

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – MAY 2012, 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 IIIB

Paper 2

Thursday 10th May 2012, 09:30-12:30

**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.**

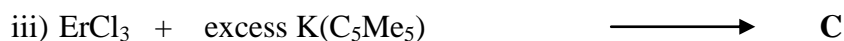
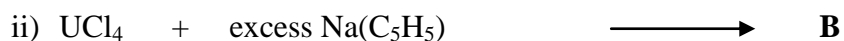
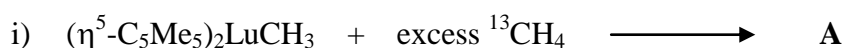
3.I7 – Lanthanide and Actinide Chemistry

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

- a) The magnetic moment μ_{eff} of the majority of Ln^{3+} complexes may be accurately predicted through the use of the Landé formula. Show that experimental values of μ_{eff} for Eu^{3+} complexes (generally 3.3 – 3.5 B.M. at 298 K) do not conform to this generalisation and explain the deviation.

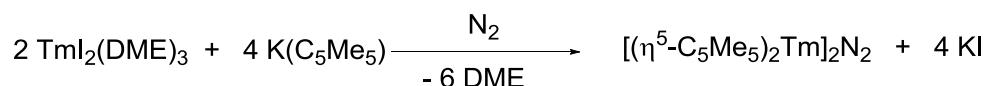
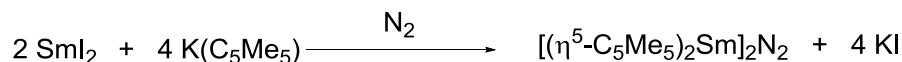
(7 marks)

- b) Identify and draw the structures of the rare earth containing products **A**, **B** and **C** in the following reactions:



(6 marks)

- c) The reactions shown below result in the formation of bimetallic complexes. Both complexes feature a side-on bound dinitrogen ligand that bridges symmetrically between the lanthanide centres.



(DME = 1,2-dimethoxyethane)

With reference to the electronic configurations of both Sm and Tm, propose an explanation of the following N_2 bond lengths:

$$[\text{Sm}] = 1.09 \text{ \AA} \text{ and } [\text{Tm}] = 1.59 \text{ \AA}.$$

(6 marks)

QUESTION CONTINUED OVERLEAF

d) Explain the following observations:

i) The compound YbCl_3 is **stable** in aqueous solution, whilst the compound YbI_2 is **unstable** in aqueous solution. (2 marks)

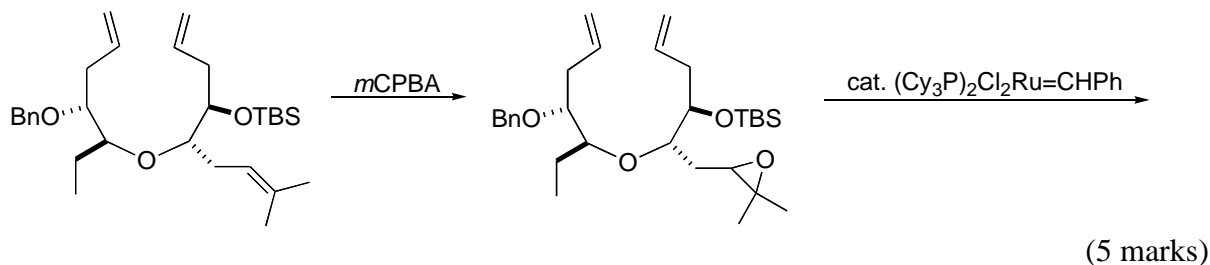
ii) The complex $[\text{Nd}(\text{OAr})_4]^-$ ($\text{OAr} = 2,6\text{-dimethylphenoxide}$) is tetrahedral, whereas the complex $[\text{Pt}(\text{tpy})\text{Cl}]^+$ is square planar ($\text{tpy} = \text{terpyridine}$). (4 marks)

e) Discuss the use of Gd^{3+} ions in Magnetic Resonance Imaging, with particular reference to the complexes often used and their mechanism of action. (6 marks)

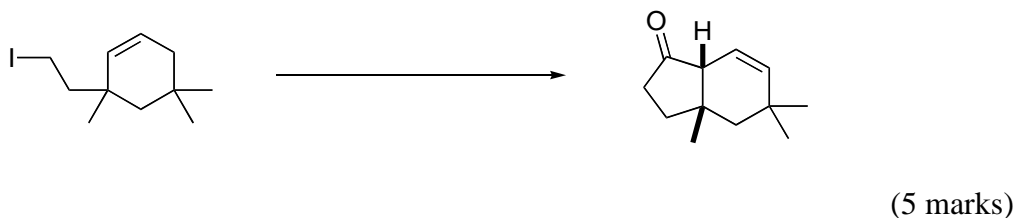
3.O1 – Organometallic Complexes in Organic Synthesis

Answer any **FIVE** of the six parts a)-f) of this question.

