

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JUNE 2014, 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 16th June 2014, 14:00-16:15

**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 **ALL** parts of this question.

a) Explain **TWO** of the following. Draw curly arrow mechanisms to illustrate your answers.

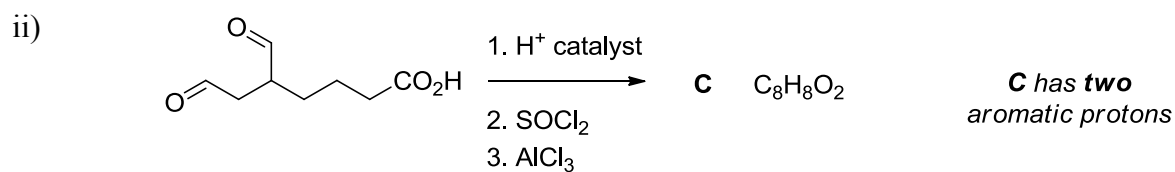
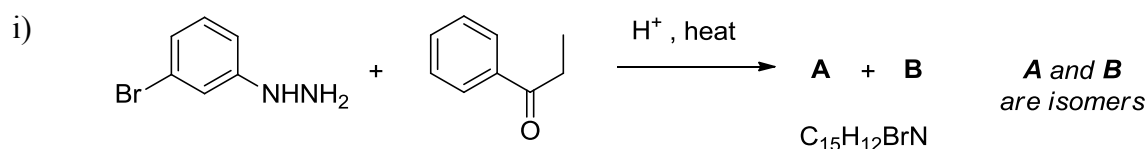
i) The conjugate acid of pyrrole has a much lower pK_a value than the conjugate acid of pyridine.

ii) Diels–Alder reactions of furan with electron-deficient alkenes are readily reversible.

iii) Dimethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate is a good reducing agent.

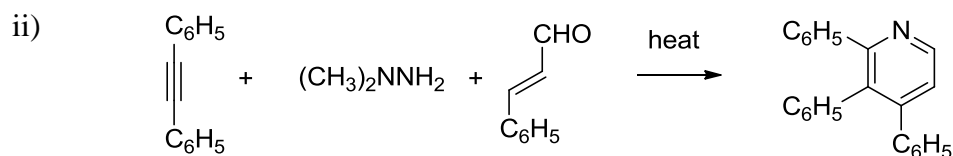
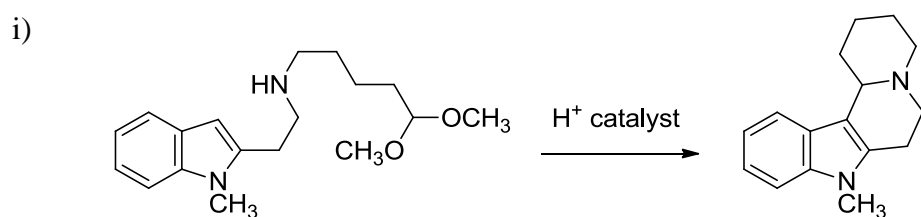
(5 marks each)

b) Identify the product(s) of **ONE** of the following reactions, and give a mechanism for the formation of the product(s).



