IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 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 IIIA

Paper 2

Thursday 15th January 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.

3.I1 – Inorganic Mechanisms and Catalysis

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

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

The first hydroformylation reactions of 1-alkenes were carried out with $[Co_2(CO)_8]$, which forms the actual catalyst $[CoH(CO)_4]$ in situ upon reaction with hydrogen.

   i) Discuss the mechanism of the reaction between $[Co_2(CO)_8]$ and H_2.
(3 marks)
   ii) Draw a plausible catalytic cycle for the hydroformylation of 1-butene using $[CoH(CO)_4]$ as the catalyst and describe each step.
(6 marks)
   iii) What types of selectivity must be considered in this reaction and how may this be influenced.
(3 marks)

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

A new industrial process for the production of 1-octene involves the reaction of butadiene and methanol to give 1-methoxy-2,7-octadiene as the first step, which is catalysed by catalyst A. Catalyst A consists of a Pd^0 source and PPh_3.
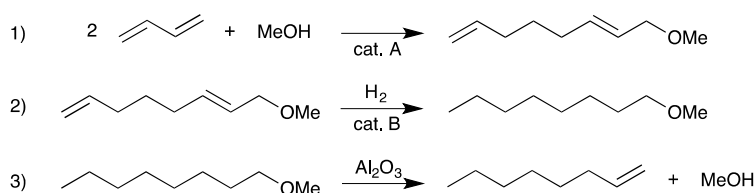
   i) The first step in the catalytic cycle for reaction 1) is shown below. Explain and discuss the mechanism of this first step.
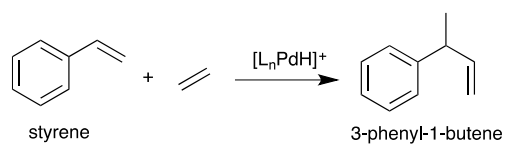

(3 marks)

   ii) The product, 1-methoxy-2,7-octadiene, from reaction 1) is hydrogenated in reaction 2) to methyl octyl ether, which is subsequently cleaved in reaction 3) over Al_2O_3 to give 1-octene and methanol. Suggest a suitable catalyst B for the hydrogenation reaction and draw the mechanism and explain each step.
(5 marks)

c) The ruthenium complex $[Ru(H)(Cl)(PPh_3)_3]$ is an efficient catalyst for the hydrogenation of aldehydes. Draw a catalytic cycle for the hydrogenation of propanal to propanol using this catalyst.
(5 marks)

d) The hydrovinylation of styrene yields 3-phenyl-1-butene as shown below and is catalysed by palladium hydride species $[L_nPdH]^+$. Draw a catalytic cycle for this reaction and explain each step. Which types of selectivity have to be considered?
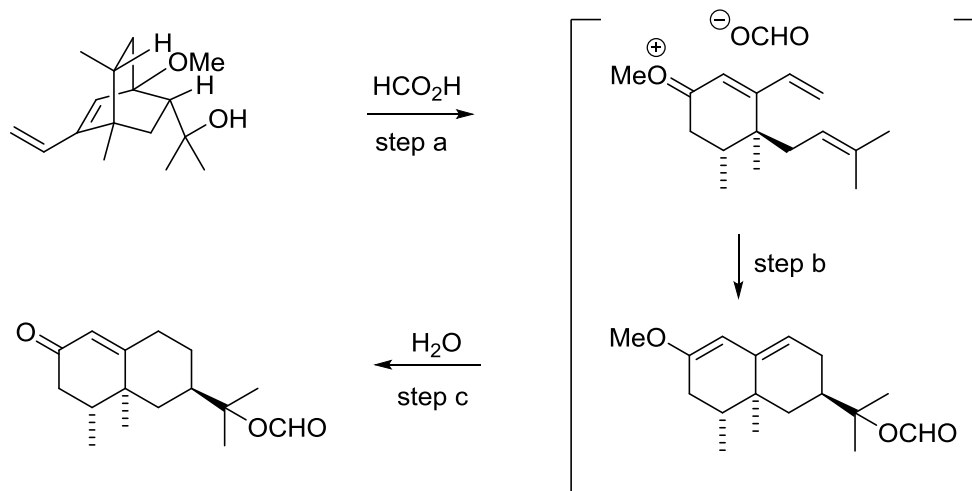

styrene   3-phenyl-1-butene

(5 marks)

## 3.O12 – An Introduction to Reaction Stereoelectronics

Answer **BOTH** parts of this question.

a) Consider the following transformation:

i)   Write out a curly arrow mechanism for the whole transformation (steps a-c).