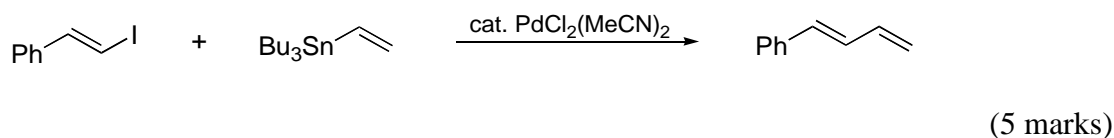
- a) Consider the two-step reaction scheme shown below. Write down the structure of the product of the second step. Why was the first step necessary?



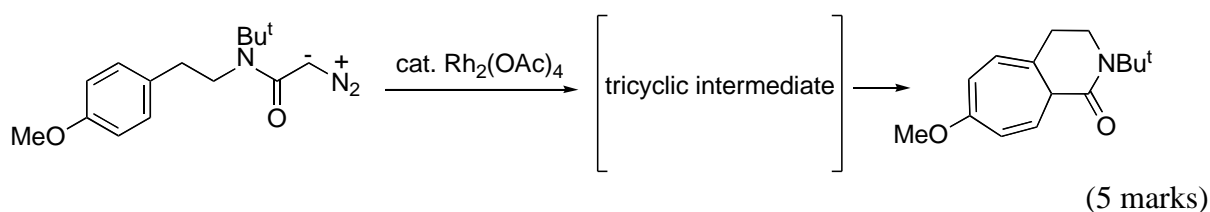
- b) Suggest reagents for the following transformation. What type of reaction is this?



- c) Draw a catalytic cycle to explain the following reaction.

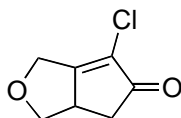


- d) Write down the structure of the tricyclic intermediate formed during the course of the reaction illustrated below. What type of pericyclic reaction transforms the intermediate into the product?



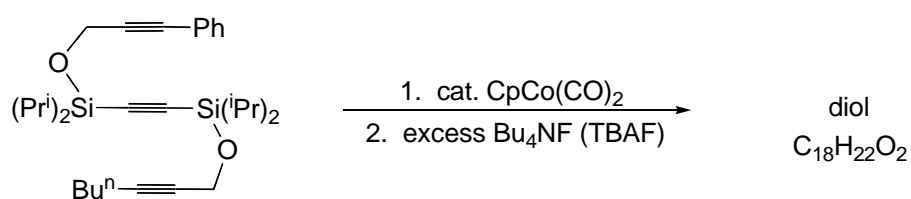
QUESTION CONTINUED OVERLEAF

- e) Write down the structure of an enyne that could be used as a starting material for the synthesis of the molecule shown below. Suggest reagents for the transformation of the enyne into the target molecule.



(5 marks)

- f) Write down the structure of the diol product of the following reaction scheme. What was the role of the silicon linkers in the overall transformation?



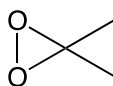
(5 marks)

3.08 – Carbohydrate Chemistry

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

- a) With reference to a specific compound in each case, describe the use of the following reagents in glycosidation reactions. In each case briefly describe the mechanism of the reaction and the factors that control the anomeric stereoselectivity of glycosidation.

A. Dimethyldioxirane **A**

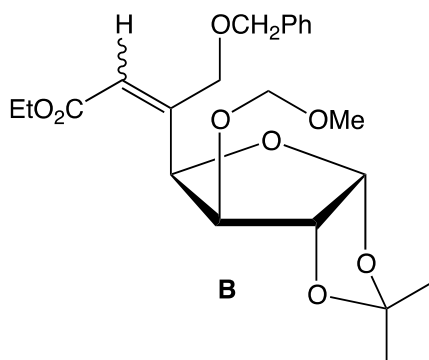


A

B. Tetraethylammonium bromide (Et₄NBr)

(16 marks)

