IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – MAY 2011, 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
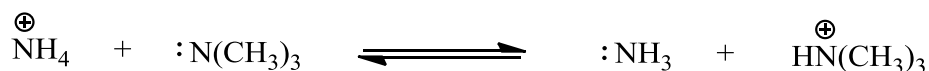
Paper 3

Friday 13th May 2011, 09:30-12:30

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

3.I8 – Solvents and Solvent Effects

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

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

For the equilibrium reaction at 25°C:

$$\overset{\oplus}{N}H_4 \;\; + \;\; :N(CH_3)_3 \;\; \rightleftharpoons \;\; :NH_3 \;\; + \;\; \overset{\oplus}{H}N(CH_3)_3$$

ΔG_{rxn} in water has been measured as -3 kJ/mol, indicating that ammonia and trimethylamine have very similar basicities. However, ΔG_{solv} of the reactants is -331 kJ/mol while ΔG_{solv} for the products is -242 kJ/mol.

i) Draw a thermochemical cycle for this reaction and clearly label the ΔG of each step.

(4 marks)

ii) Calculate ΔG_{rxn} for the reaction taking place in the gas phase.

(2 marks)

iii) Which is the stronger base in the gas phase, NH_3 or $N(CH_3)_3$? Briefly explain your choice.

(2 marks)

iv) Explain how solvation effects equalize the basicities of these two molecules in water.

(2 marks)

v) Draw the likely transition state for this reaction.

(2 marks)

vi) Plot on the same graph the reaction free energy diagram for this reaction in both water and the gas phase. Clearly label every ΔG.

(6 marks)

vii) The relative solvation of which two states determines the solvent effect on the rate of reaction?

(1 mark)

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

The copper complex $Cu(acac)_2$, acac=acetylacetonate, displays large solvatochromic shifts in different solvents. The λ_{max} for this complex in various solvents has been measured (see table below).

Solvent	λ_{max} (nm)
Acetonitrile	571
Dichloromethane	515
Dimethylsulfoxide	617
Tetrahydrofuran	571
Water	602

i) Explain how this result could be used to develop a solvatochromic scale.

(1 mark)

ii) Draw the most likely configuration for the solvated complex. Briefly explain how this configuration affects λ_{max}.

(4 marks)

iii) Briefly explain why the energy of transition is lower in more polar solvents.

(1 mark)

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

The Mentshukin reaction of tripropylamine with iodomethane was found to follow the Kirkwood theory. Reaction rate data in various solvents were obtained at 30°C (see table below).

Solvent	ε	k_2 (s^{-1} M^{-1})
Toluene	2.3	$1.0*10^{-4}$
Dichloromethane	8.4	$1.0*10^{-2}$
Acetone	21.5	$3.5*10^{-2}$
Nitrobenzene	37.3	$5.0*10^{-2}$

i) Derive a LSER (Linear Solvation Energy Relationship) for this reaction using the Kirkwood parameter, $\dfrac{\varepsilon-1}{2\varepsilon+1}$.

(3 marks)

ii) What would you expect the rate of reaction constant to be in chlorobenzene ($\varepsilon = 5.4$)?
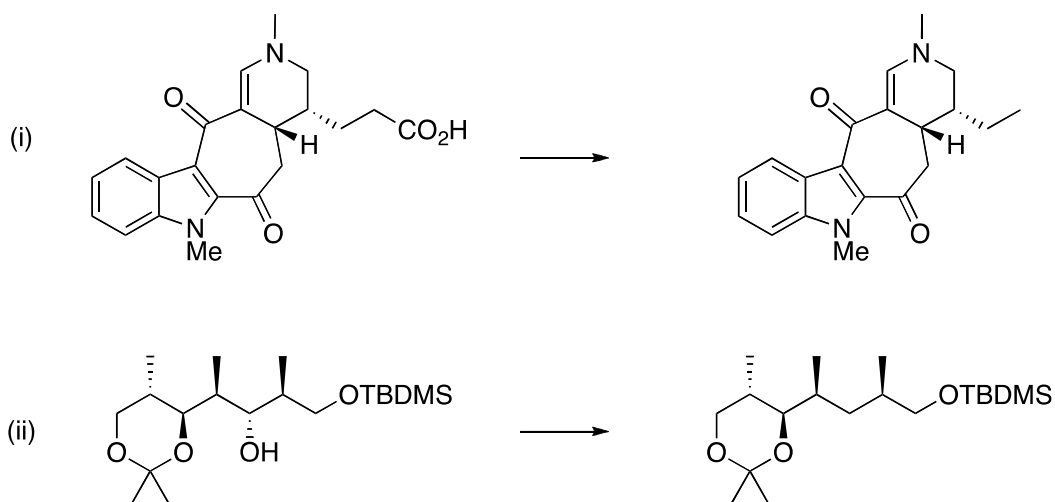
(1 mark)

