

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JANUARY 2013, 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

Thursday 10th January 2013, 14:00-16:00

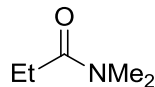
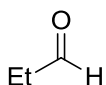
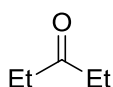
**PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT
THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING
OF ANY PRIOR CORE COURSE.**

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

2.01 – Organic Synthesis Part 1

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

- a) Explain the relative reactivity of the three carbonyl containing compounds below to nucleophiles (e.g. MeMgCl) and place in order of most reactive to least reactive.

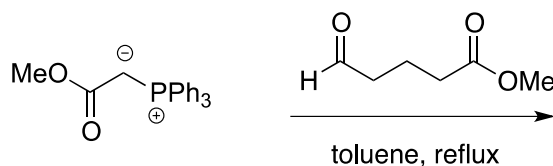


(4 marks)

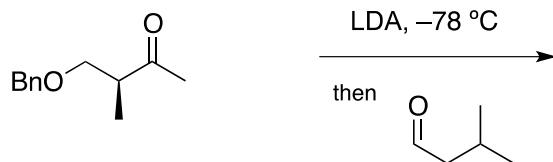
- b) Give the organic product of **THREE** out of the FIVE transformations i) to v) below after work-up. In each case the reaction is worked up with a source of aqueous H^+ to isolate the desired product. Provide a mechanism for the formation of each product and identify any selectivity features.

(5 marks each)

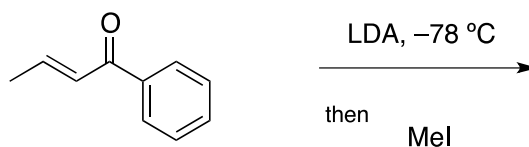
i)



ii)

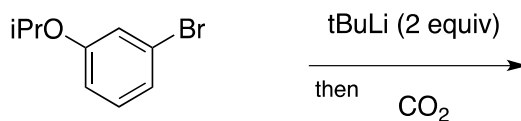


iii)

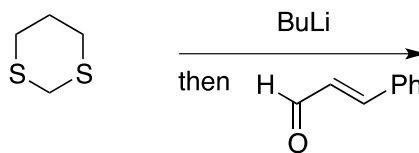


QUESTION CONTINUED OVERLEAF

iv)



v)



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

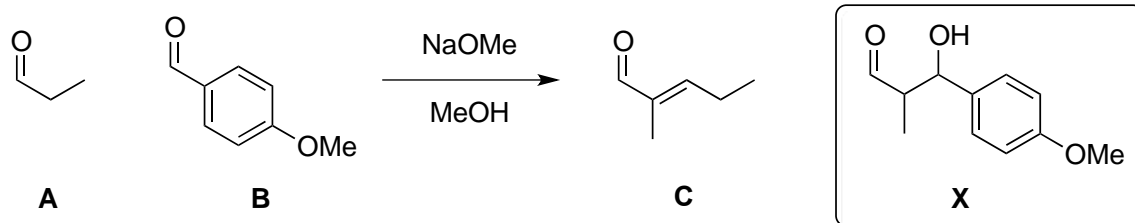
In the reaction scheme shown below, the product shown **C** was formed and not the desired target **X** in the box.

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

(4 marks)

ii) Suggest an approach to form the desired product **X** from **A** and **B**.

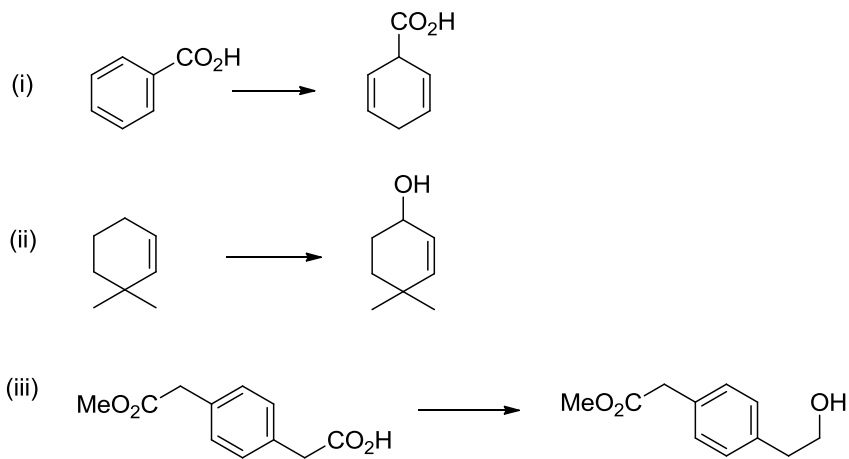
(2 marks)



