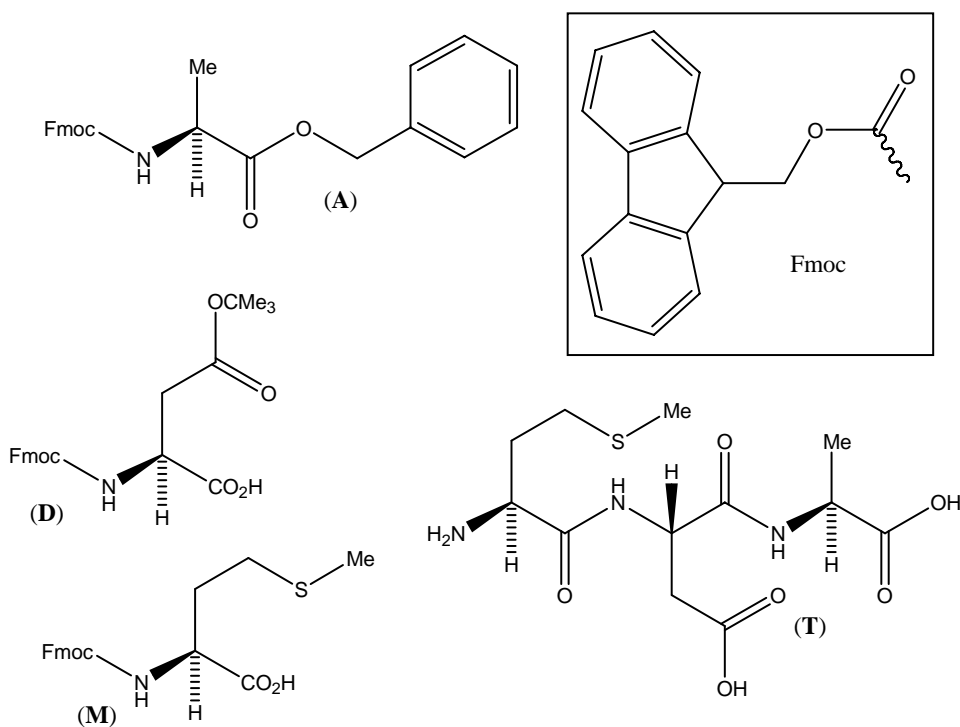
4. 1,3-Butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) is an important monomer for polymer synthesis. Discuss the polymerisation chemistry of 1,3-butadiene by providing a critical analysis of the information in parts (a) - (d).
- (a) 1,3-Butadiene can be polymerised by heating with small amounts of AIBN ($\text{NCCMe}_2\text{N}=\text{NCMe}_2\text{CN}$). Give the mechanism for this process. Describe the role of AIBN and explain why the polymerisation process is fast.
- (b) 1,3-Butadiene can be polymerised by heating with small amounts of strong acid. Give the mechanism for the process and explain the factors affecting the choice of acid. Why can ethene not be polymerised by these conditions?
- (c) 1,3-Butadiene can be polymerised by treatment with small amounts of butyl lithium ($\text{CH}_3(\text{CH}_2)_3\text{Li}$). However, ethene cannot be polymerised by treatment with butyl lithium.
- (d) Describe the regiochemistry and stereochemistry issues of addition to individual butadiene units in the polymerisation of this monomer. Why does the control of isomer formation affect the properties of the resulting polymers?

5. (a) Deprotection of *t*-Boc(Me₃COCO-) and Fmoc amino acid derivatives (see part (b) below) is based upon the selective generation of stabilised reactive intermediates. Give a specific example of the deprotection of:

- (i) a *t*-Boc amino acid derivative; and
- (ii) an Fmoc amino acid derivative.

In each case, provide a detailed mechanism for the deprotection reaction and discuss the nature of the stabilization of the relevant reactive intermediate.

- (b) Describe a synthesis of tripeptide (**T**) from the monomers (**A**), (**D**) and (**M**) shown below. In your answer, include the reaction conditions that could be used for each step and the mechanistic details of the chemistry involved.



END OF PAPER