iii) The reaction rate constant in methanol ($\varepsilon = 32$) was found to be $k_2 = 2.2 * 10^{-5}$ s^{-1} M^{-1}. Explain this result.
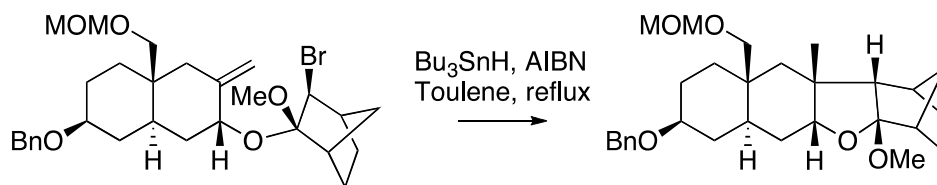
(2 marks)

3.O5 – Reactive Intermediates 2

Answer **ALL** parts of this question.

a) Suggest a radical-based method for carrying out **ONE** of the following transformations, giving reagents and a mechanism. More than one step may be required.
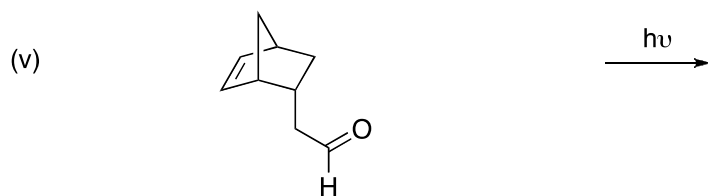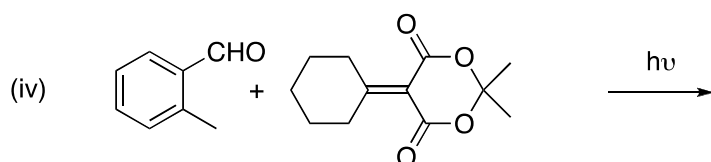
(i)

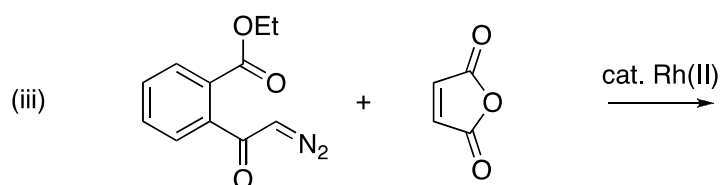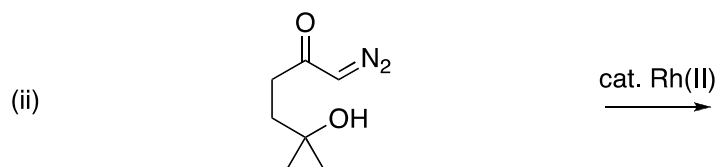(ii)

(5 marks)

b) Provide a mechanism for the following transformation commenting on any aspects of selectivity.

Bu₃SnH, AIBN
Toulene, reflux

(5 marks)

c) Give the products and mechanisms for **THREE** of the following reactions, noting carefully important regiochemical or stereochemical aspects.

(i) $Ph\diagup Ph$ + $\underset{H}{\overset{N_2}{\diagdown}}CO_2Et$ $\xrightarrow{\text{cat. Rh(II)}}$

(ii) (structure: ketone with pendant N_2 and OH groups) $\xrightarrow{\text{cat. Rh(II)}}$

(iii) (structure: aromatic ring bearing OEt ester and α-diazoketone N_2) + (maleic anhydride) $\xrightarrow{\text{cat. Rh(II)}}$

(iv) (2-methylbenzaldehyde, CHO) + (cyclohexylidene Meldrum-type dioxinedione) $\xrightarrow{h\upsilon}$

(v) (norbornene with pendant acetaldehyde CHO group) $\xrightarrow{h\upsilon}$
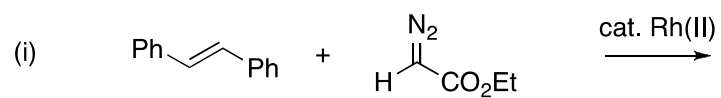
(5 marks each)

3.O10 – Molecular Modelling

Answer any **TWO** of the three questions a), b) or c) of this question.

