IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2010, 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 14th January 2010, 14:00-16:00

Answer ONE question from each attended course

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

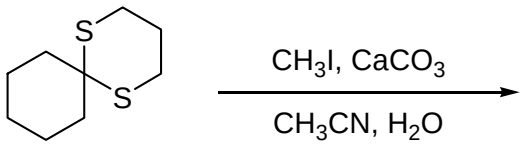
2.O1 – Organic Synthesis Part 1

Q1. Answer part a) **OR** part b)

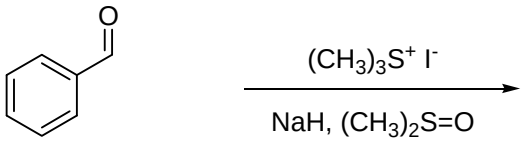
a) Give the products of **ALL** of the transformations i) – v) below, and provide a mechanism for each transformation.

(3 marks for correct product and 2 marks for correct mechanism for each part)

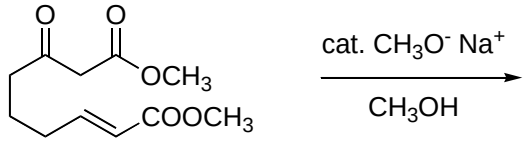
i)



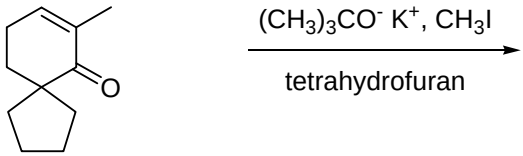
ii)



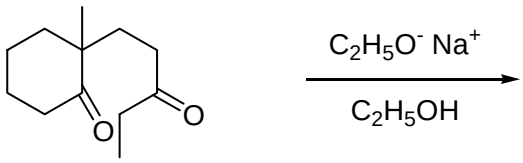
iii)



iv)



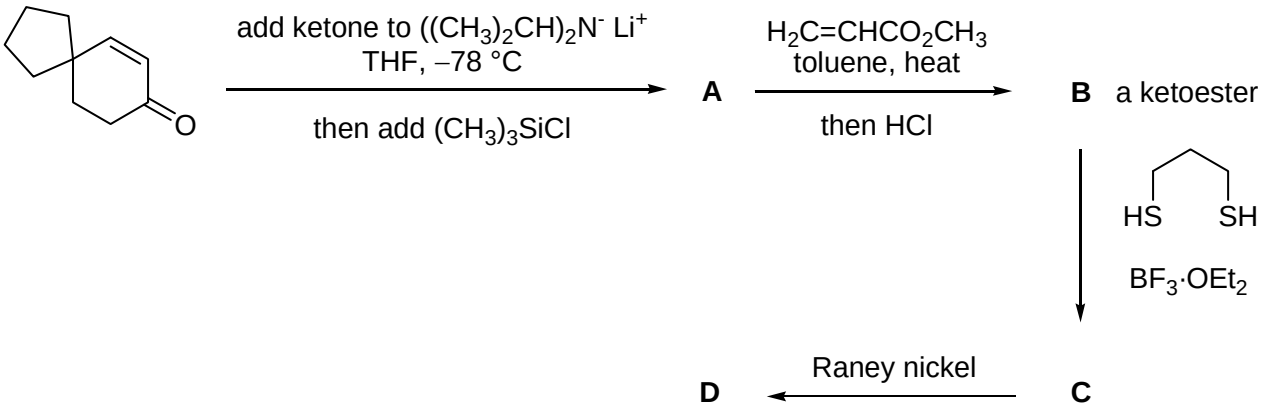
v)



QUESTION CONTINUED OVERLEAF

b) For the synthesis sequence shown below, provide structures for the lettered intermediates **A**–**D**, and draw a mechanism for the conversion of **B** into **C**.

(5 marks for each lettered structure,
5 marks for **B**→**C** mechanism)



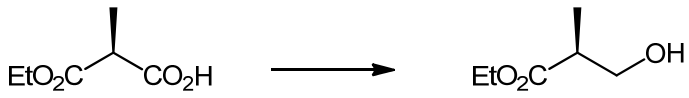
2.O1 – Organic Synthesis (Functional Group Interconversions)

Q2. Answer part a) **AND** part b)

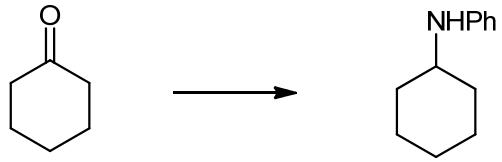
a) Suggest reagents to carry out **TWO** of the following transformations. In each case, give a mechanism and explain any issues of selectivity.

