

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JANUARY 2016, 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 14th January 2016, 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) Explain the following terms:

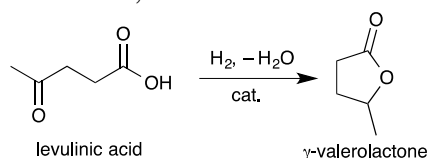
- i) *in situ* catalysts
- ii) TOF
- iii) catalyst resting state

(6 marks)

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

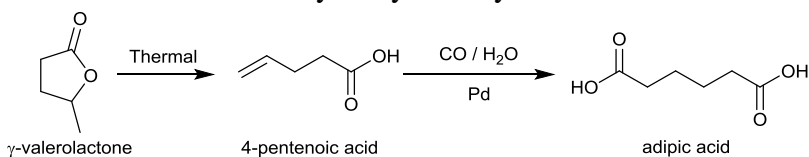
Levulinic acid, easily obtained from sugars such as fructose, is of great interest as a renewable platform chemical.

- i) The hydrogenation of levulinic acid results in the formation of γ -valerolactone. Identify the key steps involved, and draw the structure of the intermediate.



(3 marks)

- ii) Thermal conversion of γ -valerolactone results in 4-pentenoic acid, which can undergo a palladium-catalysed hydroxycarbonylation reaction to give adipic acid. Draw the mechanism for the hydroxycarbonylation reaction.



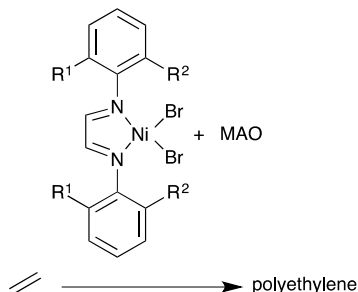
(6 marks)

- iii) What selectivity needs to be considered in the hydroxycarbonylation reaction, and how could it be controlled?

(3 marks)

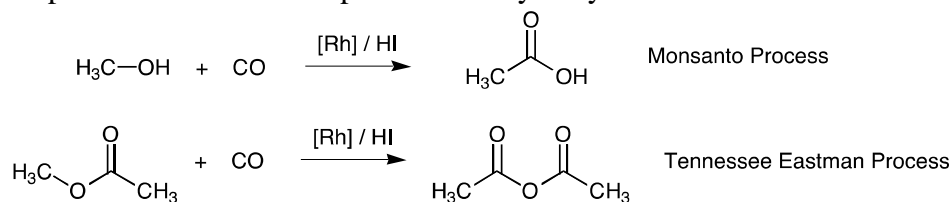
QUESTION CONTINUED OVERLEAF

- c) Nickel(II) alpha-diimine complexes, in combination with the co-catalyst methyl aluminoxane (MAO), are very active catalysts for the polymerisation of ethylene. The chain length of the polymer product is dependent on the substituents R^1 and R^2 . Explain this observation.



(7 marks)

- d) The carbonylation of methyl acetate to acetic anhydride (Tennessee Eastman Process) is catalysed by a homogeneous rhodium-based catalyst. The mechanism of this process is analogous to the Monsanto process, the rhodium-catalysed carbonylation of methanol to acetic acid. Draw a catalytic cycle for the Tennessee Eastman Process and explain the individual steps in the catalytic cycle.

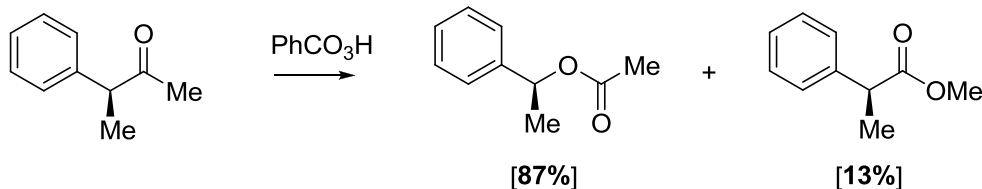


(7 marks)

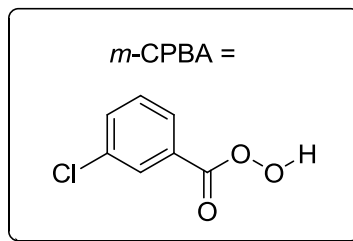
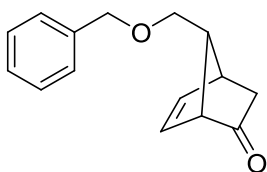
3.O12 – An Introduction to Reaction Stereoelectronics