(4 marks)

ii) Show how the stereochemistry of the starting material is important for the success of the initial Grob fragmentation (step a) and indicate the key orbital interactions involved.

(3 marks)

iii) Indicate the key orbital interactions involved in the vinologous Prins reaction (step b).

(3 marks)

b) Give a mechanism for **THREE** of the following transformations. Indicate all products and show any stereoelectronic control.
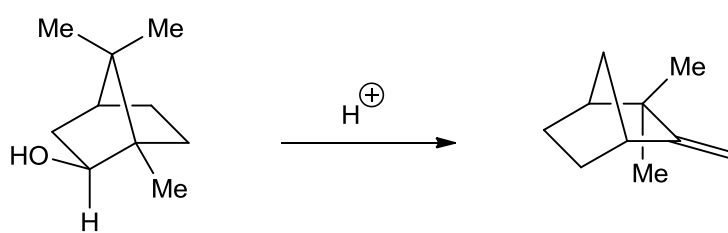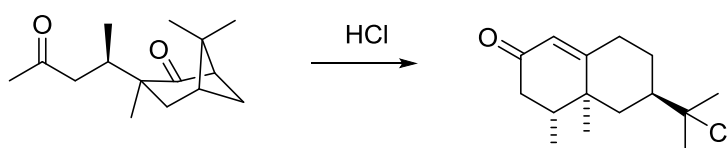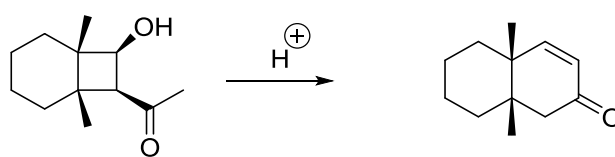
i)
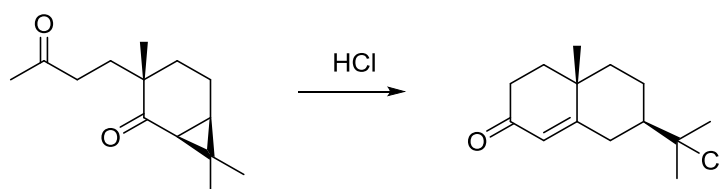
(5 marks)

ii)

(5 marks)

iii)

(5 marks)

iv)

(5 marks)

5

3.O3 – 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 poly(methyl methacrylate) chains:

> 5 chains of degree of polymerization 10
> 25 chains of degree of polymerization 100
> 50 chains of degree of polymerization 500
> 30 chains of degree of polymerization 1000
> 10 chains of degree of polymerization 5000
> 5 chains of degree of polymerization 50000
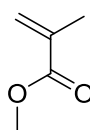
methyl methacrylate

Calculate the number and weight average molecular weight of this collection of polymer chains. Would doubling the number of polymer chains with the lowest degree of polymerisation have more influence on the number average or weight average molecular weight?
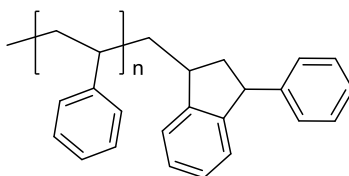
(4 marks)

ii) What type of polymer architecture will be created on polymerization of 2-((2-bromopropionyl)oxy)ethyl acrylate (shown below) in the presence of an ATRP initiator? Explain why, including an illustrative structure. Suggest a suitable initiator.

(4 marks)
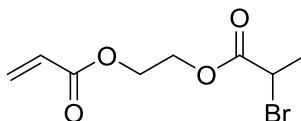
iii) The propagation step in the cationic polymerization of polystyrene is often terminated by the formation of the indane endgroup shown below. Provide a mechanism which explains this termination. Can polymerization be re-initiated from the products of this termination reaction?

(4 marks)

iv) Consider the two polymers **(1)** and **(2)** below.

