IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – MAY 2010, 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

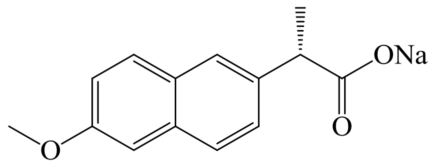
Friday 7th May 2010, 14:00-17:00

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

3.I8 – Solvents and Solvent Effects

Answer parts (a) **AND** (b) **AND EITHER** part (c) **OR** part (d)

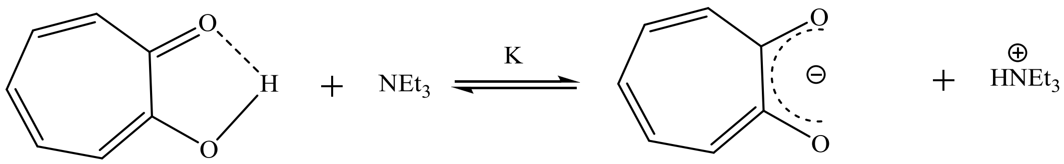
a) (*S*)-Naproxen (shown below) is a common anti-inflammatory agent. The final purification step for this compound involves recrystallisation from water. Rank the solvents acetone, ethanol and hexane in order of their effectiveness as anti-solvents. Give a brief justification for each solvent.



(3 marks)

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

The reaction between tropolone and triethylamine is shown below.



i) The equilibrium constant (*K*) has been measured in chloroform, diethyl ether, dimethylsulfoxide, *n*-heptane and tetrachloromethane. List these solvents in order of their ability to increase the equilibrium constant for the reaction.

(3 marks)

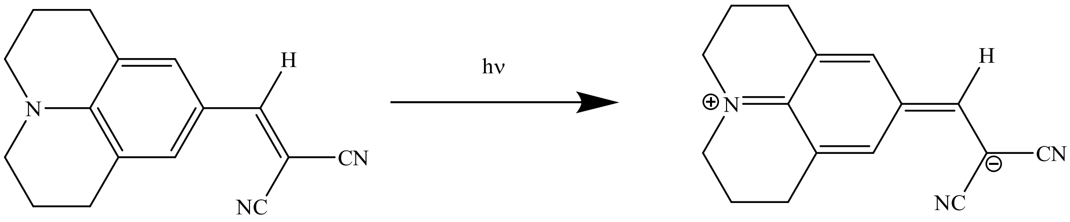
ii) With reference to the reaction steps and the interactions influencing free energy and solvation, provide a detailed explanation for your ordering in part (i).

(11 marks)

QUESTION CONTINUED OVERLEAF

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

9-(Dicyanovinyl)julolidine (DCVJ) is used as a solvatochromic probe because of the interesting properties of its highly polar excited state (absorbance spectrum).



DCVJ

i) Explain how DCVJ can be used as an indicator of solvent polarity. Would the DCVJ absorbance shift to longer or shorter wavelengths as solvent polarity is increased?

(4 marks)

ii) DCVJ can also be used as an indicator of solvent viscosity (a "molecular rotor"). Which bond in the excited state can rotate to indicate solvent viscosity? How might solvent viscosity affect this rotation?

(2 marks)

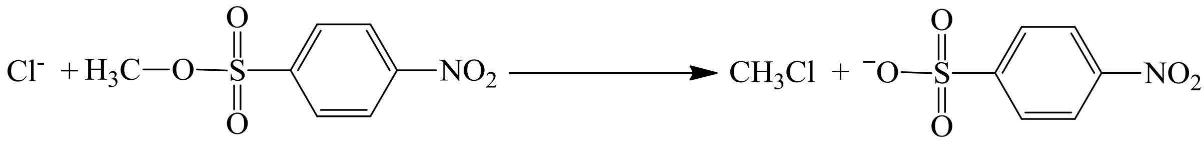
iii) Which will be more affected by strong hydrogen-bond donating solvents, the ground or the excited state of DCVJ, and why?

