

University of Canterbury

## End-of-year Examinations 2008

Prescription Number(s): CHEM 242  
BCHM 206

Paper Title: Organic Chemistry

Time Allowed: Two hours

Number of pages: Seven

**Section A;** Answer **ALL** questions in this section.  
(Worth 40% of the total mark.)

**Section B;** Answer **ALL** questions in this section.  
(Worth 60% of the total mark.)

***TURN OVER***



## SECTION A

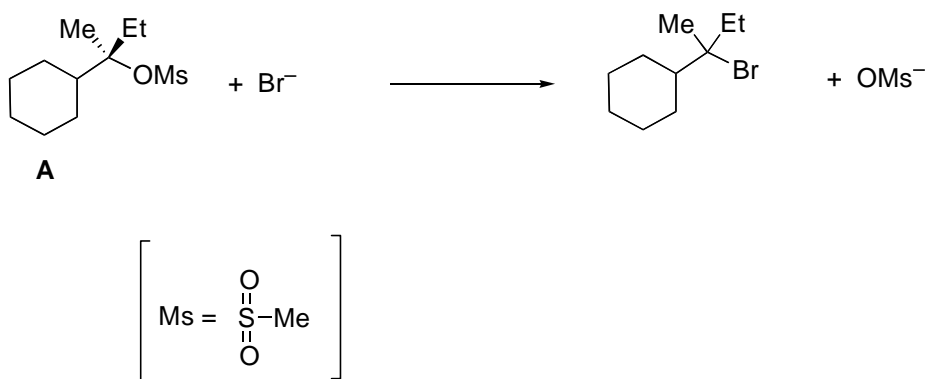
(Answer **ALL** questions in this section. Worth 40% of the total marks)

1. (5 marks)

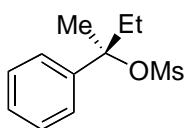
By means of structural diagrams illustrate the  $S_N1$  and  $S_N2$  mechanisms for substitution.

2. (14 marks)

For the following substitution reaction:



- (a) Would you expect this reaction to proceed via an  $S_N1$  or an  $S_N2$  mechanism? Explain your answer.
- (b) Draw a reaction energy-profile diagram for this reaction. Label key structures and energy differences.
- (c) Use this energy-profile diagram to account for the following observations.
- (i) The reaction rate does not change if  $\text{I}^-$  is used instead of  $\text{Br}^-$ .
  - (ii) The product of the reaction is not able to rotate plane polarised light.
  - (iii) The reaction rate is faster if the following starting material is used instead of compound A:

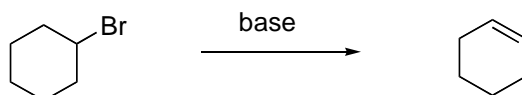


- (iv) The reaction takes place at a faster rate in methanol than in acetone.

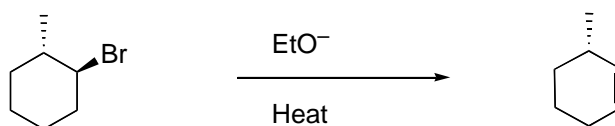
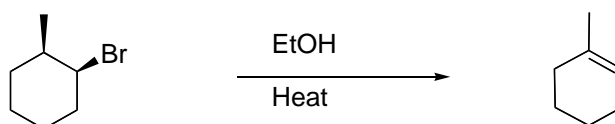
**TURN OVER**

3. (10 marks)

- (a) The following compound is capable of elimination by both E1 and E2 mechanisms. Use structural diagrams to illustrate these two mechanisms. Explain how the choice of base will determine whether the reaction proceeds via an E2 or an E1 mechanism.

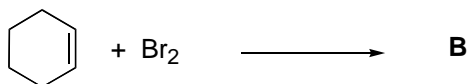


- (b) Use your answer to part (a) to explain why the two elimination reactions below give rise to different products.



4. (5 marks)

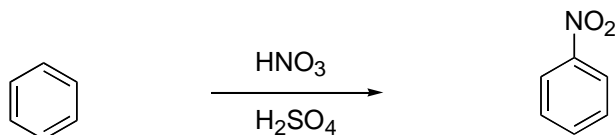
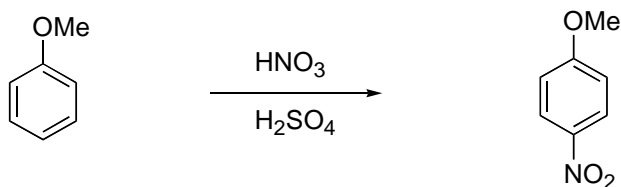
For the following addition reaction:



give the structure of compound **B**. Provide a mechanism for its formation and use this mechanism to explain whether **B** represents a single substance or a mixture of stereoisomers.

