IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2015, 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 IIB

Organic Chemistry

Tuesday 16th June 2015, 14:00-17:00

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 **ALL** parts of this question.

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

i) Treatment of pyrrole with sodium hydride followed by iodomethane gives 1-methylpyrrole, whereas treatment of pyrrole with methylmagnesium bromide followed iodomethane gives 2-methylpyrrole.

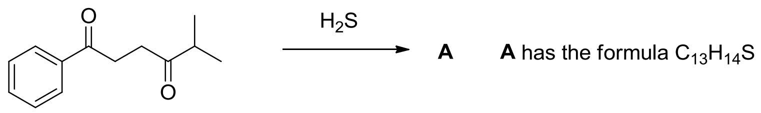
ii) Quinoline undergoes electrophilic aromatic substitution (S_EAr) preferentially at the 5- and 8-positions.

iii) Treatment of pyridine *N*-oxide with phosphorus oxychloride ($POCl_3$) gives 2-chloropyridine.

(5 marks each)

b) Identify the product of **ONE** of the following reactions, and write a mechanism for its formation.

i)



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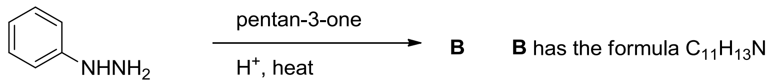
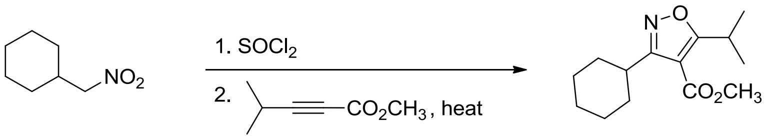


(5 marks each)

c) For **ONE** of the following reactions, give a mechanism for the formation of the product shown.

i)



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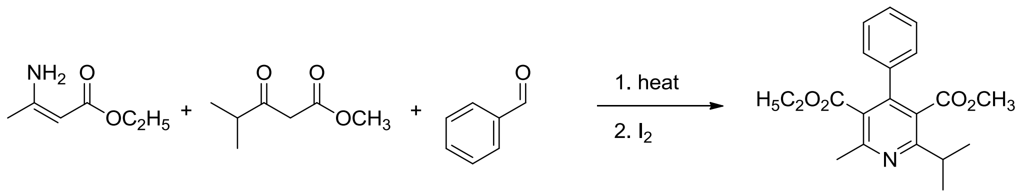
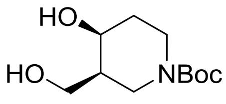
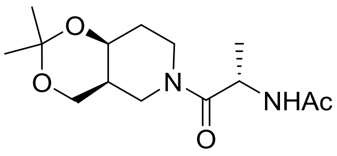


(10 marks each)

2.O3 – Bio-organic Chemistry



A



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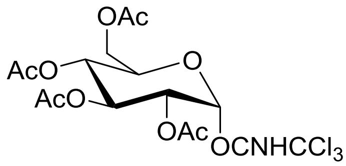

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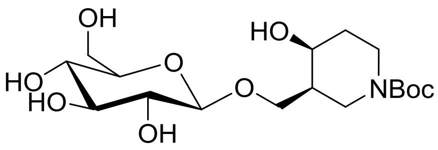

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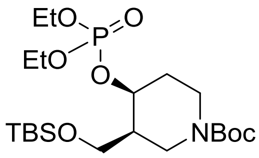

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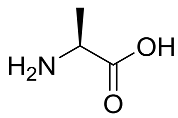


L-Alanine (Ala)

Notes: Boc = *tert*-butoxycarbonyl; TBS = *tert*-butyldimethylsilyl; Ac = acetyl.

Answer **TWO** of the following parts (a)–(c) of this question. Each part carries equal marks. Note that **more than one step** is required to achieve each transformation, including one or more protecting group manipulations.

a) Give reagents and conditions for the transformation of **A** into **B**, using Ac-Ala-OH as one of your reagents. Provide mechanisms for each step of your synthesis.

b) Give reagents and conditions for the transformation of **A** into **C**, using **E** as one of your reagents. Provide mechanisms for each step of your synthesis, and comment on any stereoselectivity observed.

c) Give reagents and conditions for the transformation of **A** into **D**, using $Et_2NP(OEt)_2$ as one of your reagents. Provide mechanisms for each step of your synthesis.

