**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JANUARY 2012, 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

**Wednesday 11th January 2012, 09:30-11:30**

**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.

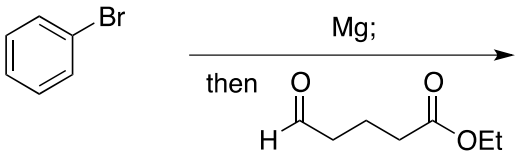
a) Define 'regioselectivity' with reference to a suitable example of a C-C bond forming reaction.

(3 marks)

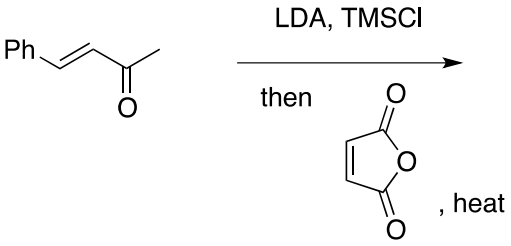
b) Give the organic product of **THREE** out of the **FIVE** transformations i) to v) below after work-up. Provide a mechanism for the formation of each product and identify any selectivity features.

(5 marks each)

i)



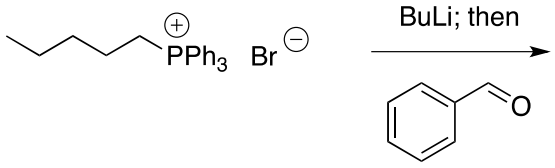

ii)



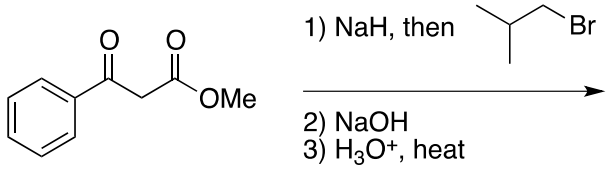

iii)


QUESTION CONTINUED OVERLEAF

iv)




v)




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

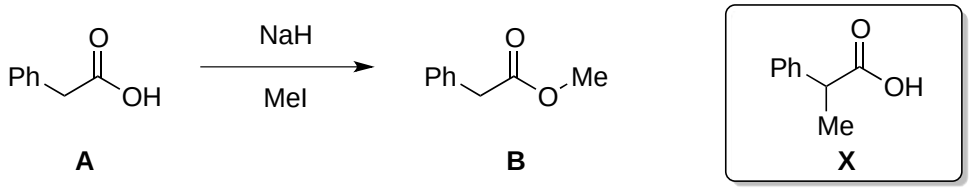
The attempted enolate alkylation of compound **A** gave the product shown **B** and not the desired target **X** in the box.

i) Explain the selectivity for product **B** over product **X** under the conditions shown and provide a mechanism.

(2 marks)

ii) Suggest a way to form desired product **X** starting from **A**, giving reaction conditions and a mechanism.

(5 marks)

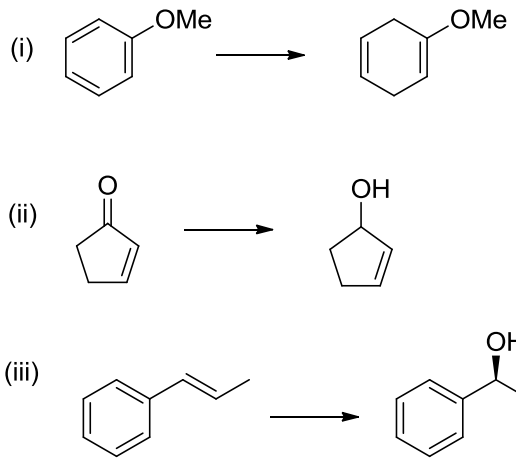



**A** **B** **X**

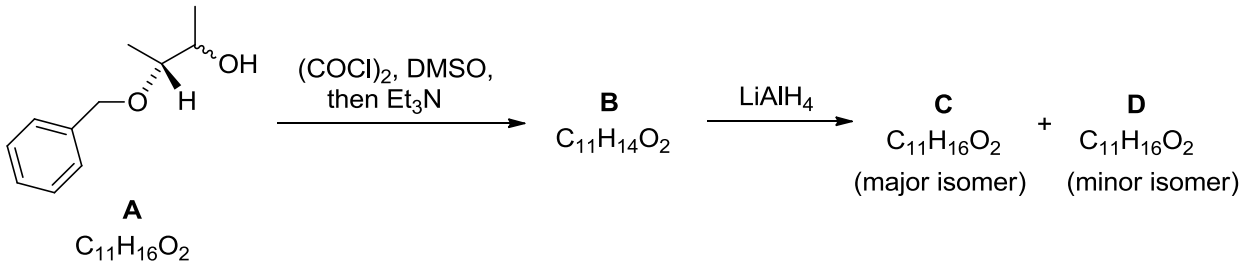
## 2.O1 – Organic Synthesis Part 1

Q2. Answer part a) **AND** part b) of this question.