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

a) Consider the following Baeyer-Villiger reaction:

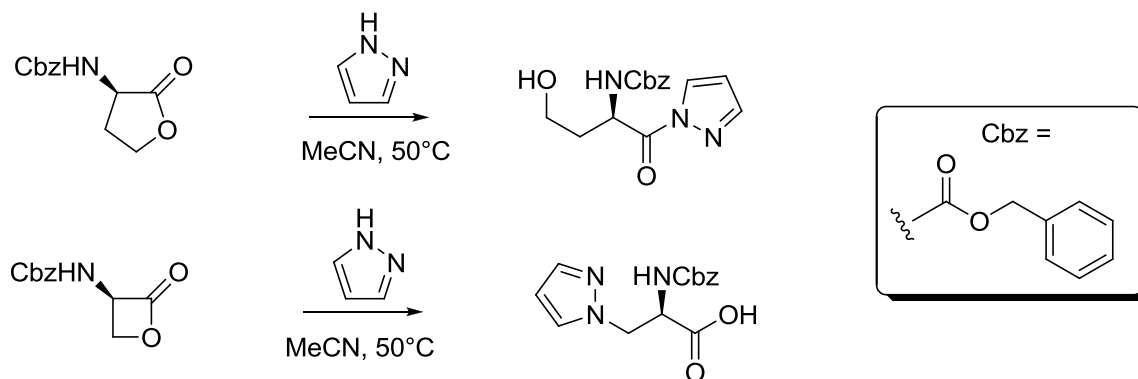


- i) Draw a mechanism for the formation of the major product. (3 marks)
- ii) Show the orbitals and highlight the key bonds that are involved in this reaction. (4 marks)
- iii) The major product is formed with essentially complete retention of stereochemistry. Explain. (3 marks)
- iv) Explain why the major product is favoured with reference to a representation of the transition state for the key 1,2-migration step. (3 marks)
- v) When the following ketone is treated with *m*-CPBA it undergoes a Baeyer-Villiger reaction. Predict the product and suggest why epoxidation of the double bond does not occur under these conditions. (5 marks)



QUESTION CONTINUED OVERLEAF

- b) Consider the two following lactone ring-opening reactions that take place under identical reaction conditions:



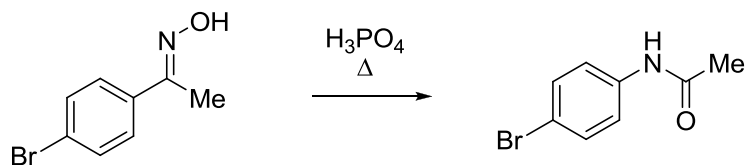
- i) Draw a mechanism for each transformation.

(4 marks)

- ii) Suggest one or more reasons for the contrasting behaviour of the two lactones.

(3 marks)

- c) Write a mechanism for the following rearrangement reaction. Explain why the stereochemistry of the starting material is important. Include in your answer diagrams of the key orbitals.



(7 marks)

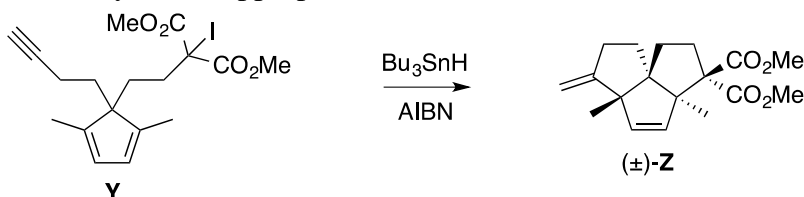
3.05 – Reactive Intermediates

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

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

- i) Discuss the possible cyclisation modes of the 5-hexenyl radical and identify the preferred cyclisation mode. (10 marks)

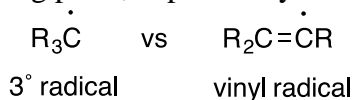
- ii) Consider the conversion of **Y** into (\pm)-**Z**, providing an annotated curly arrow mechanism, commenting on any aspects of reactivity, selectivity and stereochemistry where appropriate.