(2 marks)

QUESTION CONTINUED OVERLEAF

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

The nucleophilic substitution reaction shown below is known to proceed through an S_N2 mechanism.



Solvent	α	k_2 (s^{-1} M^{-1})	ln (k_2)
Acetone	0.08	0.0030	-5.8
Acetonitrile	0.19	0.0010	-6.9
Butanol	0.84	$1.5*10^{-6}$	-13.4
Dichloromethane	0.13	0.0018	-6.3
Tetrahydrofuran	0	0.0067	-5.0

Rate data were obtained in various solvents, and it was discovered that the reaction rate constant depended solely on the Kamlet-Taft α parameter.

i) Give the LSER equation and calculate any system specific parameters using the above data.

(3 marks)

ii) Explain the observed α dependence using the Hughes-Ingold Rules.

(2 marks)

iii) Describe the specific interaction(s) within the reaction mechanism that are affected by α. How do these interactions affect the rate of reaction?

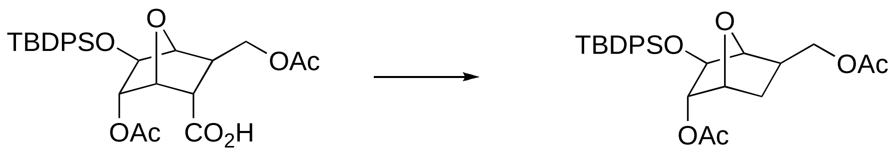
(3 marks)

3.O5 – Reactive Intermediates 2

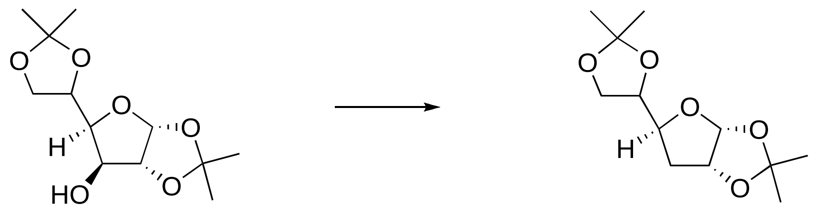
Answer **ALL** parts, (a)-(c)

a) Suggest a radical-based method for carrying out **ONE** of the following transformations, giving reagents and a mechanism.

(i)



(ii)

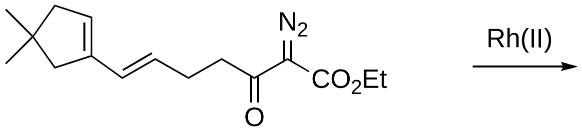


(5 marks)

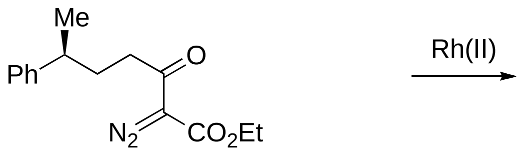
QUESTION CONTINUED OVERLEAF

b) Give the products and the mechanisms for **THREE** of the following reactions, noting carefully (a) the spin multiplicity of the reactive intermediate, (b) any other intermediates beyond the carbene, nitrene or photoexcited state and (c) any important regiochemical or stereochemical aspects.

(i)

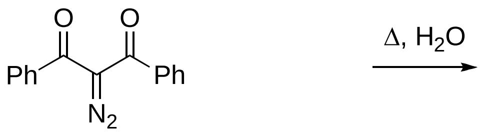


(ii)

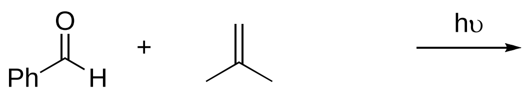


(iii)

(iv)



(v)



(5 marks each)

3.O10 – Molecular Modelling

Answer **EITHER** part a) **OR** part b).

a) Organic molecular modelling can be characterised by the following six major themes;

1. Molecular scales
2. Molecular coordinates
3. Visualisation
4. Structure analysis
5. Structure and property prediction
6. Reactivity and potential energy surfaces.

Discuss the characteristic features of any **FOUR** of these aspects. Do **NOT** include in your discussion explicit case-studies, but **DO** include any relevant concise examples illustrating any issues involved in any theme.

