IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 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

ADVANCED CHEMISTRY THEORY IIIA

Organic Chemistry

Monday 10th January 2011, 09:30-12:30

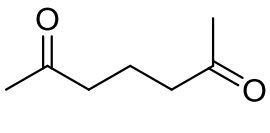
USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

3.O11 – Synthesis Part 2

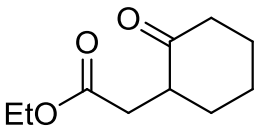
Answer **ALL** parts of this question.

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

(2 x 5 marks)



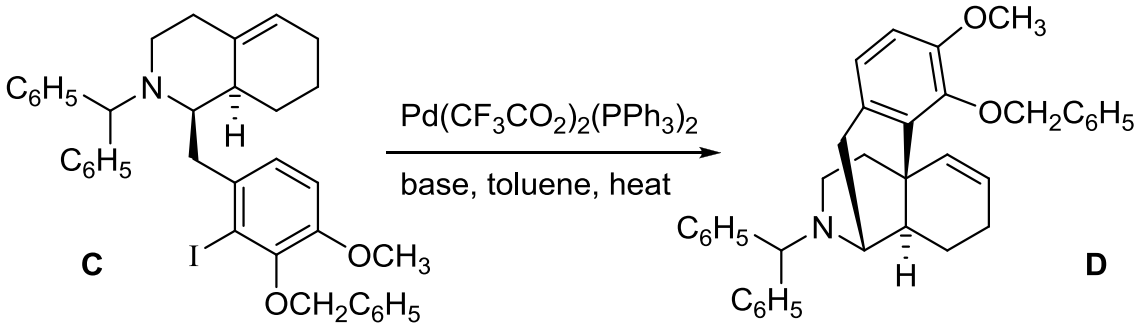
A



B

b) Give a mechanism for the intramolecular Heck reaction **C** to **D** shown below, explaining carefully the reasons for the position of the alkene double bond in the product **D**.

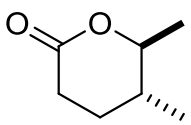
(5 marks)



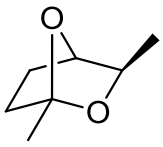
C **D**

c) Devise a synthesis of **EITHER** compound **E** **OR** compound **F** shown below. Your starting materials should have 5 carbons or fewer. Show clearly your retrosynthetic analysis, identifying synthons and synthetic equivalents where appropriate. Propose reagents for your forward synthesis.

(10 marks)



E
(racemic)



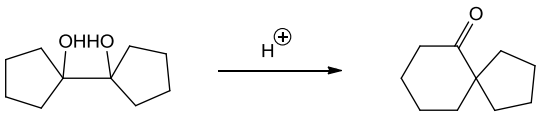
F
(racemic)

3.O12 – An Introduction to Reaction Stereoelectronics

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

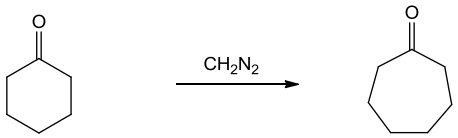
a) Answer **ALL** parts of this question.

i) Give a mechanism for the following transformation and indicate any stereoelectronic control.



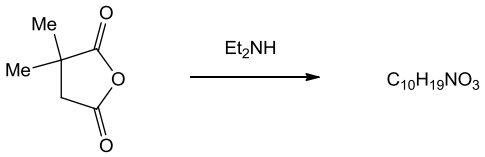
(5 marks)

ii) Give a mechanism for the following transformation and indicate any stereoelectronic control.



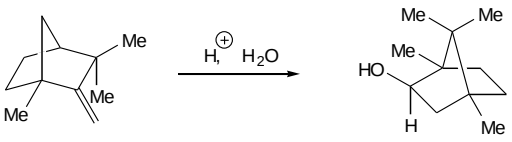
(5 marks)

iii) Predict the major product of the following reaction and explain your reasoning.



