IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 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

ORGANIC CHEMISTRY I

Monday 20th June 2011, 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.

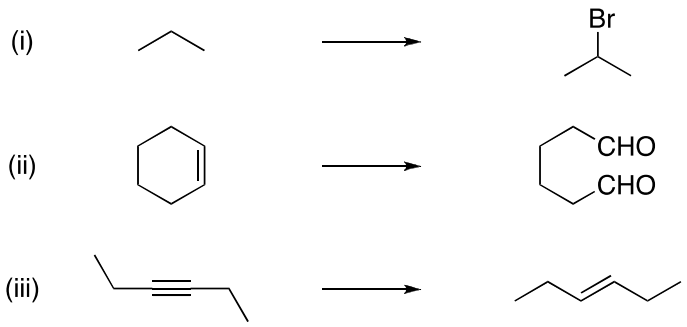
1.O2 – Alkanes, Alkenes, Alkynes

Answer **ALL** parts of this question.

a) Draw a chair conformation of cyclohexane clearly showing axial and equatorial hydrogens. Show which equatorial CH bonds are parallel to which C-C bonds.

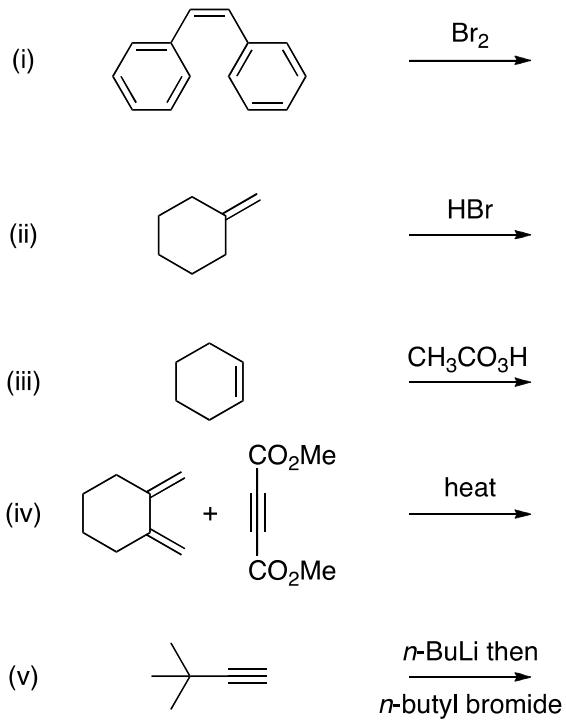
(6 marks)

b) Give reagents for **TWO** of the following reactions.



(2 marks each)

c) Give products for **THREE** of the following transformations. Provide mechanisms and give explanations for any selectivity.



(5 marks each)

1.O3 – Haloalkanes, Alcohols and Amines

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

a) Consider the reaction of 1-chloropentane with sodium cyanide.

i) Draw a curly arrow mechanism showing the formation of the product. Classify the reaction mechanism. Your answer should clearly show any intermediate or transition state.

(3 marks)

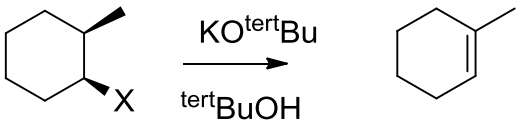
ii) What is the rate law that governs the formation of the product.

(1 mark)

iii) The rate of this reaction is accelerated when a catalytic amount of sodium iodide is added to the reaction. With reference to the mechanism, explain why and draw the energy profile diagrams for the accelerated and unaccelerated reactions.

(7 marks)

b) Consider the following reaction mechanism



1

X = Br

i) Draw the two chair conformers of compound **1**

(4 marks)

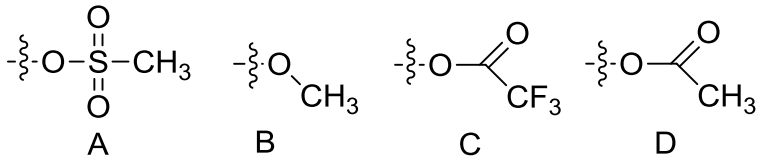
ii) Draw a curly arrow mechanism showing the formation of the product. Classify the reaction mechanism

(2 marks)

QUESTION CONTINUED OVERLEAF

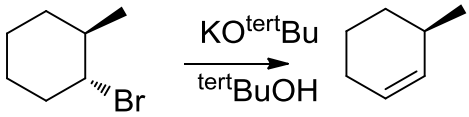
iii) The same elimination reaction was observed for the following four leaving groups (**X = A-D**). Rank them in their order of reactivity, starting with the most reactive.

Explain your reasoning.



(4 marks)

iv) When the trans isomer of **1** is used (compound **2,** shown below) a different alkene is formed as shown below and the rate of formation is much slower.

