

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JANUARY 2010, 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 IIIA

Organic Chemistry

Friday 15th January 2010, 14:00-17:00

Answer ONE question from each attended course

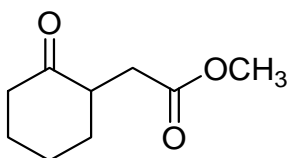
**USE A SEPARATE ANSWER BOOK FOR EACH QUESTION.
WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER
BOOK.**

3.O11 – Synthesis Part 2

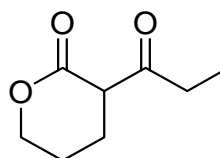
Answer **ALL** parts a), b) and c).

- a) For the dicarbonyl compounds **A** and **B** shown below, show a C-C bond disconnection. Identify the synthons implied by your disconnection, and write down the synthetic equivalents of the synthons.

(5 marks each)



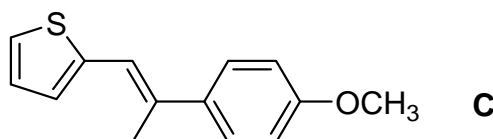
A



B

- b) Suggest a **stereospecific** synthesis of the alkene **C** shown below. Your synthesis must involve the use of transition metal catalysis, and you may invoke the use of any reasonable organic starting materials and organic/inorganic reagents.

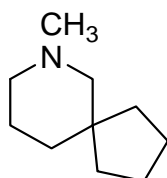
(5 marks)



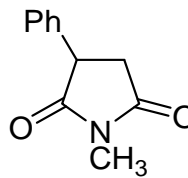
C

- c) Devise a synthesis of **EITHER** compound **D** OR compound **E** shown below. Show clearly your retrosynthetic analysis, identifying synthons and synthetic equivalents. Propose reagents for your forward synthesis.

(10 marks)



D

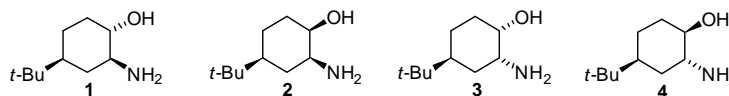


E

3.O12 – An Introduction to Reaction Stereoelectronics

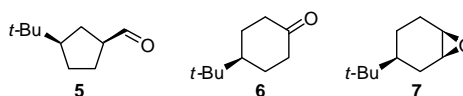
Answer part (a) and **EITHER** part (b) **OR** part (c) of this question.

- (a) (i) Draw each of the four diastereoisomeric aminocyclohexanols **1-4** (shown below) in their lowest energy conformation and explain your reasoning.



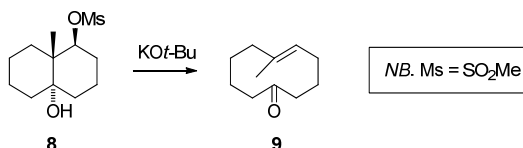
(4 marks)

- (ii) Treatment of each of **1, 2, 3** and **4** with NaNO_2/HCl (which induces diazonium salt formation) results in the selective formation of a single major product in each case. Predict which product (**5, 6**, or **7**, shown below) is formed in each reaction and explain with the aid of orbital diagrams the reasons for the selectivity in each case.



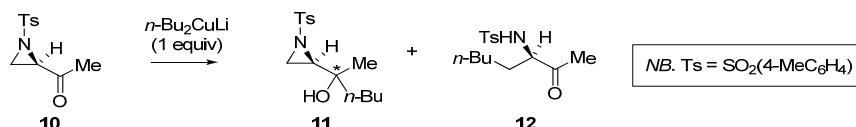
(11 marks)

- (b) Draw a mechanism for the base-induced Grob fragmentation **8** \rightarrow **9**. Include in your answer an annotated 3D structure of the alkoxide intermediate showing the orbitals involved in the reaction and hence account for the product stereochemistry.



(10 marks)

- (c) Consider the following reaction which involves the addition of a *n*-butyl cuprate reagent to aziridinyl ketone **10**.



- (i) Assuming that the reaction proceeds with Felkin-Anh control, indicate the relative stereochemistry of the major diastereoisomer of the *tert*-alcohol product **11**. Show your working.