2.O1 – Organic Synthesis Part 1

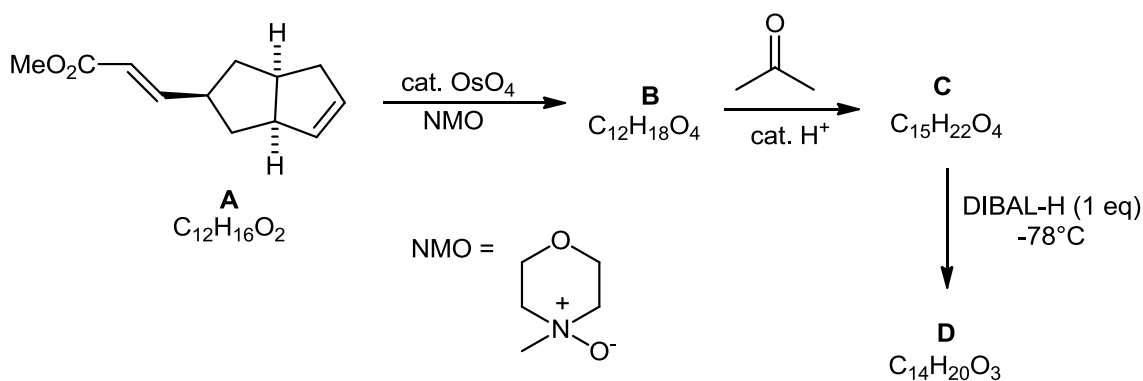
Q2. Answer **BOTH** parts of this question.

- 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) For the synthetic sequence below:

- Suggest a structure for **B**, including stereochemistry. (3 marks)
- Give a mechanism for the formation of **B** from **A** and explain any issues of selectivity. (4 marks)
- Suggest a structure for **C**. (1 mark)
- Suggest a structure for **D**. (1 mark)
- Give a mechanism for the formation of **D** from **C** and explain any issues of selectivity. (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:

- Boltzmann distribution
- Spin angular momentum
- Zeeman interaction

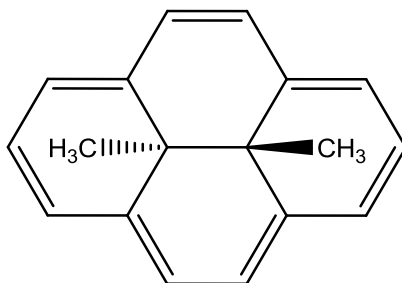
(6 marks)

ii) Explain two ways to increase the sensitivity in NMR.

(2 marks)

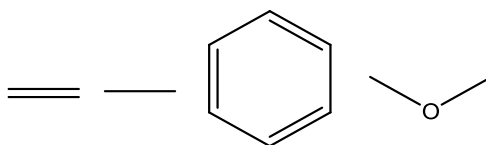
iii) Explain why the ^1H NMR chemical shift of the methyl groups are -4.25 ppm in the structure below.

(1 mark)



iv) For the following molecules rearrange in order of increasing ^1H NMR chemical shift.

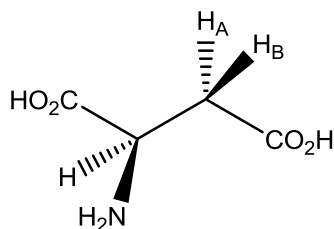
(1 mark)



QUESTION CONTINUED OVERLEAF

- v) Describe the splitting for H_A and H_B . With the aid of a Newman projection give an explanation for these splitting patterns.

(3 marks)



- vi) Propose the structure of the molecule, $C_8H_{12}O_2$, which has the following 1H NMR spectrum

| Chemical Shift (ppm) | Multiplicity | Integration | J Coupling (Hz) |
|----------------------|--------------|-------------|-----------------|
| 0.92 | d | 6H | 7.0 |
| 1.84 | m | 1H | 7.0 |
| 1.91 | t | 1H | 1.5 |
| 2.42 | d | 2H | 1.5 |
| 3.81 | d | 2H | 7.0 |

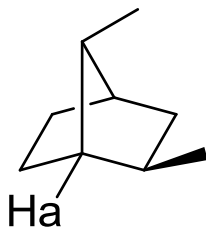
and infra-red stretching peaks at 1742 and 2150 cm^{-1} . Give a brief explanation for your proposed structure. (s=singlet, t=triplet, q=quartet, m= multiplet)

(6 marks)

- b) Answer **BOTH** parts of this question.

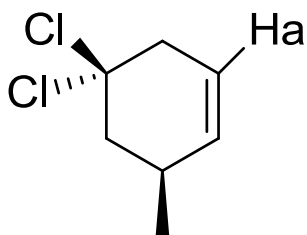
- i) Draw the splitting pattern for H_a . Include all couplings for H_a up to and including 3J .

(3 marks)



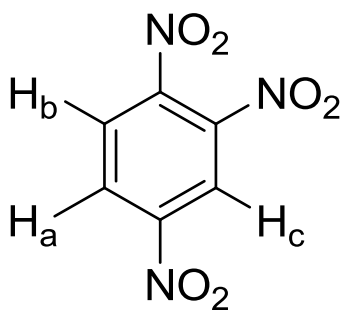
QUESTION CONTINUED OVERELAF

- ii) What is the chemical shift and splitting pattern for H_a up to and including 4J ?
(3 marks)



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

- i) What is the approximate chemical shift and splitting pattern for H_a up to and including 4J ?
(2 marks)



- ii) What is the approximate chemical shift for all the protons in the molecule shown below? Draw the splitting pattern for H_a . Include all couplings for H_a up to and including 3J .
(4 marks)