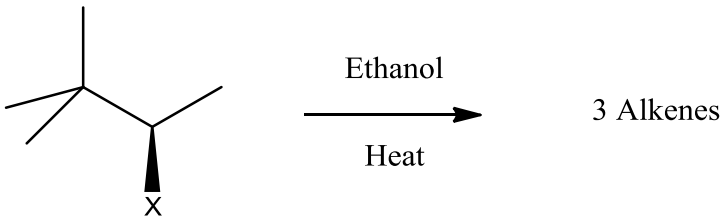


2

Explain this observation. Your answer should include a mechanism and clearly show the transition state or intermediates formed.

(4 marks)

c) Consider the following reaction



3

i) Briefly state why **3** is an optically active compound.

(2 mark)

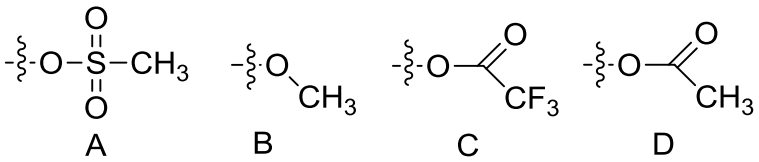
ii) Show the structures of the 3 alkenes formed from the reaction when X is iodine, and draw the mechanism for their formation in each case. Which product will predominate.

(8 marks)

QUESTION CONTINUED OVERLEAF

iii) The same elimination reaction was observed for the following four leaving groups (**X = A-D**). Rank them in their order of reactivity, starting with the most reactive.

Explain your reasoning.



A B C D

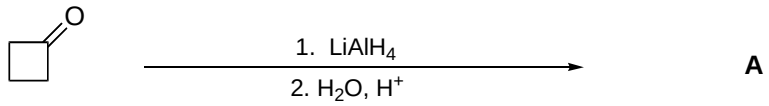
(4 marks)

1.O4 – Carbonyl and Carboxyl Groups

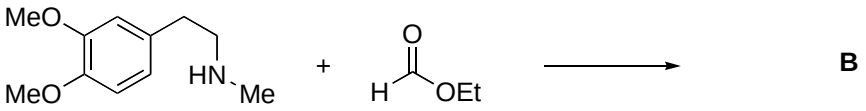
Answer **ALL** parts of this question.

a) Draw the structure of the product obtained for **TWO** out of the following **THREE** reactions.

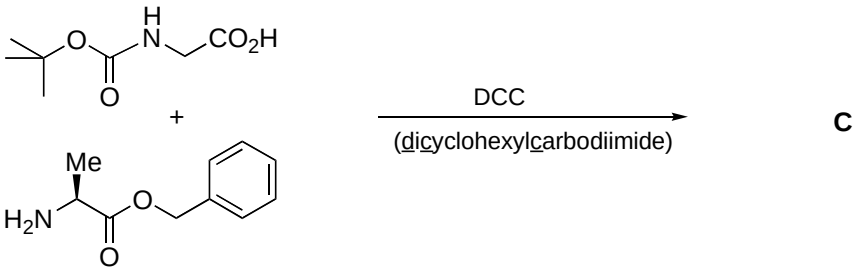
(6 marks)

(i) 

A

(ii) 

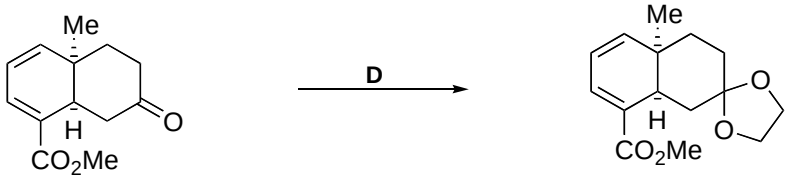
B

(iii) 

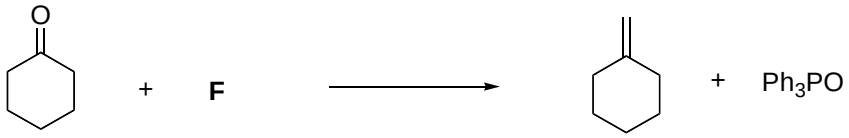
C

b) Provide the missing reagents for **TWO** of the following **THREE** reactions.

(6 marks)

(i) 

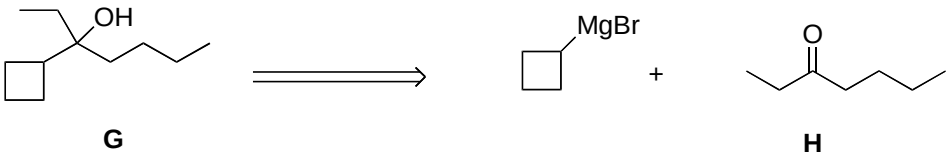
(ii) 

(iii) 

QUESTION CONTINUED OVERLEAF

c) Alcohol **G** shown may be synthesised from cyclobutylmagnesium bromide and 3-heptanone **H** in one step. Suggest two alternative one-step syntheses of **G** based on Grignard reagents and carbonyl compounds. Also, propose a two-step synthesis of **H** in which one of the steps involves a Grignard reagent and a carbonyl compound.

(7 marks)



G **H**

d) Provide a curly arrow mechanism for the transformation shown below.

(6 marks)