(6 marks per theme plus 1 bonus mark)

b) The so-called Pirkle reagent is shown below. Discuss how molecular modelling can illuminate various aspects of the properties of this molecule, including in your answer specific discussion of any **FOUR** of the following aspects.

(6 marks per item plus 1 bonus mark)

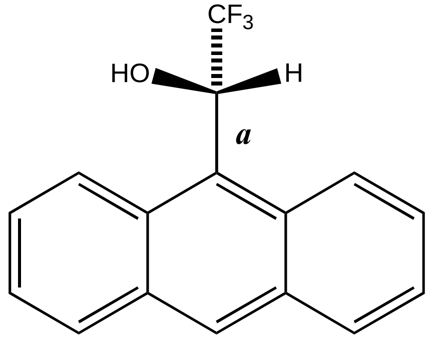
i) How any intra/inter molecular hydrogen bonding and other weak interactions can be revealed using modelling techniques.

ii) How the equilibrium conformation and barrier to rotation about the bond marked ***a*** might be rapidly predicted (including discussion of any one approximation in the modelling which might influence the prediction), and how this prediction might be compared with experiment.

iii) The issues involved in predicting the energetics of intermolecular dimer formation of this species using the molecular mechanics method.

iv) The issues involved in predicting the thermodyamics of intermolecular dimer formation of this species using quantum mechanics based methods.

v) Discuss **TWO** modelling methodologies that might be used to predict the outcome of electrophilic nitration of this species.

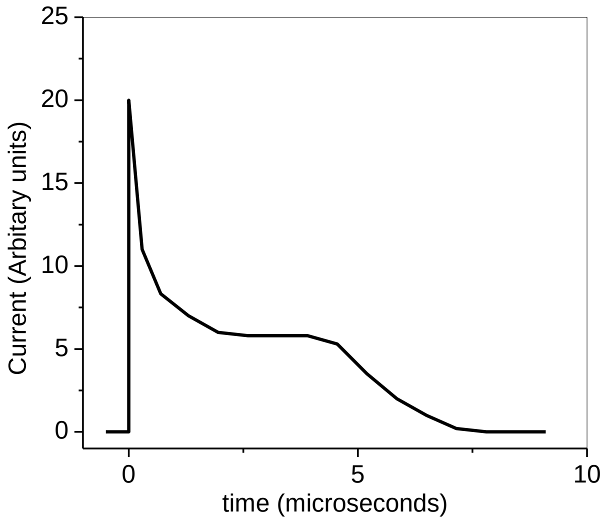


3.P6 – Molecular Electronic Materials

Answer part a) **AND EITHER** part b) **OR** part c)

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

The figure below shows data obtained from a time-of-flight (ToF) experiment for a hole-transporting arylamine polymer.



i) Explain, with the aid of a relevant equation what is meant by charge carrier mobility.
(2 marks)

ii) With the aid of suitable diagrams, describe the ToF technique that is used for the determination of charge carrier mobility.
(5 marks)

iii) Estimate the hole mobility for the arylamine polymer from the data in the figure above. You can assume a device thickness of 180 nm and an applied voltage of 120 volts.
(4 marks)

iv) Discuss, with the aid of a suitable graph, the statement: "The hole mobility in organic semiconductors is often observed to be greater in magnitude than the corresponding electron mobility."
(3 marks)

QUESTION CONTINUED OVERLEAF

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

i) The space charge limited current (J_{SCLC}) is given by the following equation:

$$J_{SCLC} = \frac{Q}{t} = \frac{\varepsilon_r \varepsilon_o \mu V^2}{d^3}$$

Derive the above equation, stating clearly any assumptions used.

(6 marks)

ii) The following electrical characteristics were obtained for a polymer film sandwiched between two electrodes. The terms *J* and *E* refer to the current density and electric field strength respectively.

J (A/m^2)	0.025	0.06	0.1	0.2	0.33
E (V/nm) $\times 10^{-3}$	1.5	2.3	3.1	3.8	5.4

Show that these data are consistent with the space charge limited current model.