a) An article published in 2006 has the intriguing title "Tetra-*t*-butylethylene, fantasy, fake, or reality?" (DOI: 10.1007/s11224-006-9061-x). This molecule (**1**) has thus far resisted all attempts at its synthesis. Describe how you would go about modelling the geometry and stability of this species. Include in your answer the following aspects:

   i) How to predict the central C=C bond length, including in your answer brief details of any algorithm that would be used for this prediction based on a total calculated energy for the system.
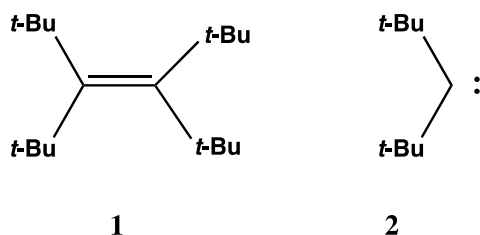
   (3 marks)

   ii) How to assess whether it might be made by dimerization of di (*t*-butyl) carbene (**2**).

   (3 marks)

   iii) Describe one pro OR one con of attempting to use **each** of the following general modeling techniques for **1**; molecular visualization, molecular mechanics and density functional molecular orbital methods

   (6 marks)

1   **2**

   (+ 0.5 bonus mark)

b) A general form of the Pirkle reagent (**3**) is shown on page 7. Answer the following three questions about how you would go about modelling this system, using any of the following general modeling techniques; molecular visualization, molecular mechanics and density functional molecular orbital methods.

   i) Describe a suitable method for obtaining the energy of dimerization of such a system. Distinguish in your answer methods which include entropy and those that do not.

   (4 marks)

   ii) Describe **two** modelling methods for probing the location(s) of any intermolecular hydrogen bonding involving the OH group.

   (4 marks)

iii) Describe how you might go about identifying any significant intramolecular (non-covalent) interactions involving the groups X and Y (normally X=Y=H) and obtaining approximate estimates of their strengths, using an appropriate modelling technique as listed above
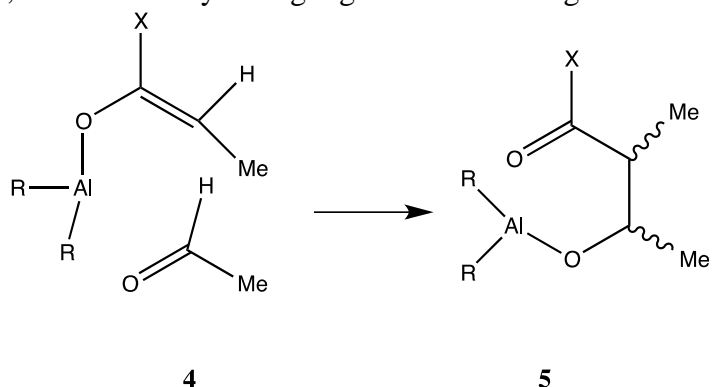
(4 marks)
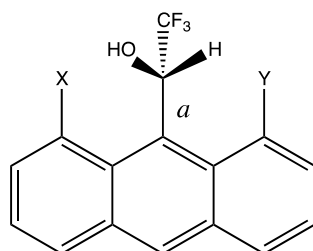
3

(+ 0.5 bonus mark)

c) A synthetic chemist wants to know how they might best control the stereochemical outcome of the reaction **4** to **5**. Using any of the following general modeling techniques, molecular visualization, molecular mechanics and density functional molecular orbital methods as appropriate, describe how you might go about modeling the following three aspects:

4   **5**

i) The procedure involved in estimating the rate constant for the reaction (R=Et, X=Me) at 298K. Include in your answer any aspects of the conformation of the system.

(4 marks)

ii) How you would go about estimating factors determining the relative concentrations of the two diastereomers of **5** that might form, for the case X=Me?

(4 marks)

iii) The synthetic chemist suggests a group X that they think might result in more than 90% of a single stereochemical isomer of **5**. How would you go about assessing that prediction and what special characteristic must X have to give such an outcome?

(4 marks)

(+ 0.5 bonus mark)

3.P6 – Molecular Electronic Materials

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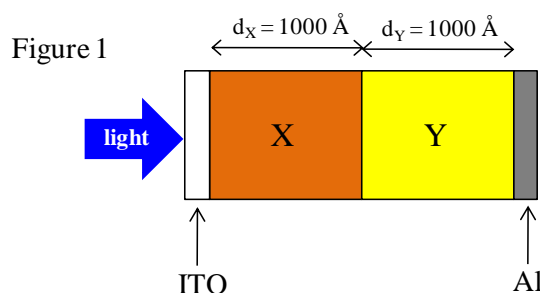
a) Answer **ALL** parts of this question.

