

University of Canterbury

End-of-year Examinations 2009

Prescription Number(s): CHEM 242
BCHM 206

Paper Title: Organic Chemistry

Time Allowed: Three hours

Number of pages: SEVEN

Answer **ALL** questions

The following abbreviations have been used:

Me = CH₃-; Et = CH₃CH₂-; ^tBu = (CH₃)₃C-;
Ph = C₆H₅-; eq. = number of equivalents

Aqueous work-up procedures are implied throughout, with concomitant protonation or deprotonation of charged intermediates. Assume reactions are carried out at room temperature unless otherwise indicated. All formulae depicting chiral molecules refer to racemic mixtures, unless a single enantiomer is explicitly specified.

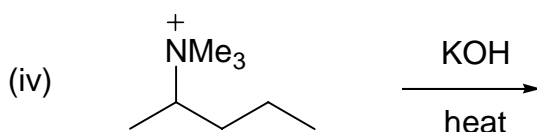
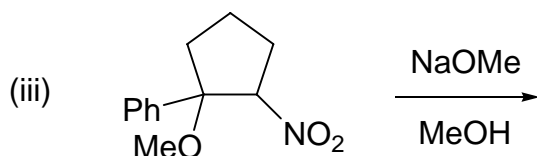
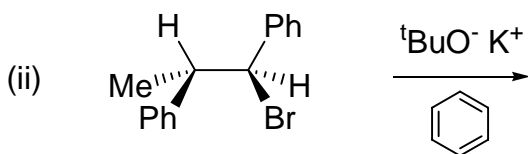
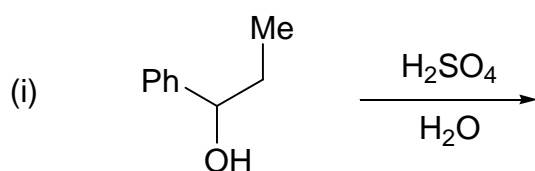
TURN OVER

1. (a) (5 marks)

Explain briefly the differences between the stereochemical outcomes of S_N1 and S_N2 reactions.

(b) (3 × 5 marks)

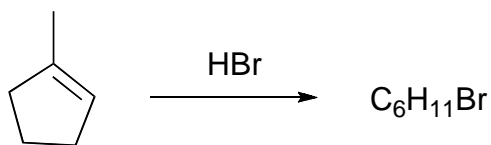
The following elimination reactions all give alkenes as the products. For **THREE** of them predict the structure of the product and give a reaction mechanism in each case. In your answer you should state clearly in each case which type of elimination mechanism you think is occurring (e.g. E1, E2 or E1_{CB}) and give a reason for your choice.



2. (a) (5 marks)

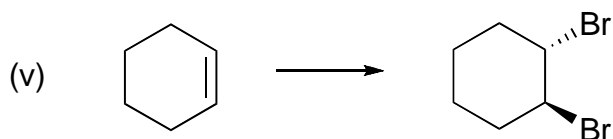
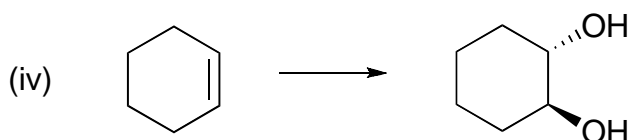
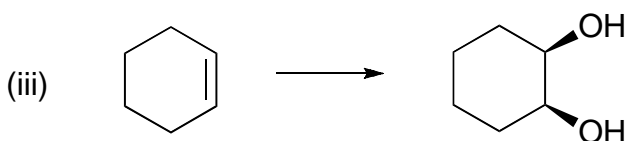
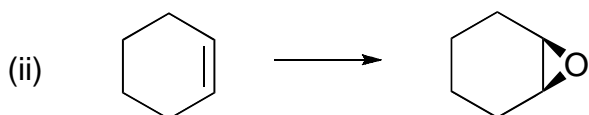
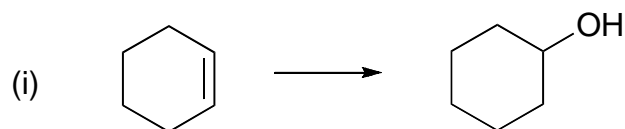
Predict the structure of the product formed in the following synthetic transformation.

Give a mechanism for this reaction and explain why only one regioisomer is formed.



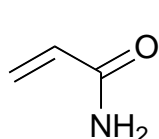
(b) (3 × 5 marks)

For **THREE** of the following examples suggest reagents that may be used to achieve the required synthetic conversion. In each case you choose you should give a mechanism for the reactions involved, and, if appropriate, comment on any stereochemical aspects of this process. Note: more than one step may be required.

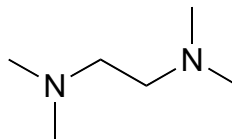


3. (a) (14 marks)

Acrylamide (structure shown below) is an important monomer for the formation of polymeric gels for use in biochemical studies. It is polymerised using TEMED (structure also shown below), which is added to the mixture at the last minute to initiate the polymerisation process.