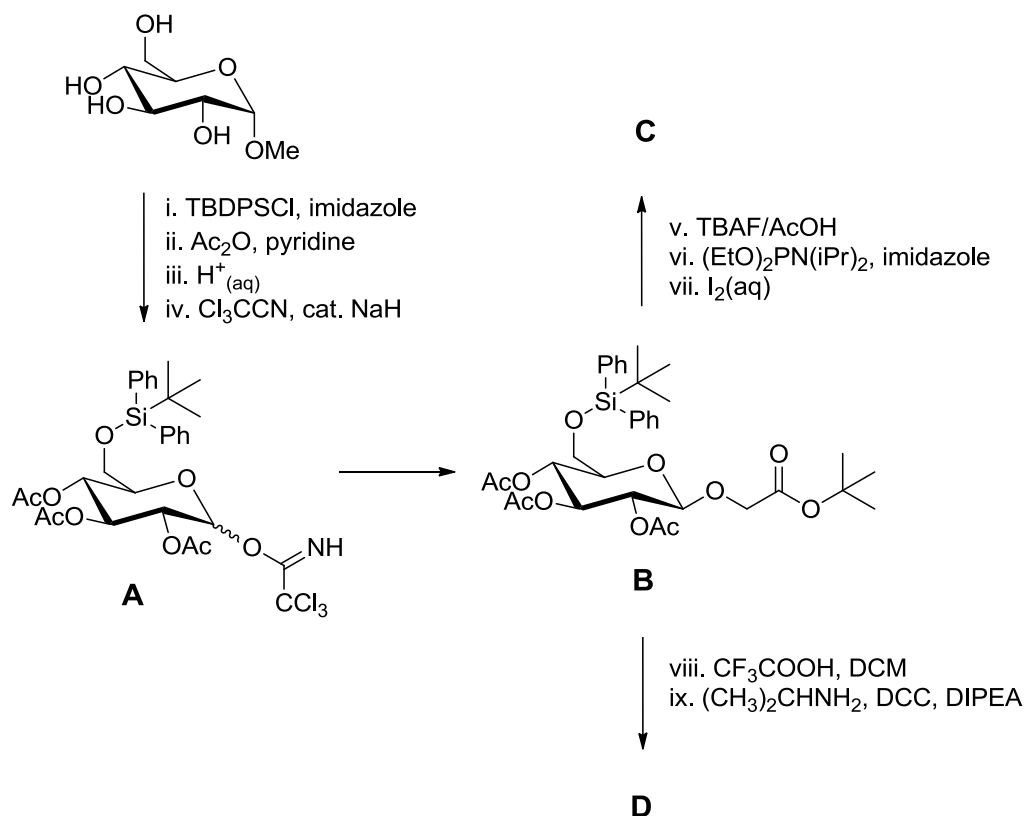
(5 marks)

c) For **EITHER** i) **OR** ii) below, give a detailed mechanism for the formation of the product shown.



(10 marks)

2.O3 – Bio-organic Chemistry



Notes: DCC = *N,N'*-dicyclohexylcarbodiimide; DIPEA = *N,N*-diisopropylethylamine; TBAF = $(^t\text{Bu})_4\text{NF} \cdot (\text{H}_2\text{O})_3$; TBDPS = *tert*-butyldiphenylsilyl; DCM = dichloromethane.

Answer **THREE** of the following parts (a)-(d) of this question. 8 marks for each part, plus 1 bonus mark.

- Identify the product formed in each step leading to formation of **A**, and provide a mechanism for step (iv).
- Provide reagents and a mechanism for the conversion of **A** to **B**, providing rationalisation for any observed selectivity.
- Identify the product formed in each step leading to formation of **C**, and provide a mechanism for step (vi).
- Identify the product formed in each step leading to formation of **D**, and provide a mechanism for step (ix).

2.O4 & 2.O5 – Pericyclic Reactions/Conformational Analysis

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

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

- i) Show one example of a sigmatropic reaction involving a hydrogen atom and occurring with only suprafacial components. Indicate in your answer the numbering and nomenclature, and how the pericyclic selection rules might be applied to your example.

(4 marks)

- ii) Show one example each of molecules where cyclic and acyclic atropisomerism is observed. In your answer indicate the bond or bonds about which any conformational rotation may be occurring

(2.5 marks for each example)

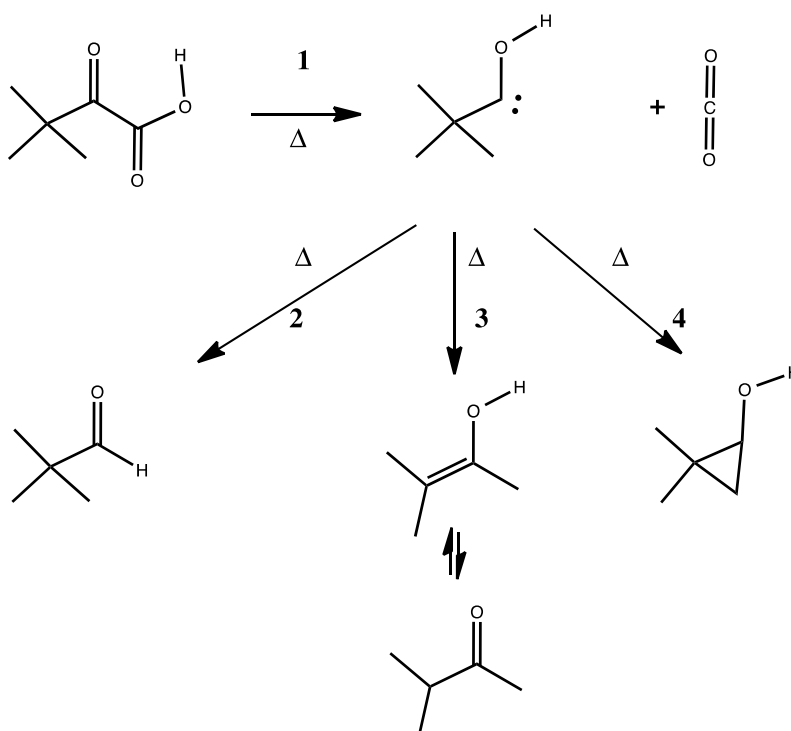
Discuss also how the relationship of atropisomerism to conformational and configurational isomerism might be defined.

