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 IIB

Monday 20th June 2011, 14:00-16:00

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

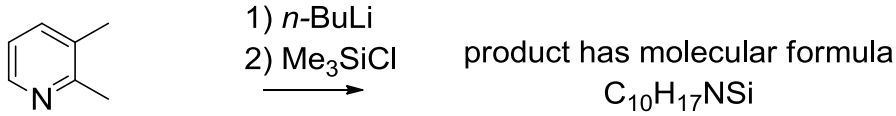
USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

2.O2 – Heteroaromatics

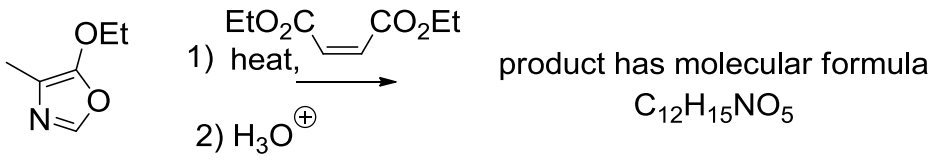
Answer **BOTH** part a) **AND** part b) of this question.

a) Predict the (major) products of **THREE** of the following reactions. Draw a mechanism for your selected transformations and explain any selectivity.

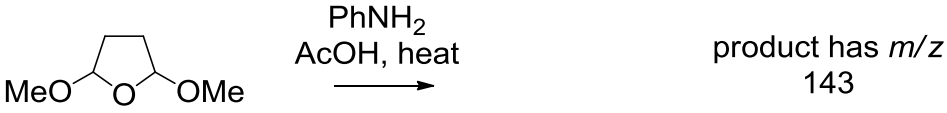
i)



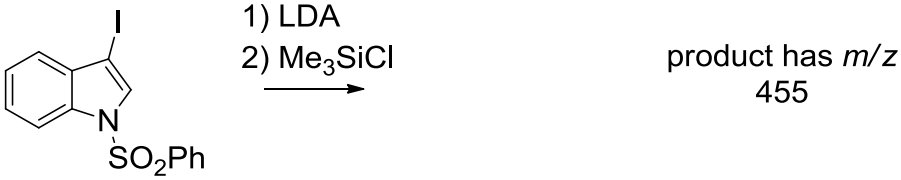
ii)



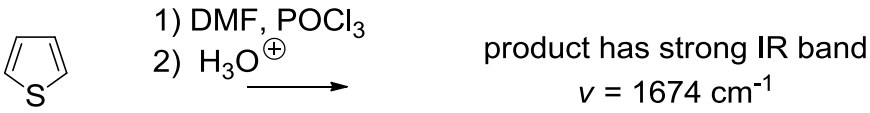
iii)



iv)



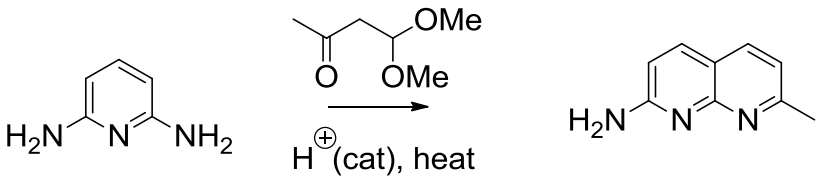
v)



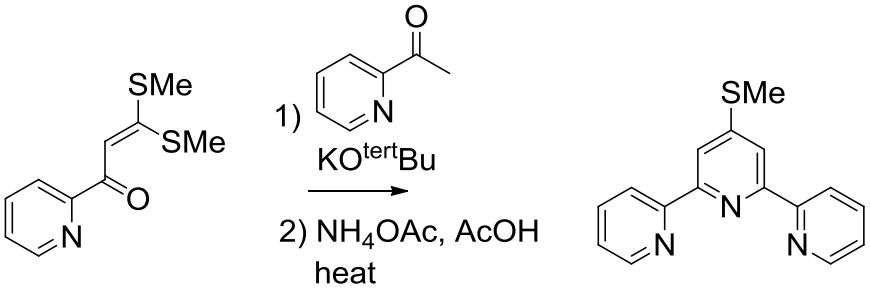
(5 marks each)

b) Give a mechanism for **ONE** of the following transformations:

i)



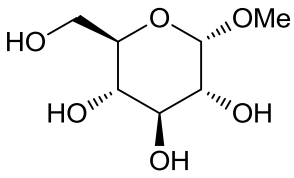
ii)



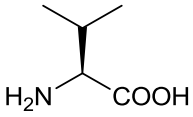
(10 marks)

2.O3 – Biological Chemistry

The following information is provided for reference:



α-methyl-D-glucoside.



L-Valine (Val)

Answer any **TWO** of the three parts a), b) and c) of this question.

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

i) Identify each of the protecting groups in molecule **A** (below).

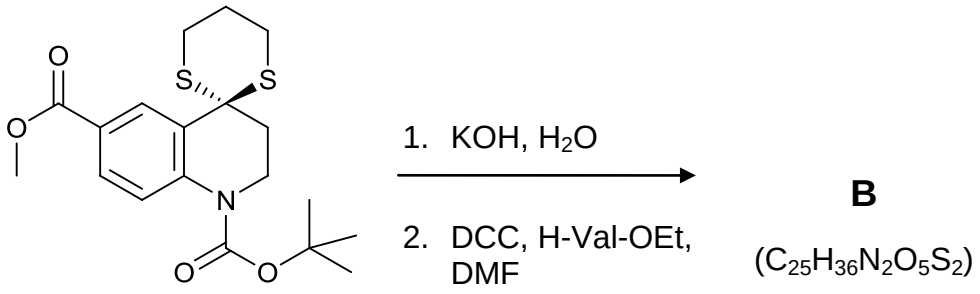
(3.5 marks)

ii) Draw the reaction product **B**. Note that DCC is dicyclohexylcarbodiimide, (C_6H_{11})-N=C=N-(C_6H_{11}).