Acrylamide

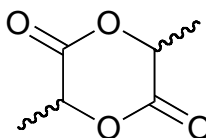


TEMED

- (i) Provide a detailed mechanism for the polymerisation reaction of acrylamide carried out at room temperature with a trace amount of TEMED as an initiator. (7 marks)
- (ii) Explain why the acrylamide polymerisation can be done at room temperature and atmospheric pressure, whilst ethene does not polymerise under these reaction conditions. (4 marks)
- (iii) Is the polymerisation reaction of acrylamide under thermodynamic or kinetic control? Explain your reasoning. (3 marks)

(b) (6 marks)

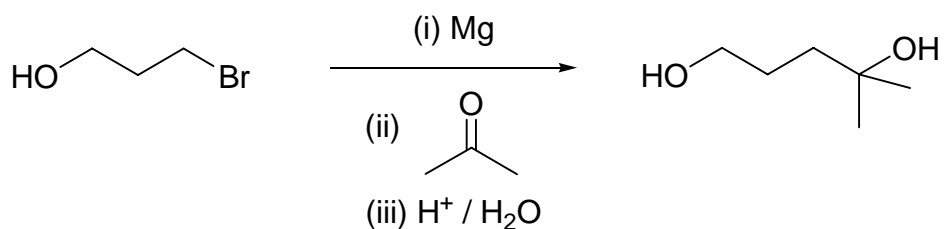
Poly lactide is a biodegradable polymer formed from a renewable resource (corn starch). What is the structure of poly lactide produced by base catalysed ring opening and polymerization of the lactide monomer (shown below) using NaOH as a catalyst? Provide a mechanism for its formation.



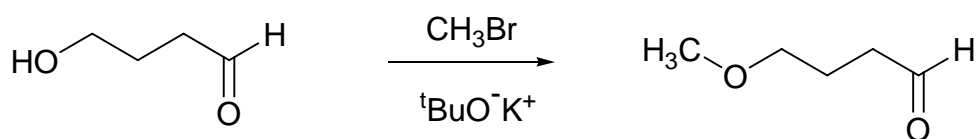
Lactide monomer

4. The reactions of organic molecules are often complicated by the presence of more than one type of functional group. In the proposed synthetic sequences shown below explain what the problems are, and suggest alternative reagents and conditions that could be used overcome them.

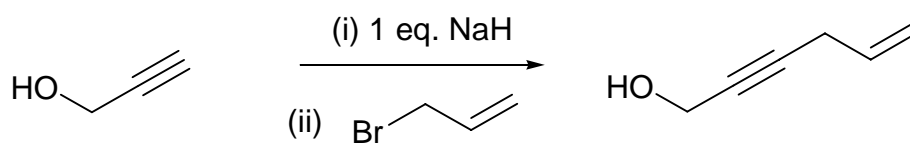
(a) (7 marks)



(b) (7 marks)



(c) (6 marks)



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

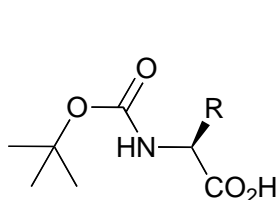
(a) (8 marks)

Deprotection of Boc and Fmoc protected amino acids (shown below), is based upon the selective generation of stabilised reactive intermediates. Give a specific example of the deprotection of:

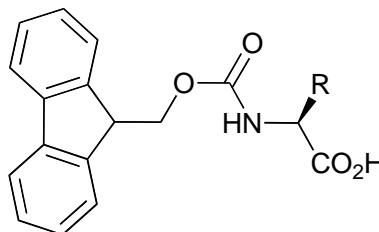
EITHER: (i) a Boc protected amino acid derivative;

OR (ii) an Fmoc protected amino acid derivative.

For your chosen example, provide a detailed mechanism for the deprotection reaction and discuss the nature of the stabilization of the relevant reactive intermediate.



a Boc protected amino acid



an Fmoc protected amino acid

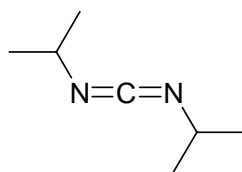
(b) (12 marks)

Different reagents can be used to increase the efficiency of amide formation during peptide synthesis. Give a specific example of the uses of:

(i) A diimide coupling reagent, such as DIC. (6 marks)

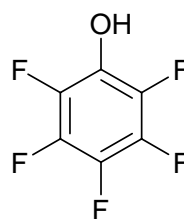
(ii) An activated ester, such as a pentafluorophenol ester. (6 marks)

In both cases you should provide a detailed mechanism for the coupling reaction that forms the new amide bond.



DIC

diisopropylcarbodiimide



pentafluorophenol

END OF PAPER