IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2015, for Internal Students of the Imperial College of Science, Technology and Medicine

This paper is also taken for the relevant examination for the Associateship

ADVANCED CHEMISTRY THEORY IIA

Organic Chemistry

Tuesday 13th January 2015, 14:00-15:30

PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING OF ANY PRIOR CORE COURSE.

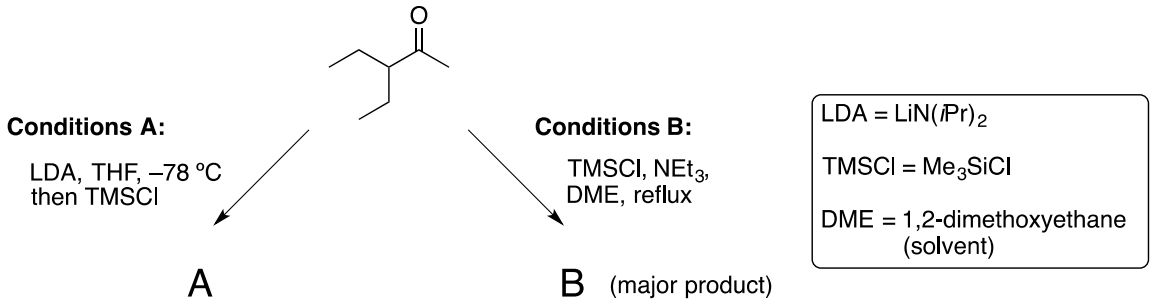
USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

2.O1 – Organic Synthesis Part 1

Q1. Answer **ALL** parts of this question.

a) For the reaction scheme shown below:

i) Provide structures for the lettered products **A** and **B**.
ii) State what type of selectivity is observed.
iii) Under conditions B, explain why compound **B** is the preferred product.

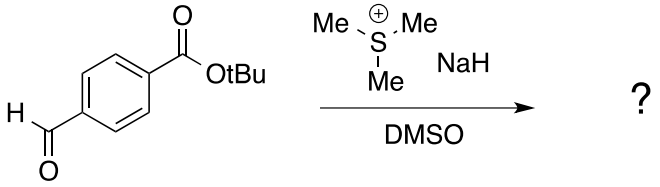


(8 marks; 4 marks for part i; 4 marks for ii/iii)

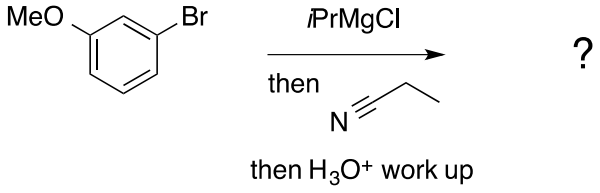
b) Give the organic product for **TWO** out of the transformations i) to iii) below. In each case you can assume an appropriate workup procedure is undertaken to isolate the organic product. Provide a mechanism for the formation of the product and identify any selectivity features involved in the reaction.

(5 marks each)

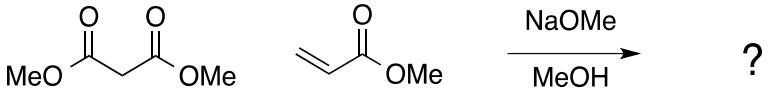
i)



ii)



iii)



QUESTION CONTINUED OVERLEAF

c) Answer **BOTH** parts of this question.

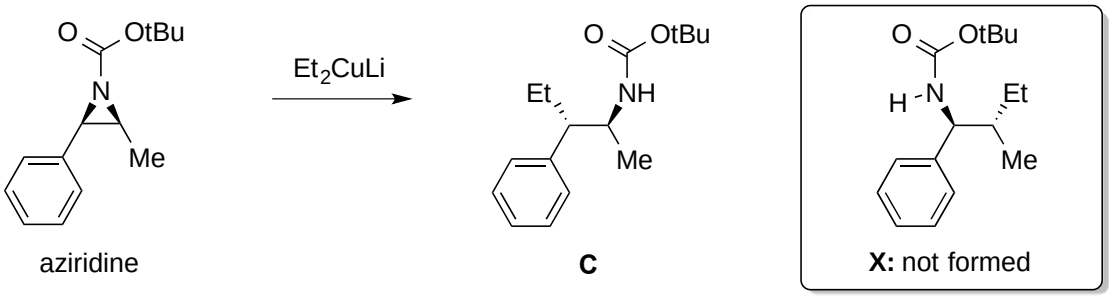
In the reaction scheme shown below, the aziridine starting material was treated with the cuprate reagent shown, to open the strained aziridine ring. The product **C** was formed and not the desired target **X** in the box.

i) Provide a mechanism for formation of **C** and explain the stereochemical and regiochemical outcomes. Explain the selectivity for product **C** over product **X**.

(5 marks)

ii) The reaction was also attempted with EtLi, instead of Et_2CuLi, but the reaction was unsuccessful as the aziridine ring opening did not occur. Suggest a possible explanation as to why a different reaction outcome was observed with EtLi.

(2 marks)



aziridine **C** **X:** not formed

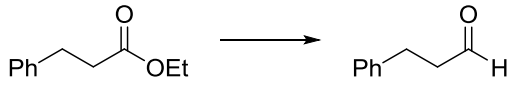
2.O1 – Organic Synthesis Part 1

Q2. Answer **BOTH** parts of this question.

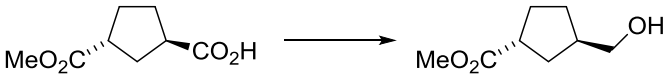
a) Suggest reagents and any specific conditions to carry out **TWO** of the following transformations. In each case, provide a mechanism and explain the key mechanistic features that lead to any selectivity that is required.

(6 marks each)

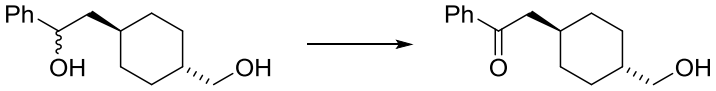
(i)



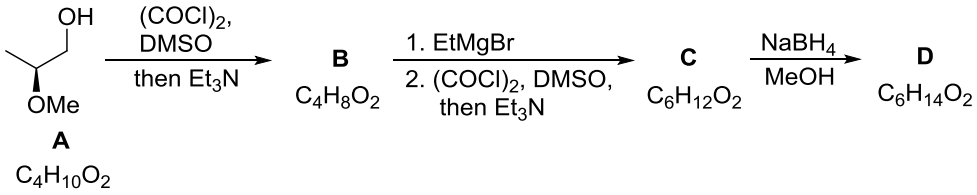
(ii)



(iii)



b) For the synthetic sequence shown below:



i) Suggest a structure for **B** (mechanism not required).

(1 mark)

ii) Suggest a structure for **C** (mechanisms for its formation not required).

(2 marks)

iii) Suggest a structure for **D** (mechanism not required).

(1 mark)

iv) Compound **D** is formed as predominantly one stereoisomer. Predict the configuration of this major stereoisomer, and give a rationale for the stereochemical outcome.

(5 marks)

v) Suggest an alternative reagent or change in reaction conditions that would convert **C** into a different predominant stereoisomer of **D** from that obtained using $NaBH_4$. Give a stereochemical rationale to support your answer.

(4 marks)

Note: You may assume a standard aqueous quench/work-up procedure at each stage of the synthesis. DMSO = dimethylsulfoxide.