(2 marks)

b) The following sequence of reactions has recently been reported.¹ For **each** of the four numbered reactions, answer the following **two** questions for each. (14 marks)

- i) Identify whether the numbered step is a pericyclic reaction and if it is classify the reaction into one of four major categories of pericyclics.

- ii) Suggest an arrow-pushing mechanism and identify how many electrons are involved in the mechanism. If it is pericyclic, discuss which of the selection rules it might be expected to follow and any stereochemical implications that might be inferred.

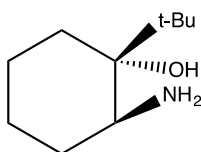


QUESTION CONTINUED OVERLEAF

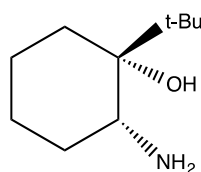
¹ DOI: 10.1039/c2sc21555a For further analysis, see DOI: [10042/a3uyv](https://doi.org/10.1002/a3uyv)

c) Answer the following **four** questions.

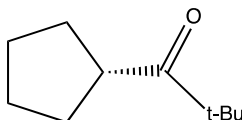
- i) Draw the **two** possible chair conformations for each of the reactants **1** and **2** in a manner that clearly indicates whether the three substituents in each conformation are axial or equatorial.



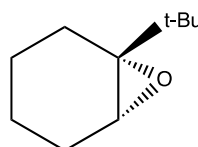
1



2



3



4

(1 mark per conformation)

- ii) Suggest for both **1** and **2** which conformation is likely to be present in the greater concentration in solution, giving your reasons.

(1 mark each)

- iii) When each of the compounds **1** and **2** are treated with nitrous acid (HNO_2), one of them gives product **3** and the other gives product **4**. Clearly indicate which product arises from which reactant, giving your reasons. Show which conformation of **1** or **2** is involved in the mechanism (no arrow-pushing mechanism for the reaction between nitrous acid and **1** or **2** is required)

(2.5 marks each)

- iv) Using just the orbital overlap/bond orientation term in the theory of conformational analysis, suggest one contributing reason why the preferred conformation of vicinal (1,2)-difluoroalkanes tends to be *gauche*, whereas that of vicinal-dibromoalkanes tends to be *anti* (Figure below)

(3 marks)

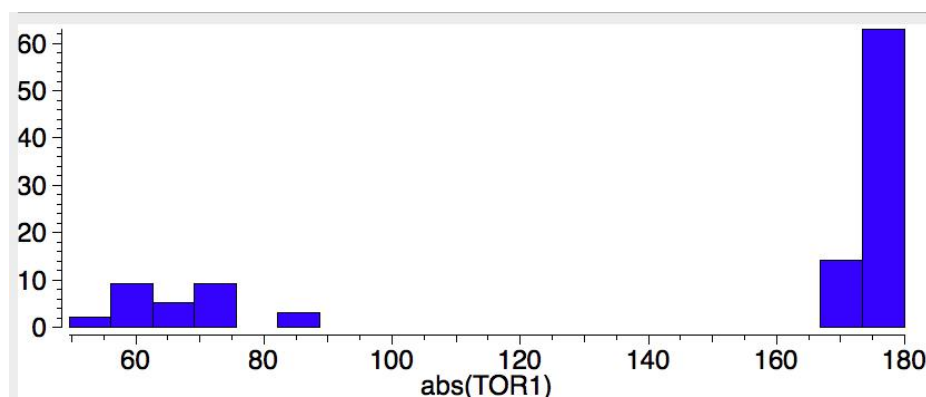


Figure: The torsional distribution about the central C-C single bond in acyclic vicinal dibromoalkanes as obtained from the Cambridge crystal structure database. The left axis shows the number of entries for each torsional band.