Figure 1

Figure 1 shows a bilayer solar cell based upon a photoactive layer comprising two semiconducting polymers X and Y sandwiched between an indium tin oxide (ITO) anode and an aluminium (Al) cathode. Polymer X has a thickness of 1000 Å and polymer Y has a thickness of 1000 Å. A photocurrent is generated when the device is illuminated with monochromatic light of appropriate wavelength.

i) Explain, with the aid of a suitable diagram why the energy conversion efficiency of bilayer solar cells tends to be higher than those of single layer solar cells.

(4 marks)

ii) The exciton diffusion length is approximately 60 Å in both polymers X and Y, and the extinction coefficient at the illumination wavelength is approximately 0.003 Å^{-1} in both materials. Draw a diagram showing the exciton generation profile as a function of distance from the ITO anode, marking clearly the position of the heterojunction.

(3 marks)

iii) Show that the fraction of excitons (n) which dissociate as a result of reaching the heterojunction is approximately equal to:

$$n = 2kl\exp(-kd_x)$$

where l is the exciton diffusion length, k is the extinction coefficient and d_x is the thickness of polymer layer X.

(4 marks)

iv) Using the expression in part iii), calculate the fraction of excitons (n) that will benefit from the existence of the heterojunction when the device in Figure 1 is illuminated with light. Suggest a modification you could make to the structure of the photoactive layer to enhance n explaining your reasoning.

(4 marks)

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

   i) How do the mobilities of charge carriers in organic semiconductors typically vary with electric field?

   (3 marks)

   ii) Explain with reasons what charge carrier mobility characteristics are required for a high power conversion efficiency in:

   • An organic donor-acceptor heterojunction solar cell.
   • A single layer organic light emitting diode.

   (4 marks)

   iii) A 1.5 µm thick film of a particular semiconducting polymer was sandwiched between two electrodes. A transit time for electrons was found to be 60 ns when 7 V was applied across the electrodes. From this data calculate the mobility of the electrons.

   (3 marks)

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

   i) Distinguish between Fowler-Nordheim and thermionic-emission charge injection mechanisms.

   (4 marks)

   ii) The external quantum efficiency $\eta_{\phi(ext)}$ of an organic light emitting diode is given by the following equation:

$$\eta_{\phi(ext)} = \gamma \times \alpha \times \phi \times \beta$$

   Explain the physical meaning of each term in the above equation and suggest how you would optimize each of the terms.

   (6 marks)

3.P10 – Soft Condensed Matter

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

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

   i) With the aid of suitable graphs briefly discuss how the length scale of interactions influences the phase diagram of soft materials.

                (3 marks)

   ii) The Bjerrum length is an estimate of the interaction range between two charged colloids in a suspension. In an experiment it is observed that the colloid liquid phase becomes unstable when the interaction range is about 20 nm. Estimate the dielectric constant of the suspension assuming a colloids charge of 5 e⁻, and a temperature of 300 K.

                (3.5 marks)

   iii) For a glass, sketch the dependence of the entropy on temperature, indicating the location of the Kauzmann temperature. Briefly explain the physical meaning of this temperature.

     How does the speed of undercooling affect the entropy dependence with temperature? Justify your answer.

                (3.5 marks)

   iv) The relaxation time for configurational rearrangements in a glass is given by the Vogel-Fulcher equation,

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right)$$

     The glass transition temperature of an experiment performed on a 10^4 second timescale is 200 K. Estimate the glass transition temperature when the experimental time increases by two orders of magnitude assuming $B = 10^3$ K and $T_0 = 50$ K.

     Comment on your result.

                (5 marks)

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

  i) For a homogeneous nucleation process, sketch the dependence of the Gibbs free energy on the radius of a spherical nucleus. Justify your answer by discussing the different contributions to the Gibbs free energy.

  (3 marks)

  ii) For the process referred to in part i) the radius of the critical nucleus, r^*, is given by:

  $$r^* = \frac{2\gamma_{sl} T_m}{\Delta H_m \Delta T}$$

  Define all the terms in this equation.

  (1.5 marks)

  iii) By considering the Gibbs free energy of homogeneous nucleation, derive the equation for r^* in (ii)

  (5.5 marks)

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

  i) A colloidal suspension coagulates when the average distance between the colloids is 1 nm. Estimate the *molar* concentration of KCl needed to coagulate the suspension at 300 K assuming a dielectric constant of 78.

  (5 marks)

  ii) Experimental studies have shown that the van der Waals interactions between colloidal particles dispersed in a solvent can be repulsive, attractive or zero, depending on the composition of the colloidal particles.

  Explain these observations. Your answer should contain all the relevant equations.

  (5 marks)