(3 marks)

iii) Draw a mechanism for step 2.

(6 marks)



A

B

$(C_{25}H_{36}N_2O_5S_2)$

b) Propose a plausible synthesis of 4-O-methyl α-methyl-D-glucoside, starting from α-methyl-D-glucoside.

(12.5 marks)

QUESTION CONTINUED OVERLEAF

c) Answer **ALL** the following parts:

i) Give the structure of molecules **C** and **D** (below).

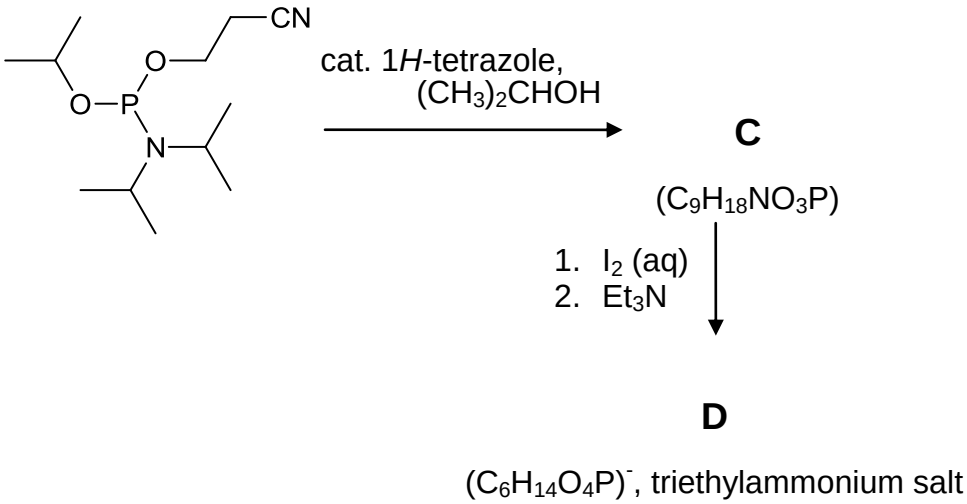
(5 marks)

ii) Provide a mechanism for the formation of **C**.

(5 marks)

iii) Provide a mechanism for the deprotection step using Et_3N.

(2.5 marks)



2.O4 and 2.O5 – Pericyclic Reactions and Conformational Analysis

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

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

i) Give **one** example of a **pericyclic ene reaction**, showing clearly the arrow pushing for your selected example, indicating whether your arrows correspond to a 4n+2 rule or a 4n electron rule for a pericyclic step and if your reaction is promoted by heat or by light.

(5 marks)

ii) How many potentially distinguishable conformations of cyclohexane are there?

(2 marks)

Describe any one of the transition states that connect any pair of these conformations, indicating **one** reason why it might be a maximum rather than a minimum in energy.

(3 marks)

b) In the reaction sequence shown below[1] which is promoted by heat, identify any **one** pericyclic reaction that might be occurring for any of the steps C to D, D to E or E to F

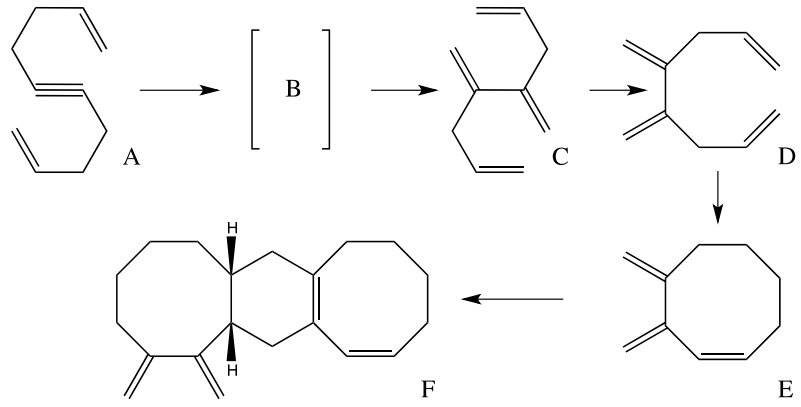
(3 marks)

Indicate the mechanism of your selected step with appropriate arrow pushing, apply the selection rule for your mechanism as appropriate for a thermal reaction and any nomenclature associated with your selected step.

(7 marks)

Suggest a structure for the intermediate B, indicating your reasoning.

(5 marks)



QUESTION CONTINUED OVERLEAF

[1] DOI: http://dx.doi.org/10.1016/S0040-4039(00)98289-3

c) For the molecule below, sketch **three** limiting conformations using a Newman projection along the central C-C bond.

(3 marks)

For TWO of these conformations, indicate the nature (*e.g.* C-X/Y, X/Y=H,F,Si) of the bonds involved in antiperiplanar alignment with respect to the C-C backbone.

(4 marks)

With reference to the orbital diagram below, indicate which if any of the $\sigma_{C\text{-}X}/\sigma^*_{C\text{-}Y}$ interaction energies E2 for these antiperiplanar alignments in your two chosen conformations are likely to be larger than the $\sigma_{C\text{-}H}/\sigma^*_{C\text{-}H}$ value in ethane, giving your reasons.

(4 marks)

Suggest which of your two chosen conformations is likely to be the lower in energy, giving your reasons.

(4 marks)