(6 marks)

- (ii) Draw a mechanism for the formation of by-product **12** and account for this mode of reactivity by reference to the structure and bonding in aziridines.

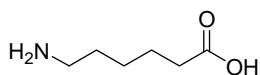
(4 marks)

3.O3 – Polymers: The Essential Guide

Answer parts (a) **AND** (b).

a) Provide synthetic schemes for the linear homopolymers (include the mechanism of the propagation step) you can form using monomers **A-C** and identify a current application in which each of the polymers is being used.

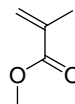
(9 marks)



A



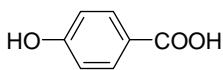
B



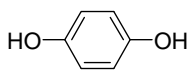
C

b) Answer any **FOUR** of the questions (i) – (vi)

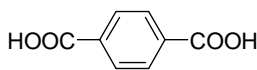
The synthesis of aromatic poly(ester)s is a polycondensation reaction.



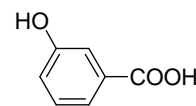
D



E



F



G

- Explain how you can control the number average molecular weight in a polycondensation reaction. Choose from the list of monomers **D-G** to illustrate your answer.
(4 marks)
- Give reasons why it is not possible to control the molecular weight distribution in a homogeneous polycondensation reaction.
(4 marks)
- Design a synthesis in which you obtain an aromatic poly(ester) with hydroxyl groups as polymer chain end groups.
(4 marks)
- Explain how you could decrease the glass transition temperature of an aromatic poly(ester) derived from monomer **D**.
(4 marks)
- The synthesis of aromatic poly(ester) dendrimers can also involve condensation reaction steps. In such processes, dendrimers are obtained with a precise molecular weight (monodisperse), whereas non-dendritic aromatic poly(ester)s made from monomers **D-G** are always obtained with a molecular weight distribution (polydisperse). Explain.
(4 marks)
- Suggest monomer(s) and draw the structure for a hyperbranched aromatic poly(ester). (Hint: You may want to consider derivatives of monomers D-G).
(4 marks)

3.04 – Introduction to Physical Organic Chemistry

Answer part a) and **EITHER** part b) or part c)

a) Answer either “true” or “false” for **ALL** of the following statements. Give a BRIEF explanation of your answer in each case.

- i) Measuring the pK_a values of an acid and a base in water allows prediction of their values in other solvents.
(2 marks)
- ii) Linear free energy relationships generally hold for reactions of *meta* and *para* substituted aromatic compounds but not for *ortho* substituted compounds.
(2 marks)
- iii) The Hammond postulate provides a theoretically proven relationship between thermodynamics and kinetics.
(2 marks)
- iv) Most chiral molecules crystallize from a racemic solution as separate D and L crystals, known as conglomerates.
(2 marks)
- v) Observation of a concave-upwards shape to a Hammett plot indicates that the reaction goes through a change in mechanism.
(2 marks)
- vi) Dimroth’s principle can be used to help separate diastereomeric molecules.
(2 marks)
- vii) Reaction intermediates are represented as maxima on an energy diagram while transition states are represented as minima.
(2 marks)
- viii) The Bronsted catalysis law allows calculation of pK_a values for very weak acids or bases where a direct measurement is not possible.
(2 marks)

QUESTION CONTINUED OVERLEAF

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

- i) The aldol reaction between acetone and aromatic aldehydes catalyzed by amino acids proceeds ten times faster for *p*-nitrobenzaldehyde than for *p*-methoxybenzaldehyde. Sketch a Hammett plot based on this information and discuss what this tells us about the transition state.

(4 marks)

- ii) A proposed mechanism for this reaction is formation of an enamine via nucleophilic attack of the amino acid on the acetone carbonyl, followed by attack of the enamine on the aldehyde carbonyl. What would the Hammett plot look like if the rate-limiting step switched from enamine attack in the case of *p*-methoxybenzaldehyde to the enamine formation for *p*-nitrobenzaldehyde.

(5 marks)

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

- i) What is the eutectic composition of a ternary system of D and L enantiomers in water for the case of a molecule that forms a racemic compound and for the case of a molecule that forms a conglomerate?

(5 marks)

- ii) From which type of system may solid phase homochirality be induced? Why can't solid phase homochirality be induced in the other type of system?

(4 marks)