(5 marks)

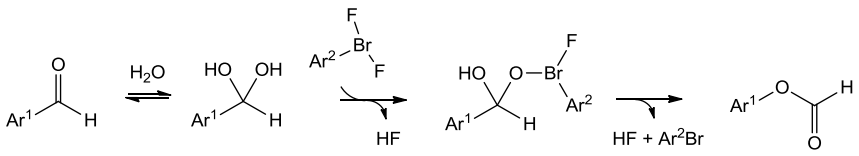
b) Write a mechanism for the following rearrangement reaction. Explain why the stereochemistry of the starting materials is important for the success of these transformations including in your answer diagrams of the key orbitals which are involved in the rearrangement steps.



(10 marks)

QUESTION CONTINUED OVERLEAF

c) The reaction shown below involving a hypervalent bromine(III) reagent offers an alternative to the Baeyer-Villiger reaction and has the advantage that it is successful for converting a wide range of benzaldehydes to their corresponding formate esters:



Give a mechanism for the final step shown. Include in your answer diagrams of the key orbitals which are involved in this fragmentation.

(10 marks)

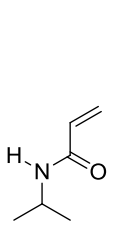
3.O3 – Polymers – The Essential Guide

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

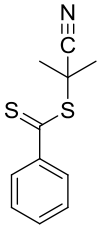
a) Answer **ALL** parts of this question

i) List the three most important criteria to define a polymerisation process as "living".
(3 marks)

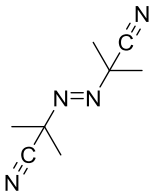
ii) Describe in mechanistic detail the initiation, propagation and termination steps of a RAFT (radical addition fragmentation transfer) polymerisation of *N*-isopropyl acrylamide (**A**). Use **B** as your RAFT agent and AIBN (**C**) as your initiator.
(7 marks)



A



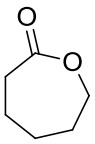
B



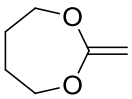
C

b) Answer any **FIVE** of the **EIGHT** questions (i) – (viii)

An aliphatic polyester with the same repeat unit structure can be synthesised by polymerising separately monomer **D** and **E** requiring different polymerisation chemistries.



D



E

QUESTION CONTINUED OVERLEAF

i) Provide mechanistic details for the initiation, propagation and termination reaction in the polymerisation of monomer **D**. Include your choice of initiator.

(3 marks)

ii) Provide mechanistic details for the initiation, propagation and termination reaction in the polymerisation of **E**. Include your choice of initiator.

(3 marks)

iii) Draw the molecular structure of the resulting polymer chain based on monomer **D** and include in your molecular representation the most abundant end groups.

(3 marks)

iv) Draw the molecular structure of the resulting polymer chain based on monomer **E** and include in your molecular representation the most abundant end groups.

(3 marks)

v) Explain how you could control the number-average molecular weight (M_n) in the polymerisation of **D**.

(3 marks)

vi) Explain how you could control the number-average molecular weight (M_n) in the polymerisation of **E**.

(3 marks)

vii) Reducing the ring size of **D** and **E** by a single methylene group (CH_2) each decreases the rate of polymerisation in each case. Explain.

(3 marks)

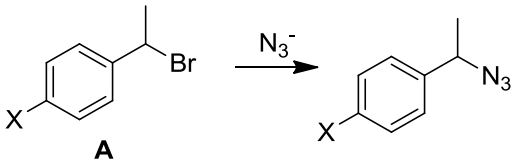
viii) Polymerising **D** at high concentrations increases M_n significantly whereas in the case of **E** the effect is rather small. Explain.

