

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 1

Tuesday 13th January 2015, 14:00-16:15

**PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT
THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING
OF ANY PRIOR CORE COURSE.**

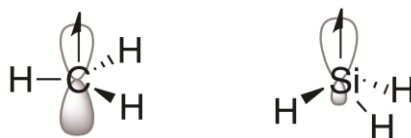
**USE A SEPARATE ANSWER BOOK FOR EACH
QUESTION. WRITE YOUR CANDIDATE NUMBER ON
EACH ANSWER BOOK.**

3.I2 – Advanced Main Group Chemistry

Answer any **FIVE** parts a) to f) of this question.

- a) Show how silylene intermediates are involved in the mechanism for the “Direct Process” for the synthesis of a chlorosilane used to make the backbone of silicone polymers. What type of undesired byproduct can also arise from this mechanism? (5 marks)
- b) Giving a specific example show how a sila-aromatic compound without bulky substituents can be prepared. Give two different types of reaction to show how the reactivity of the compound is significantly different to the carbon analogue of the compound you have described. (5 marks)
- c) A new element, Flerovium, Fl, was recently added to the Periodic Table, at the bottom of group 14. Using your knowledge of trends in Group 14 chemistry suggest how a compound containing a “triple” bond between two Fl atoms might be made. Draw a likely structure for the compound and comment on the bonding in such a compound. (Such chemistry is unlikely to be explored as only *ca.* 80 atoms of Fl have so far been made.) (5 marks)
- d) Answer **BOTH** parts of this question.

Spectroscopic data suggests that, while the radical $\text{CH}_3\cdot$ is most stable in a trigonal planar geometry, $\text{SiH}_3\cdot$ is most stable in a trigonal pyramidal geometry.

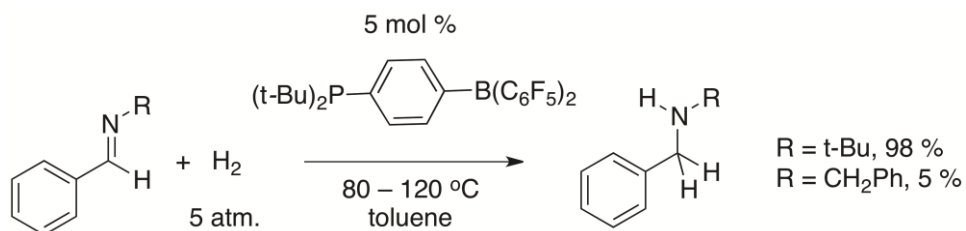


- i) Assign point groups to the two structures. (1 mark)
- ii) With the aid of molecular orbital theory, rationalise the relative stabilities of the two ground-state structures. (4 marks)
- e) Discuss the problems with generating organocalcium complexes by direct synthesis from the metal and aryl halide and outline the approaches that have been taken to overcome them. (5 marks)

QUESTION CONTINUED OVERLEAF

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

Recently a new frustrated Lewis pair was discovered that is capable of catalytically hydrogenating imines to form amines.



i) Draw a plausible reaction mechanism.

(4 marks)

ii) While the reaction is efficient for $\text{R} = \text{t-Bu}$, for $\text{R} = \text{CH}_2\text{Ph}$ the catalyst becomes almost completely ineffective, explain this observation.

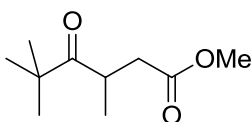
(1 mark)

3.O11 – Organic synthesis

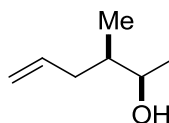
Answer **ALL** parts of this question.

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

(2 x 5 marks)



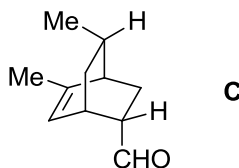
A



B

- b) Explain how compound **C** below may be disconnected using a pericyclic reaction, identifying the reactants you would use in the forward reaction. Give a mechanism for your proposed transformation, and explain the selectivity observed.

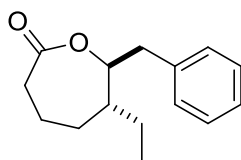
(5 marks)



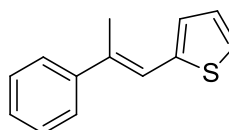
C

- c) Devise a synthesis of **EITHER** compound **D OR** compound **E** shown below. Show clearly your retrosynthetic analysis, identifying synthons and synthetic equivalents where necessary. Propose reagents for your forward synthesis.

(10 marks)



D



E

3.P9 – Photochemistry

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

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

- i) How many photons are there in a light pulse of energy 2 mJ at a wavelength of 500 nm?
(2 marks)
- ii) Biacetyl triplets are phosphorescent with a triplet state lifetime of 10^{-3} s. If the phosphorescence is quenched by a quencher Q with a diffusion-controlled rate constant of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$, what concentration of Q is required to reduce the phosphorescence by half?
(4 marks)
- iii) Explain, with the aid of a suitable diagram, what is meant by the term 'intersystem crossing'.
(3 marks)
- iv) Identify, with reference to a clearly labelled diagram, all the allowed $\pi - \pi^*$ absorption transitions of 1,3,5 hexatriene.
(3 marks)

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

- i) Compare the photophysical properties of zinc porphyrin and $\text{Ru}(\text{bpy})_3^{2+}$, highlighting the important differences between the two molecules.

You may find the following photophysical data useful.

	Porphyrin	$\text{Ru}(\text{bpy})_3^{2+}$
Lowest energy absorption maximum	620 nm	480 nm
Emission Maximum	630 nm	620 nm
Emission Quantum Yield	0.2	0.04
Emission Decay Time	6 ns	620 ns

(7 marks)

- ii) Which of the two dyes in part i) would be most useful for the initiation of photochemical reactions in solution? Explain your answer.
(3 marks)

QUESTION CONTINUED OVERLEAF

- iii) A molecular energy transfer relay is synthesised, comprising a zinc porphyrin donor coupled to a free base porphyrin acceptor. The quantum yield of energy transfer from the zinc porphyrin S_1 state to the free base porphyrin is measured to be 30 %. Determine the energy transfer rate constant.

(3 marks)

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

- i) The rate constant for electron transfer between molecular donors and acceptors is related to their spatial separation by:

$$k_{\text{et}} \propto e^{-\beta r}$$

Explain the physical origin of this relationship.

(6 marks)

- ii) The following table shows data obtained experimentally for a photosynthetic reaction centre, giving the observed rate constants for electron transfer between different co-factors and their edge-to-edge distances:

Reaction	$\text{BChl}^- \rightarrow \text{BPh}$	$\text{BPh}^- \rightarrow \text{BChl}_2^+$	$\text{BPh}^- \rightarrow \text{Q}_\text{A}$	$\text{Cyt c} \rightarrow \text{BChl}_2^+$	$\text{Q}_\text{A}^- \rightarrow \text{Q}_\text{B}$	$\text{Q}_\text{A}^- \rightarrow \text{BChl}_2^+$
r/nm	0.48	0.95	0.96	1.23	1.35	2.24
$k_{\text{et}}/\text{s}^{-1}$	1.58×10^{12}	4×10^9	1×10^9	1.58×10^8	4×10^7	63.1

Demonstrate that these data are in agreement with the expected distance dependence of the electron transfer rate constant, and determine the value of β .

Why is a chain of redox co-factors essential for the efficient function of photosynthetic reaction centres?

(7 marks)