(6 marks each)

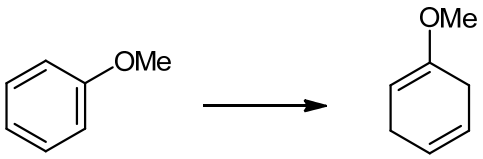
i)



ii)

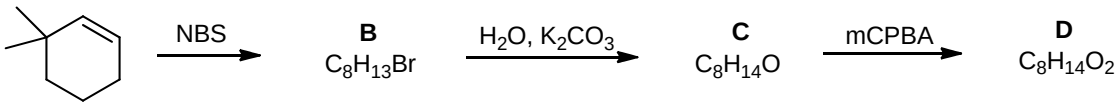


iii)



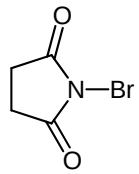
b) In the following synthetic sequence, suggest structures for compounds **B**-**D**, including stereochemistry where appropriate. Give a mechanism for the conversion of **A** to **B** and for the conversion of **C** to **D.**

(13 marks)

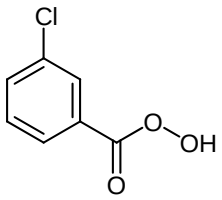


A

NBS = *N*-bromosuccinimide, *i.e.*



mCPBA = *meta*-chloroperbenzoic acid, *i.e.*



2IS.1 – Introduction to NMR Spectroscopy

Q3. Answer part a) and **EITHER** part b) **OR** c)

a) Answer **ALL** parts

i) Give a brief definition of each of the following terms:

Spin angular momentum
Magnetic quantum number
Zeeman transition

(6 marks)

ii) Propose a structure for the molecule, $C_6H_{12}O$, which has the following ^1H NMR spectrum - chemical shift, multiplicity, integration - (2.58, septet, 1H; 2.44, quartet, 2H; 1.06, doublet, 6H; 1.01, triplet, 3H) and an infra-red stretching peak at 1718 cm^{-1}. Give a brief explanation for your proposed structure.

(4 marks)

iii) Give the number of different ^{13}C resonances for the following molecule in Fig. 1.

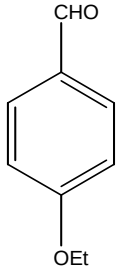


Fig. 1

(2 marks)

iv) Rank in order of increasing chemical shift, in Fig. 2, the ^1H resonances for the following molecules.

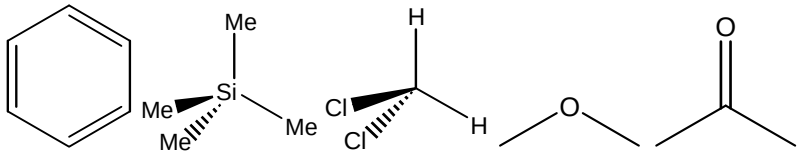


Fig. 2

(1 mark)

v) Explain why there are two different methyl resonances for the compound in Fig. 3.

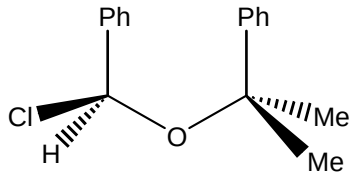


Fig. 3

(2 marks)

QUESTION CONTINUED OVERLEAF

b) Answer **ALL** parts

i) For the molecule shown in Fig. 4 draw the splitting pattern for all protons.

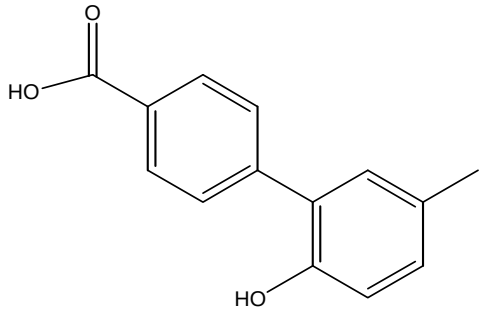


Fig. 4

(3 marks)

ii) For the molecule shown in Fig. 5 draw the splitting pattern for all protons.

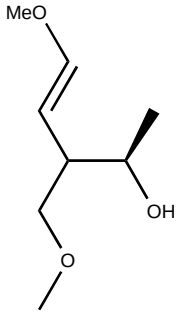


Fig. 5

(4 marks)

iii) Discuss which factors affect the magnitude of chemical shift. Give examples in each case.

(3 marks)

c) Answer **ALL** parts

i) In Fig. 6 what is the approximate chemical shift and splitting pattern for all protons?

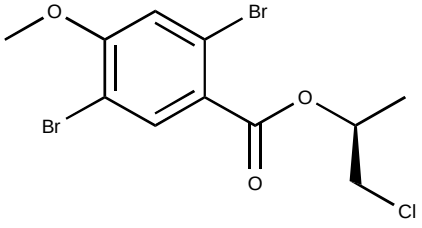
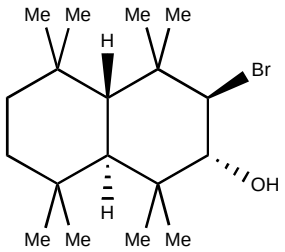


Fig. 6

(4 marks)

QUESTION CONTINUED OVERLEAF

ii) Describe the splitting pattern for all four methine protons in Fig. 7.



(3 marks)

Fig. 7

iii) Discuss the factors that affect the magnitude of spin-spin (J) coupling.

(3 marks)