IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2011, 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

Monday 10th January 2011, 09:30-11:30

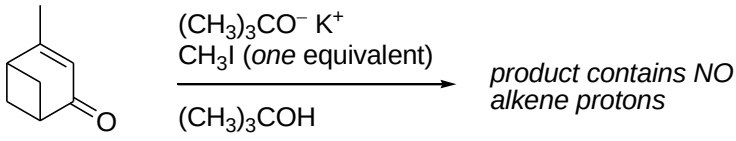
USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

2.O1 – Organic Synthesis Part 1

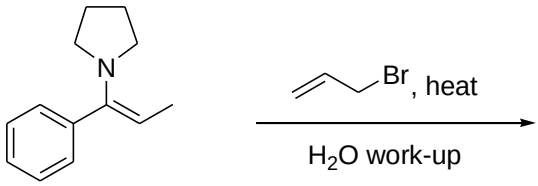
Q1. Answer part a) **OR** part b) of this question.

a) Give the organic products of **ALL** of the transformations i) – v) below, and write a mechanism for the formation of each product.
(3 marks for each correct product + 2 marks for each correct mechanism)

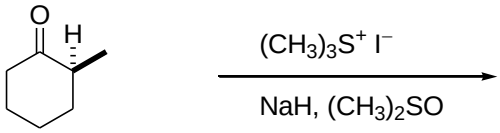
i)



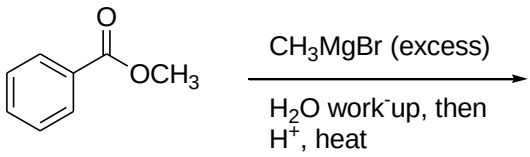
ii)



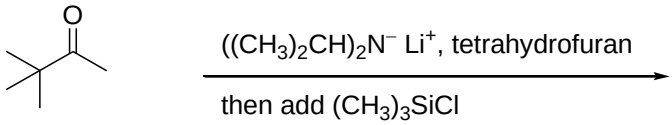
iii)



iv)



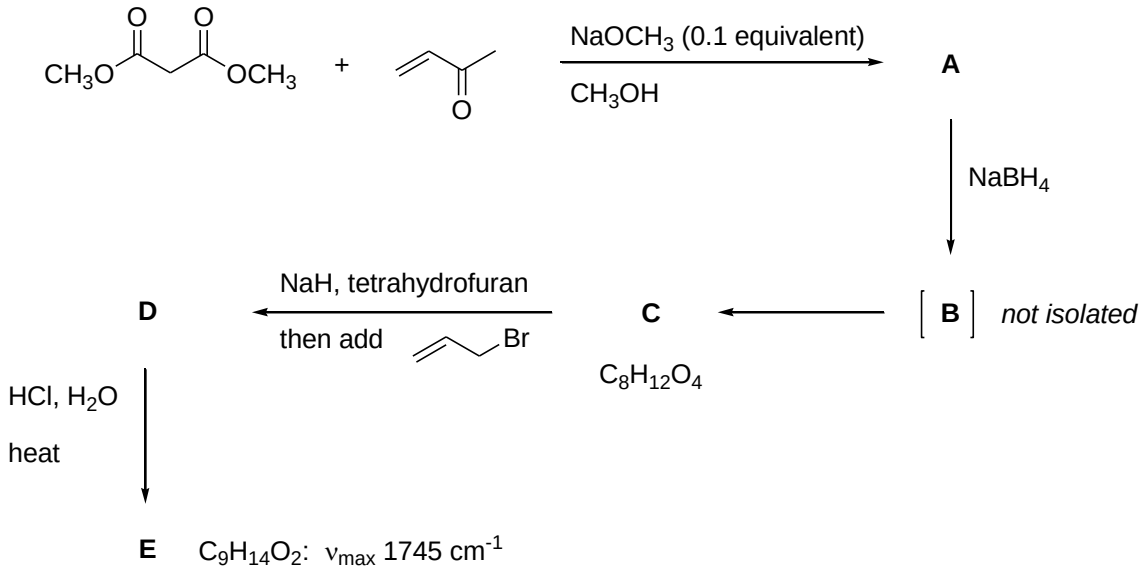
v)



QUESTION CONTINUED OVERLEAF

b) For the synthesis sequence shown below, provide structures for the lettered intermediates **A**, **C**, **D** and **E**. Draw a mechanism for the formation of **A**. Explain why **E** is formed as a mixture of diastereoisomers.

(5 marks each for structures of **A**, **C**, **D** and **E**; 3 marks for mechanism for formation of **A**; 2 marks for explanation of diastereoisomerism)