(5 marks)

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

A two component, nanostructured film comprising a blend of a poly-3-hexylthiophene (P3HT) and a fullerene derivative (PCBM) can be used as the photoactive layer in an organic solar cell. The HOMO and LUMO energies of P3HT are 4.9 eV and 2.6 eV respectively. The HOMO and LUMO energies of PCBM are 6.8 eV and 3.8 eV respectively.

i) Calculate the exciton binding energy in P3HT. You can assume an exciton radius of 6 nm and a dielectric constant of 2.9 for the P3HT polymer.

(4 marks)

ii) Explain with the aid of suitable diagrams, the function of a solar cell based upon a nanostructured film comprising a blend of P3HT and PCBM, detailing the mechanisms of operation, and explaining the need for the use of a nanostructured blend. What are the particular characteristics of the materials P3HT and PCBM that make them suitable for the fabrication of organic solar cells?

(7 marks)

3.P10 – Soft Condensed Matter

Answer part (a) and **EITHER** part (b) **OR** part (c).

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

i) Silica and toluene form glasses with very different behaviours. Silica behaves as a strong glass, whereas toluene is a prototype of a fragile glass. Sketch the temperature dependence of the viscosity for these two materials.

Explain the origin of the "strong" and "fragile" behaviour.

(3.5 marks)

ii) Upon addition of salt, a colloidal suspension precipitates forming a crystal. Assuming the characteristic interaction between colloid pairs is 5 kJ/mol, and the density of the crystal, 10^{21} colloids/m^3, estimate the Young's modulus of the crystal.

Will the crystal resist strong deformations? Justify your answer.

(3.5 marks)

iii) Addition of polymer to a colloidal suspension increases the "attractive" interaction between the colloids. This attractive interaction also increases with temperature.

Explain this observation and write an approximate equation that describes the colloid-colloid interaction.

(4 marks)

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

The free energy of mixing of a binary polymer mixture can be quantified using mean field theory:

$$\frac{\Delta F}{k_B T} = \chi x_a x_b + x_a \ln x_a + x_b \ln x_b$$

i) Sketch the coexistence phase diagram, temperature vs composition, of the polymer mixture. Clearly show in your diagram: the critical point, binodal and spinodal lines, and metastable, unstable and stable regions.

(3 marks)

QUESTION CONTINUED OVERLEAF

ii) Estimate the composition on the spinodal line at T=300 K. You may consider $\chi = 800/T K^{-1}$ as the value of the interaction parameter.

(5 marks)

iii) The two figures below show examples of the patterns observed during the polymer demixing process.

Explain which compositions give rise to these two patterns?

Using an appropriate free energy diagram explain the origin and discuss the differences between these two demixing processes.

(6 marks)

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

The freely jointed model (FJC) accurately describes the force-extension curve of polymers, such as DNA, for small extensions.

The probability of the end-to-end distance for a polymer chain in the FJC model is given by:

$$P(r,N) = C\exp\left[\frac{-3r^2}{2Na^2}\right]$$

i) Show that the extension force predicted by the FJC model is:

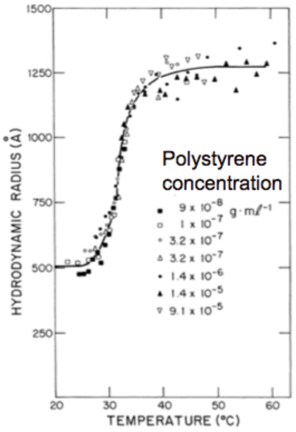
$$f = -k_B T \frac{3r}{Na^2}$$

Justify all your working.

(7 marks)

QUESTION CONTINUED OVERLEAF

ii) The figure below shows the variation of the hydrodynamic radius of polystyrene with temperature.



Explain the origin of the transition observed in this experiment.

(4 marks)

iii) Assuming a degree of polymerization for polystyrene of 10^4 and a monomer length of 0.67 nm, estimate the end-to-end distance of the polymer at the theta temperature.

(3 marks)