a) Suggest reagents to carry out **TWO** of the following transformations. In each case, explain the key mechanistic features that lead to any selectivity that is required.
(6 marks each)




b) In the synthetic sequence shown below, stereoisomer mixture **A** was converted into **B** using the reagents shown. Reaction of **B** with $LiAlH_4$ gave isomeric products **C** (major isomer) and **D** (minor isomer).




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

ii) Suggest structures for **C** and **D**. What is the relationship between them?
(3 marks)

QUESTION CONTINUED OVERLEAF

iii) Explain why formation of **C** is preferred over formation of **D**.

(5 marks)

iv) When $Zn(BH_4)_2$ is used instead of $LiAlH_4$ in the reaction with **B**, a mixture of **C** and **D** is again obtained, but in a different ratio. Explain which isomer, **C** or **D**, you would expect to predominate in this product mixture.

(4 marks)

## 2IS.2 – Introduction to NMR and EPR Spectroscopy

Answer part a) and **EITHER** part b) **OR** part c) of this question.

a) Answer **ALL** parts of this question.

i) Give a brief definition of the following terms:

- Gyromagnetic ratio
- Chemical shift standard
- Ring current

(6 marks)

ii) In a $^{1}$H NMR spectrum, recorded on an 800 MHz spectrometer, a doublet is split by 0.00875 ppm and has a chemical shift of 7.7 ppm. What is the value of the splitting in Hz? Identify a type of proton that gives rise to this signal.

(2 marks)

iii) Propose the structure of the molecule, $C_6H_{10}O_2$, which has the following $^{1}$H NMR spectrum

| Chemical Shift (ppm) | Multiplicity | Integration | J Coupling (Hz) |
|---|---|---|---|
| 2.08 | s | 3H | |
| 2.22 | dt | 2H | 6,8 |
| 4.31 | t | 2H | 6 |
| 5.01 | dd | 1H | 2,12 |
| 5.09 | dd | 1H | 2,18 |
| 5.89 | ddt | 1H | 18,12,8 |

and an infra-red stretching peak at 1752 $cm^{-1}$. Give a brief explanation for your proposed structure. (s=singlet, d=doublet, t=triplet, q=quartet)

(5 marks)

iv) For protons, what is the Zeeman effect and how does this relate to sensitivity in NMR?

(2 marks)

v) Explain, with the aid of an example, what is meant by the term diastereotopic protons.

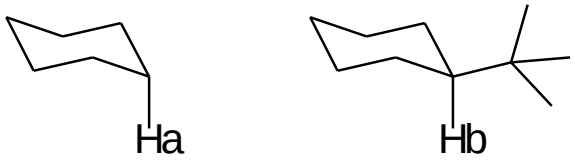
(4 marks)

QUESTION CONTINUED OVERLEAF

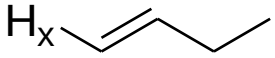
b) Answer **ALL** parts of this question

i) Explain why Ha (below, left) is a single peak at room temperature but why $H_b$ (below, right) is a multiplet at room temperature.

(3 marks)




ii) What is the approximate chemical shift for all protons in the molecule shown below? Draw the splitting pattern for $H_x$. Include all long range couplings for $H_x$ include up to $^4J$.

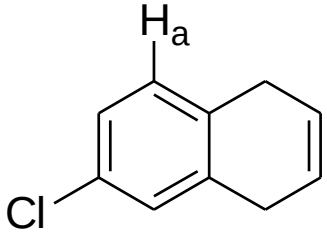



(3 marks)

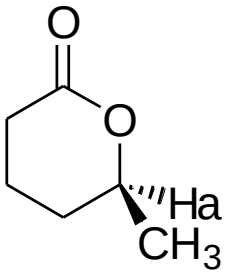
c) Answer **ALL** parts of this question

i) What is the approximate chemical shift (below) and splitting pattern for $H_a$, include up to $^4J$?

(3 marks)




ii) What is the chemical shift (below) and splitting pattern for $H_a$, include up to $^3J$?




(3 marks)