IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 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

ORGANIC CHEMISTRY I

Thursday 20th June 2013, 09:30-11:45

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.

Year 1/0613 Turn Over

1.O2 – Alkanes, Alkenes, Alkynes

Answer ALL parts of this question.

a) Draw Newman projections showing the eclipsed and staggered conformations of ethane and comment on their relative energies.

(8 marks)

b) Give suitable reagents for **THREE** of the following transformations.

(2 marks each)

c) For **ONE** of the following transformations provide an annotated curly arrow mechanism and explain any issues of selectivity.

(ii)
$$\xrightarrow{\text{heat}}$$
 $\xrightarrow{\text{OMe}}$ $\xrightarrow{\text{HCI}}$ $\xrightarrow{\text{HCI}}$ $\xrightarrow{\text{CI}_{\text{A}}}$ $\xrightarrow{\text{CH}_3}$ (11 marks)

1.03 - Haloalkanes, Alcohols and Amines

Answer ALL parts of this question.

- a) Discuss the mechanism in which tertiary alkyl halides undergo elimination when heated in protic solvents. Include in your answer:
 - i) The terminology and rate law used to describe the reaction.

(2 marks)

ii) The mechanism of formation of the product including clear drawings of any intermediates or transition states involved paying particular attention to any stereochemical issues.

(3 marks)

iii) The energy profile diagram for the reaction.

(2 marks)

iv) Explain with reasoning how you expect the rate of reaction to change as the structure of the starting halide is changed from tertiary to secondary to primary.

(3 marks)

b) Give the products of **TWO** of the following four reactions.

(4 marks)

(ii)
$$H_3C$$
 \overline{OTs} $KOBu^t$

(iii) OH
$$\frac{SOCl_2, pyr}{}$$

c) Consider the following reaction scheme:

In all answers **clearly show the stereochemistry** of the product.

i) Give the structure of product **A**, and determine its absolute stereochemical descriptor (*R* or *S*).

(3 marks)

ii) Draw the structure of product **B**.

(2 marks)

iii) Identify product **C** and draw a curly arrow mechanism to show its formation.

(2 marks)

- iv) Identify reagent \mathbf{D} , and show the stereochemistry of the final product \mathbf{E} (2 marks)
- v) Suggest alternative reagents and conditions for the transformation of **B** to **E**.

(2 marks)

1.04 - 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)
$$CO_2Me$$
 LiAlH₄ A

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

D

(6 marks)

(iii)
$$CO_2Me$$
 CO_2Me

QUESTION CONTINUED OVERLEAF

c) Compound **G** was recently converted into compound **H** in three steps that used all six of the reagents shown in the box below. Write down the reagents that were used in each of the three steps 1, 2 and 3.

(6 marks)

d) Provide a curly arrow mechanism for the reaction shown below, which is promoted by the base potassium *tert*-butoxide and proceeds *via* a five- membered cyclic ester.

(7 marks)