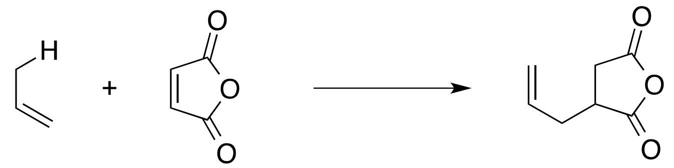
2.O5 – Pericyclic Reactions

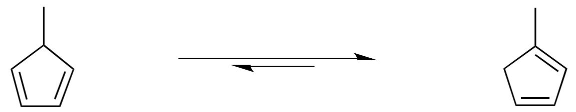
Answer **ALL** parts of this question.

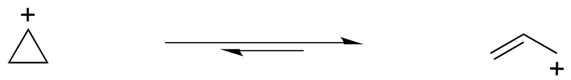
a) Define the term electrocyclic reaction.

(4 marks)

b) For **TWO** of the following **THREE** thermal reactions, draw a curly arrow mechanism and write down the class of pericyclic reaction to which it belongs.

i) 

ii) 

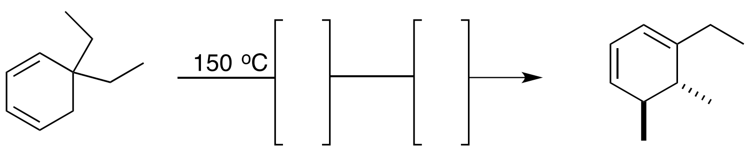
iii) 

(4 marks each)

c) Carry out a Woodward-Hoffmann analysis of the following reaction to show that it is thermally allowed.

(5 marks)

d) The thermal reaction illustrated below takes place in three steps and involves two electrocyclic reactions and one sigmatropic rearrangement. Write down the structures of the two intermediates and explain how you deduced the stereochemistry of the second intermediate.



(8 marks)

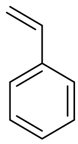
2.O6 – Fundamentals of Polymer Chemistry

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

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

i) Consider the following distributions of polystyrene chains:

5 chains of degree of polymerisation 10
25 chains of degree of polymerisation 25
30 chains of degree of polymerisation 40
15 chains of degree of polymerisation 70
10 chains of degree of polymerisation 100



styrene

Calculate the number and weight average molecular weight of this collection of polymer chains.

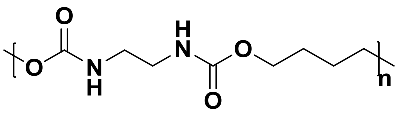
(5 marks)

ii) Anionic polymerisation of methyl methacrylate often exhibits a side reaction eliminating a methoxy anion. Show the mechanism for this reaction. Comment on the effect of the reaction on polymer molecular weight and yield.

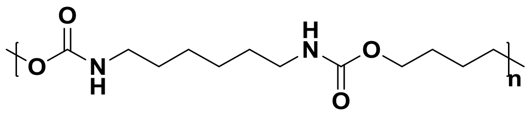
(4 marks)

iii) Which of the two polymers (1) and (2) below would you expect to exhibit the higher glass transition temperature? Explain your reasoning (2 marks). Suggest a synthesis of polymer (1) from appropriate monomers (2 marks). In this synthesis, one of the two monomers is in excess to the ratio 1:1.05 and the extent of reaction is 0.99. What is the number average molecular weight of the resulting polymer? (3 marks)

(7 marks)



(1)

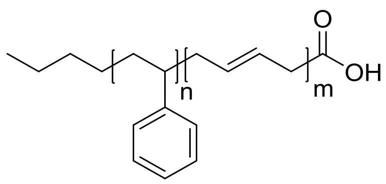


(2)

QUESTION CONTINUED OVERLEAF

iv) The copolymer **(3)** of precise block lengths n and m, shown below, can be easily synthesised by sequential addition of the two monomers using the same polymerisation mechanism. Propose a mechanism, reagents and conditions. Suggest the appropriate initiator and chain terminator for this polymerisation?

(5 marks)



(3)

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

i) Compare the reactivity of a styrene monomer with the reactivity of a vinyl acetate monomer in radical polymerisation, and account for the faster propagation rate of vinyl acetate radical polymerisation.

(2 marks)

ii) For the table below, describe the copolymer architecture of any two of the three combinations of monomers.

(2 marks)

Monomer 1	r_1	Monomer 2	r_2
Styrene	0.80	Isoprene	1.68
Styrene	55	Vinyl Acetate	0.01
Styrene	0.04	Maleic anhydride	0.015

c) The monomer below was polymerised with both an AIBN initiator, and also with a CuCl/$CHCl_3$/bipyridine mixture. Discuss both polymerisation mechanisms, and compare the polydispersities and polymer architecture arising from both polymerisations.

(4 marks)