(15 marks)

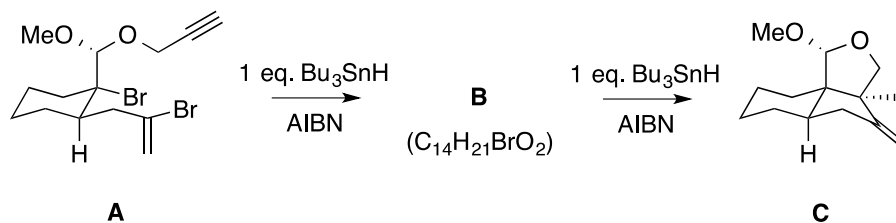
b) Answer **ALL** parts of this question.

- i) A carbon-centred vinyl radical (below) is less stabilised than a carbon-centred tertiary radical. Using your understanding of the stability of carbon-centred tertiary radicals as a starting point, explain why.



(10 marks)

- ii) Consider the conversion of **A** into **C** via **B** (where the latter is an isolable intermediate). Provide a structure for compound **B**, and provide annotated curly arrow mechanisms for the transformation of **A** into **B** and then **B** into **C**.



(15 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

Consider a gas consisting of N diatomic molecules

- i) Write an expression for the total partition function of a molecular fluid in terms of the molecular partition function, stating the different degrees of freedom.

You may assume ideal gas behaviour.

(2 marks)

- ii) Using the equipartition theorem write an equation for the heat capacity of 1 mol of non-interacting molecules.

You may neglect electronic contributions.

(3 marks)

- iii) One molecule of carbon dioxide adsorbs in a porous material. The pore volume is 10^3 nm^3 and the temperature 200 K.

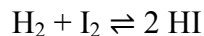
Estimate the number of thermally accessible translational energy levels.

$$m_{\text{O}}=16 \text{ g/mol}, m_{\text{C}}=12 \text{ g/mol}$$

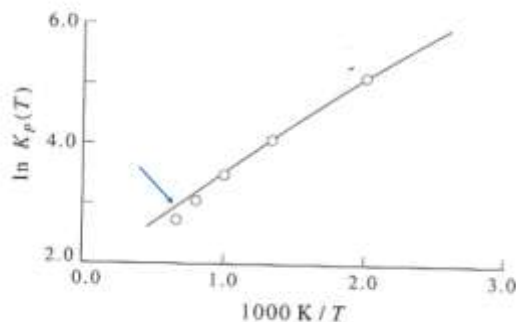
(5 marks)

QUESTION CONTINUED OVERLEAF

- iv) The diagram below shows the temperature dependence of the equilibrium constant of the gas phase reaction:



The circles are experimental data and the line represents the statistical thermodynamics prediction. Briefly explain the origin of the deviation between theory and experiment (see arrow).



(2 marks)

- v) Write the statistical mechanics equation for the chemical reaction in part iv). State clearly all the variables needed to quantify the equilibrium constant.

(4 marks)

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

- i) The rotational energy of one diatomic molecule is,

$$u^r = \frac{h^2}{8\pi^2 I} J(J+1)$$

and the degeneracy for each energy level is $2J+1$.

Show that the rotational partition function is given by

$$q^r = \frac{8\pi^2 I k_B T}{\sigma h^2}$$

(5 marks)

QUESTION CONTINUED OVERLEAF

- ii) What is the physical origin of the factor, σ , appearing in the rotational partition function of part i)?

What values does σ take for CO and N₂ molecules?

(4 marks)

- c) Answer **BOTH** parts of this question

- i) Consider a molecule that can access “two” possible energy levels with energies 0 and u , respectively. Each level has double degeneracy.

Derive the statistical thermodynamics equation for the entropy of N molecules in the canonical ensemble. What is the entropy of the system in the high temperature limit?

(6 marks)

- ii) The van der Waals equation corrects the pressure of a fluid by taking into account the interactions between particles, $u = -a N / V$ and the volume occupied by the particles, $n b$.

Write the partition function of a monoatomic fluid consisting of interacting atoms, using the energy, u , volume correction, $n b$, given above.

Hint: The translational partition function for ideal particles is:

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

(3 marks)