    A. Which polymer would you expect to exhibit the higher glass transition temperature? Explain your reasoning.

    (2 marks)

    B. Suggest a synthesis of polymer **(1)** from appropriate monomers.

    (2 marks)

    C. In this synthesis, one of the two monomers is in excess to the ratio 1:1.06 and the extent of reaction is 1. What is the number average molecular weight of the resulting polymer?
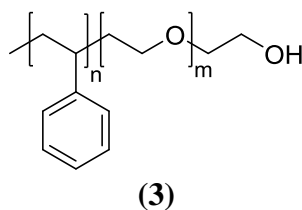
    (3 marks)

(1)

(2)
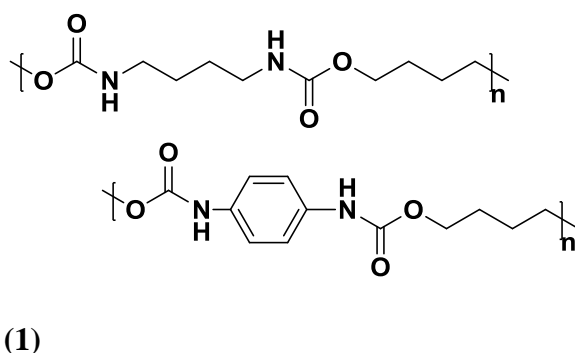
v) Why is styrene a better monomer than propylene for free radical polymerisation?

(1 mark)
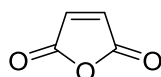
b) Answer **ALL** parts of this question.

The copolymer **(3)** of precise block lengths n and m, shown below, can be easily synthesized by sequential addition of monomer using the same polymerization mechanism. Propose a mechanism, reagents and conditions. Why is a crown ether often required during the synthesis?

(5 marks)

(3)

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

Discuss the suitability of maleic anhydride (shown below) for polymerisation by radical, anionic and cationic methods. Propose a co-monomer which will improve polymerisation for one of the methods.

(5 marks)

3.P11 – Statistical Thermodynamics

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

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

   i) Consider a system consisting of N atoms. Each atom can access n different energy levels. State the total number of microstates available and the total entropy for the system.

(2 marks)

   ii) For the system discussed in question i), how many microstates contain the most probable state? You can assume that $n=N$.

(2 marks)

   iii) Consider a system containing 1 mol of particles. Each particle can access *three* different energy levels. Sketch the variation of the entropy, S, and the heat capacity, Cv, with temperature, stating clearly the limiting behaviour of S and Cv as $T \rightarrow 0$ and $T \rightarrow \infty$.

(3 marks)

   iv) For the three energy level system considered in question iii), derive the internal energy in the canonical ensemble. Assume that the particles are distinguishable, and that the levels have energies 0, u_1, and u_2 and degeneracies *1, 2* and *1*.

(4 marks)

   v) Calculate the number of thermally accessible energy levels of 1 argon atom trapped in a cavity of volume 1 cm^3 at 300 K.

   [Data: $m_{Ar} = 39.95$ g/mol]

(2 marks)

   vi) Use the equipartition principle to estimate the internal energy of 1 mol of molecular nitrogen at 3500 K. State clearly all the approximations you make.

   [Data: vibrational temperature of N_2: 3340 K; Rotational temperature of N_2: 3 K]
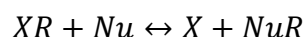
(3 marks)

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

i) Statistical mechanics provides a route to derive a microscopic equation for the temperature. Starting from the molecular translational partition function for a monoatomic ideal gas

$$q_t = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V \,,$$

show that the temperature is defined by $T = \dfrac{2}{3}\dfrac{U}{N k_B}$ where U is the kinetic energy. (Note, all terms in the above equations have the meanings given in the lectures).

(6 marks)

ii) Write the statistical thermodynamics equation for the equilibrium constant of the following nucleophilic substitution reaction:

$$XR + Nu \leftrightarrow X + NuR$$

Clearly explain the meaning of all the symbols in your equation, and identify the entropic and enthalpic terms.

(3 marks)

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

i) Show that the partition function of the one-dimensional oscillator is given by:

$$q = \frac{\exp\!\left(-\dfrac{q_v}{2T}\right)}{1 - \exp\!\left(-\dfrac{q_v}{T}\right)}$$

where all terms have the meanings given in the lectures.

(4 marks)

ii) Show that at very high temperatures the partition function converges to the classical limit result.

(1 mark)

iii)
A spectroscopic experiment indicates that O_2 molecules can access about 50 rotational energy levels. Estimate the temperature at which the experiment was performed. Would the equipartition principle be a valid approach to estimate the rotational energy in this experiment?

[Data: m_O = 16 g/mol; bond length O_2 = 0.121 nm]

(4 marks)