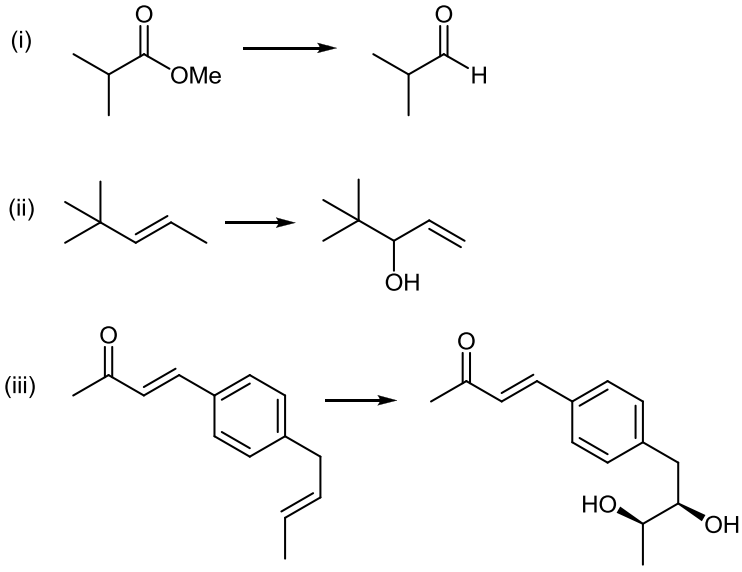


2.O1 – Organic Synthesis Part 1

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

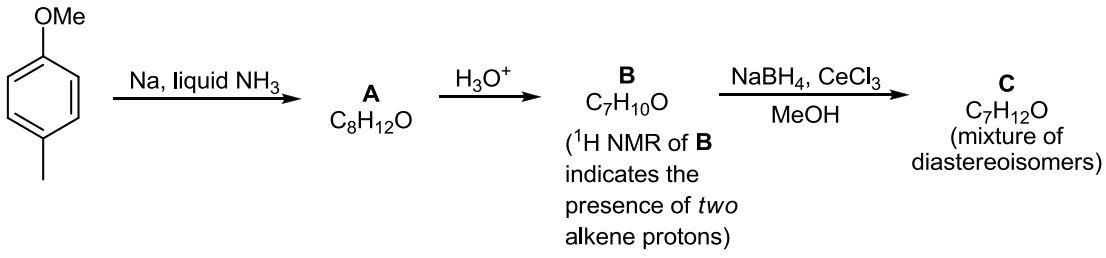
a) Suggest reagents to carry out **TWO** of the following transformations. In each case, give a mechanism and explain any issues of selectivity.

(6 marks each)



b) In the synthetic sequence below, identify compounds **A, B**, and **C**. Give a mechanism for the formation of **A** and for the formation of **B**, explaining any issues of selectivity. In the formation of **C**, briefly explain the mechanistic role of the $CeCl_3$.

(13 marks)



2IS.1 – Introduction to NMR 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:

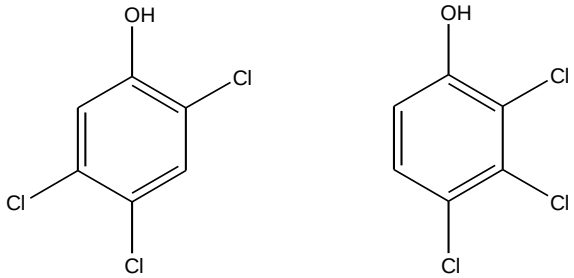
- Spin quantum number
- Gyromagnetic ratio
- Boltzmann distribution

(6 marks)

ii) Propose a structure for the molecule, $C_5H_{10}O$, which has the following ^1H NMR spectrum – (chemical; shift, multiplicity, integration) 0.90, doublet, 6H; 1.90, nonet, 1H; 2.42, doublet, 2H; 9.64, singlet, 1H and an infra-red stretching peak at 1731 cm^{-1}. Give a brief explanation for your proposed structure.

(3 marks)

iii) Explain how ^1H NMR spectroscopy could be used to determine the difference between the two isomers in **A**.



A

(1 mark)

iv) In the ^1H NMR spectrum on a 300 MHz spectrometer, two peaks are split by 0.03 ppm and have a chemical shift of 7.3 ppm. What is the value of the splitting in Hz? Identify the type of proton that gives rise to this signal.

(2 marks)

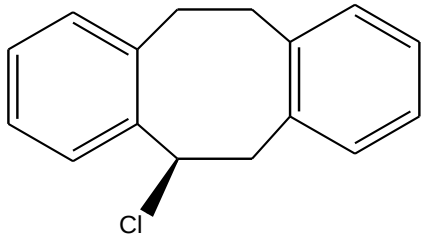
v) What is the Zeeman effect and how does this relate to sensitivity in NMR?

(3 marks)

QUESTION CONTINUED OVERLEAF

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

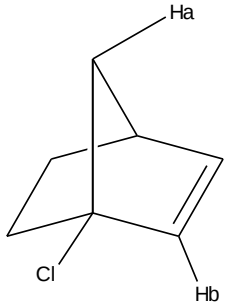
i) What is the approximate chemical shift for all protons for the molecule shown in **B**?



B

(3 marks)

ii) For the molecule shown in **C,** draw the expected splitting pattern for Ha, and state the approximate chemical shift for Hb.



C

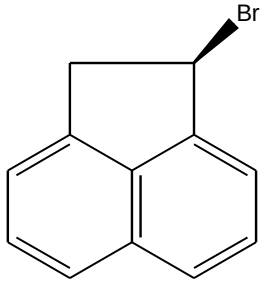
(3 marks)

iii) Discuss which factors affect the magnitude of chemical shift.

(4 marks)

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

i) In the molecule, shown in **D,** what is the approximate chemical shift for all protons?

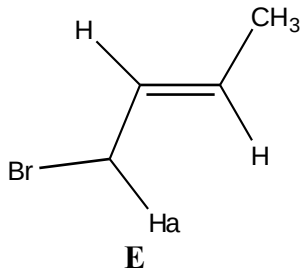


D

(3 marks)

QUESTION CONTINUED OVERLEAF

ii) Describe, for the molecule in **E,** the expected splitting pattern for Ha and estimate its chemical shift.



E

(3 marks)

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

(4 marks)