5. (6 marks)

(a) Give the mechanism of the following nitration reaction.

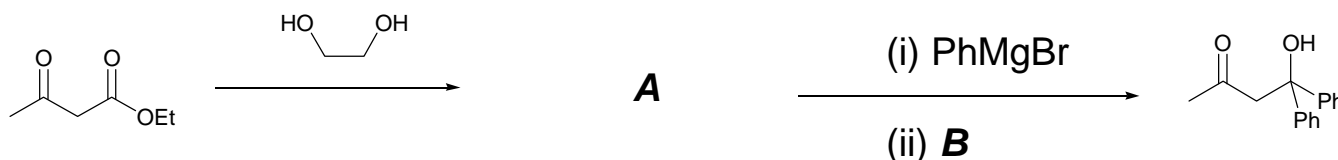
(b) When an OMe-substituted benzene is used instead of benzene as the starting material, the reaction is *faster* and gives rise to mainly *one isomer* of the product. Explain these observations.**TURN OVER**

## SECTION B

(Answer **ALL** questions in this section. Worth 60% of the total marks.)

6. (10 marks)

The synthetic procedure shown below requires the use of protecting groups.

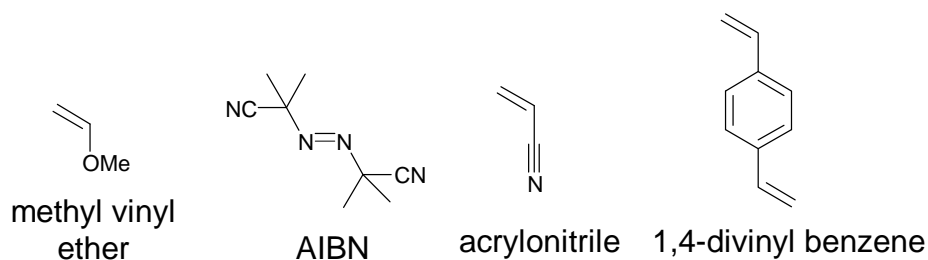


- Give the structure of **A**.
- Give the reagent **B** required to complete the synthetic scheme.
- Briefly explain why this reaction requires the use of protecting groups.

7. (25 marks)

Methyl vinyl ether is an important monomer that is used in the formation of polymers.

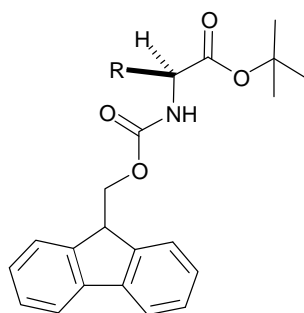
- Provide a detailed mechanism for the polymerisation reaction of methyl vinyl ether carried out at 80°C with a trace amount of AIBN as an initiator.
- It is possible to increase the rigidity of a polymer formed from methyl vinyl ether by adding a small amount of 1,4-divinyl benzene. Explain this observation.
- Is the polymerisation reaction of methyl vinyl ether under thermodynamic or kinetic control? Explain your reasoning.
- The radical polymerisation of a 1:1 mixture of methyl vinyl ether with acrylonitrile gives a co-polymer. Give the structure of the repeating unit of this polymer, and explain why this structure is formed.



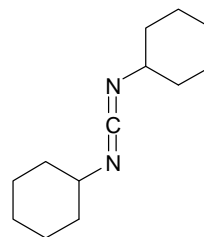
8. (25 marks)

The synthesis of peptides requires the use of both protecting groups and reagents to activate coupling of amines and carboxylic acids to form amide bonds.

- (a) Shown below is an example of an Fmoc and t-Butyl protected amino acid. Describe how you would remove each of these protecting groups *separately*. In each case, give a detailed mechanism and discuss the nature of any stabilisation of the relevant intermediates.
- (b) DCC (Dicyclohexyldiimide) is used as a coupling reagent for the formation of amide bonds in peptide synthesis. Give the mechanism of amide bond formation using DCC and discuss why this reagent is used.



Fmoc and t-Butyl protected  
amino acid



DCC

**END OF PAPER**