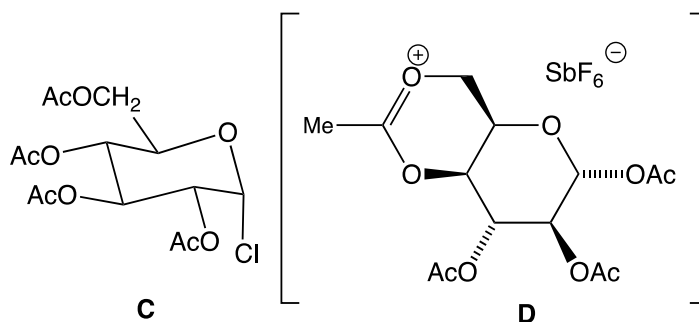
- b) In the total synthesis of sphingofungin E, a natural product, D-glucose was utilised as the starting material. A key intermediate was **B**. Suggest a method for the conversion of D-glucose into **B**.



(9 marks)

QUESTION CONTINUED OVERLEAF

- c) The glucose derivative **C** was found to undergo a rearrangement on reaction with the powerful Lewis acid antimony pentachloride. Prior to the addition of water, a salt that crystallised from the solvent dichloromethane was found to be the acetoxonium hexafluoroantimonate **D**. Suggest a mechanism for the reaction. Hint: Look closely at the stereochemistry at all centres of salt **D** and remember there are several steps in the process.



Finally, what do you expect salt **D** to produce on being allowed to react with water?
(9 marks)

3.P1 – Modern Analytical Chemistry

Useful equations that might be needed to answer questions a), b), and c)

$n\lambda = d(\sin\alpha + \sin\beta)$	$t_q = \frac{1}{k_F + k_q[Q] + k_{NR}}$	$NA = n \sin \theta \cong \frac{D}{2f}$
$A = -\log T = \log \frac{P_0}{P} = \epsilon bc$	$\phi_f = \frac{k_r}{k_a} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_f}{\tau_r}$	$A = \frac{d\beta}{d\lambda} = \frac{n}{d \cos(\beta)}$
$F = k f_f P_0 2.303 \epsilon bc$	$\frac{n_{upper}}{n_{lower}} = \exp\left(-\frac{\Delta E}{kT}\right)$	$r = \frac{\lambda f}{n\pi R}$

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

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

- i) Write equations for both absorbance with respect to the initial radiant power and the fluorescence radiant power. Define all terms present. (2.5 marks)
- ii) Using the equations defined in i), explain why fluorescence spectroscopy is potentially more sensitive than absorption spectroscopy. (3 marks)
- iii) List 6 assumptions made when using the absorption law. (3 marks)
- iv) An absorption spectrometer contains a malfunctioning wavelength selector. The output was found to be producing two wavelengths with power P_0 and P_0 . Starting with the Beer-Lambert law, derive an equation that can correct for this in terms of incident power, extinction coefficient, sample path length, and concentration. (5 marks)
- v) Assume a fluorescence spectrometer is used in iv) rather than an absorption spectrometer. How would the fluorescence radiant power be affected by the two incident wavelengths? (2.5 marks)

QUESTION CONTINUED OVERLEAF

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

i) Describe what is meant by a *population inversion*. Use an energy level diagram in your answer.

(1 mark)

ii) Using the Boltzmann distribution describe why thermal excitation is not effective in order to achieve a *population inversion*.

(3 marks)

iii) Why cannot lasing be achieved with a “two level system”? Use energy level diagrams in your answer.

(3 marks)

iv) How can a “two level system” be modified in order to achieve lasing?

(2 marks)

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

i) The three-dimensional fluorescence autocorrelation function can be defined as follows:

$$G(\tau) = \frac{1}{N} \left(\frac{1}{1 + 4D\tau/\omega_1^2} \right) \left(\frac{1}{1 + 4D\tau/\omega_2^2} \right)^{\frac{1}{2}} + 1$$

What would the simplified form of this function look like for a particle undergoing one-dimensional diffusion in the x direction?

(1 mark)

ii) Using your answer in i) calculate what the y-intercept would be if there are on average either 0.01 or 21 molecules in the detection probe volume.

(2 marks)

iii) How would your answer to ii) change for three-dimensional diffusion?

(1 mark)

iv) Dr Bloggs, an experimentalist, decides that he wants to run a single molecule fluorescence experiment to determine the diffusion coefficient of an unknown sample. He runs the unknown sample and finds that this produces an autocorrelation curve. Dr Bloggs is just about to use the equation in i) to fit the data, however he quickly realizes that he does not know the value of ω_1 . Give two examples as to how Dr Bloggs can approximate ω_1 .

(5 marks)