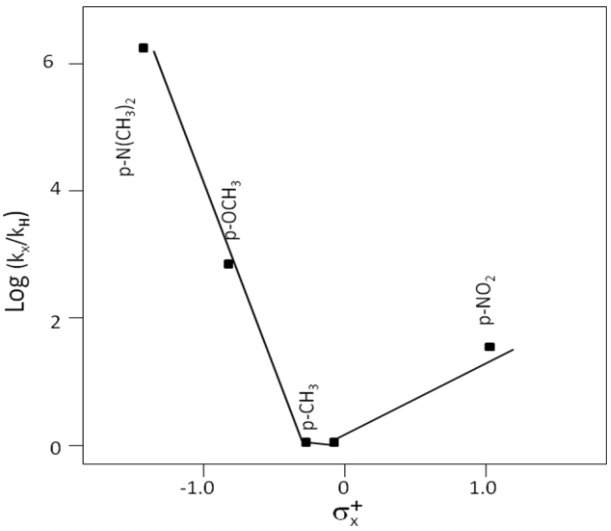
(3 marks)

3.O4 – Introduction to Physical Organic Chemistry

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

a) The substitution reaction of a series of para substituted compounds **A** was studied, resulting in the Hammett plot below.





i) Analyse and explain the shape of this plot in terms of substitution mechanisms and ρ values.

(7 marks)

ii) Explain why the dimethylamino substituted compound is more reactive than the methoxy substituted compound.

(2 marks)

iii) Comment on the reason that σ^+ was used rather than σ as the x axis parameter.

(1 mark)

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

i) The entropy of activation ($\Delta S^{\ddagger}$) of the nucleophilic substitution of the carbon-chlorine bond in 2-chloro-2-methylpropane was observed to be large and positive. What information does this provide about the mechanism for the substitution?

(2 marks)

ii) The pK_a of ethanoic acid (CH_3COOH) in water is 4.7. In what way would you expect the pK_a to change when measured in CH_3CN and why?

(2 marks)

iii) The pK_a's of ethanoic acid (CH_3COOH) and thiophenol (C_6H_5SH) are 4.7 and 6.6 respectively. The pK_a's of the conjugate acids of the two bases, pyridine (C_5H_5N) and ammonia (NH_3) are 5.5 and 9.3 respectively. Write the balanced equations (four in total) for the reaction of each acid with both bases, indicating whether the equilibrium is favoured towards the side of the acid, or conjugate acid of the base.

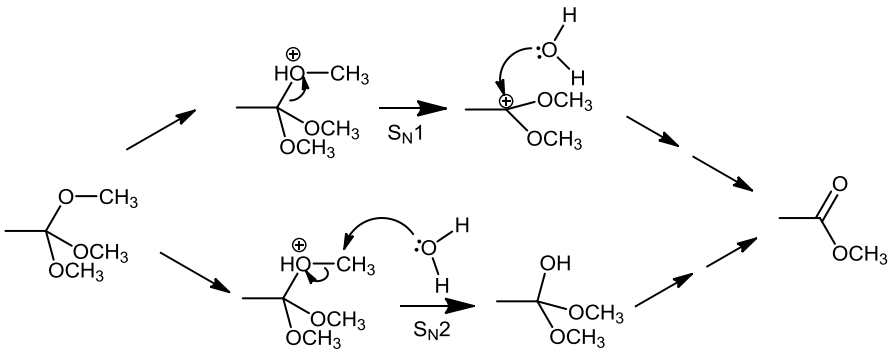
(4 marks)

QUESTION CONTINUED OVERLEAF

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

i) How can isotope labelling be used to distinguish between the two proposed mechanisms for hydrolysis of orthoesters as shown below?

(2 marks)



ii) The sulfonation of benzene is a two step process, and was observed to have a significant primary kinetic isotope effect (PKIE). Write a mechanism for the reaction, and explain the PKIE effect in terms of the rate determining step. Sketch the reaction energy profile for the reaction, indicating the relative energies of the two transition states.

(5 marks)

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

i) The Hammett plot ρ value for the reaction of chlorodiphenylmethane with ethanol is -5.09. What information does this provide regarding the rate determining step and mechanism of this reaction?

(3 marks)

ii) The two reactions A and B below have very different reaction rates. Compare the reaction transition state enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation of both reactions and predict which reaction is more favourable.

(4 marks)