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
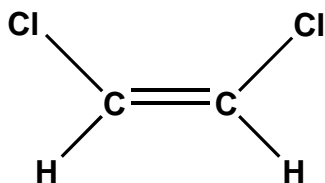
ADVANCED CHEMISTRY THEORY IIIB

Paper 2

Wednesday 5th May 2010, 14:00-17:00

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

3.I6 – Inorganic Symmetry and Spectroscopy

Answer **BOTH** part (a) **AND** part (b)

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

Determine Γ_{vib}(*cis*-1,2-dichloroethene). Show your working.

(7 marks)

Use the projection method to determine the equations for the **C-Cl stretching** vibrations. Show your working and draw a representative diagram for each of the vibrations.

(6 marks)

b) Answer **ANY TWO** parts from parts (i), (ii), and (iii).

i) From the equation given below **derive** the expansion coefficients for the (time independent) perturbed wavefunction. **Define** the perturbing Hamiltonian for a lightwave interacting with a molecule.

$$\left[H^{(0)} - E^{(0)} \right] \psi^{(1)} = \left[E^{(1)} - H^{(1)} \right] \psi^{(0)}$$

(6 marks)

ii) **Define** the closure, identity and inverse axioms for groups. **Explain** how the group multiplication table for C_3 given below, illustrates each of these axioms.

C_3	E	C_3^1	C_3^2
E	E	C_3^1	C_3^2
C_3^1	C_3^1	C_3^2	E
C_3^2	C_3^2	E	C_3^1

(6 marks)

iii) **Define** the equivalence relationship. With reference to the diagram below, **show** using diagrams that the $\sigma_v(xz)$ and $\sigma_v(yz)$ operations in the C_{2v} point group are not conjugate. **Identify** one point group in which the σ_v operations are conjugate.

x-axis comes out of the page
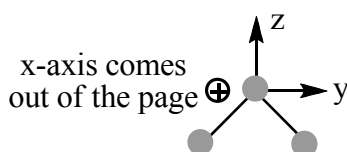
(6 marks)

3.I7 – Lanthanide and Actinide Chemistry

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

a) Read the information below and answer **ALL** parts of this question.

The ligand, **L** (Figure 1), reacts with Nd^{3+} and Yb^{3+} salts in water to form coordination complexes that display strong Infra-Red emission when sensitised with visible light. The electronic process that produces this fluorescence in the **Yb** complex (Figure 2) involves a transition from the **first** excited state to the ground state.
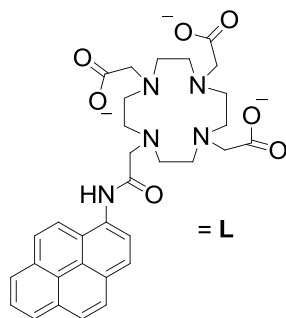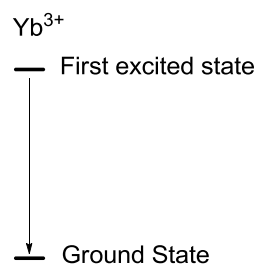

Figure 1   **Figure 2**

i) Describe the features of the macrocyclic ligand **L** which make it suitable for the purpose described.

(4 marks)

ii) State which complex (Nd or Yb) will have the higher stability constant in aqueous solution and explain your reasoning.

(4 marks)

iii) Use Hund's rules to determine the term symbols $^{(2S+1)}L_J$, of the ground **and** first excited states of the Yb complex.

(5 marks)

b) Suggest possible products from the following reactions. In your answer give your reason and include a brief discussion on the bonding and oxidation states of the products.
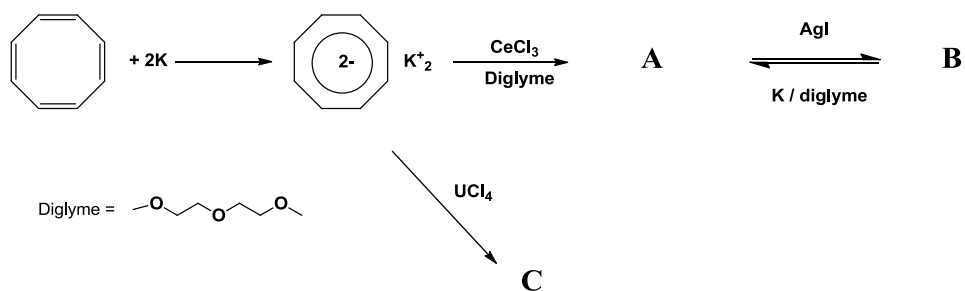
(8 marks)

c) Why are the oxo ligands of the octahedral uranium(VI) species $[UO_2Cl_4]^{2-}$ located in a *trans* configuration, while the oxo ligands of the octahedral tungsten(VI) complex $[WO_2Cl_4]^{2-}$ are mutually *cis*?
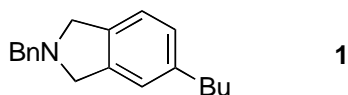
(4 marks)

d) With reference to the variable electronic structure of its ions, explain how compounds of cerium are widely employed as reagents in organic synthesis.

(4 marks)

3.O1 – Organometallic Complexes in Organic Synthesis

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

a) Arene **1** was formed by a [2+2+2] trimerisation reaction. Write down the two substrates used and suggest a metal catalyst for the reaction.

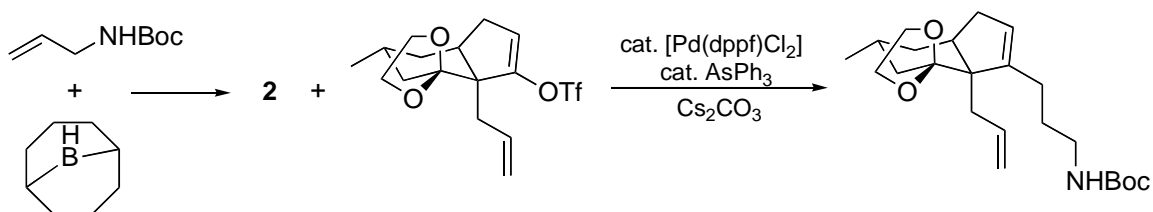$$\text{BnN} \qquad \qquad \text{Bu} \qquad \qquad \textbf{1}$$

(5 marks)

b) The following reaction has been described as a molybdenum-mediated hetero-Pauson-Khand reaction. Write down the product of the reaction.

$$\xrightarrow{\text{Mo(CO)}_3\text{(DMF)}_3}$$
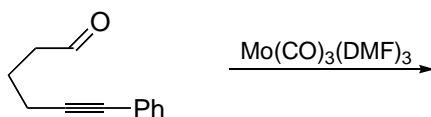
(5 marks)

c) Name the types of the two reactions involved in the sequence shown below. Write down the structure of **2**.

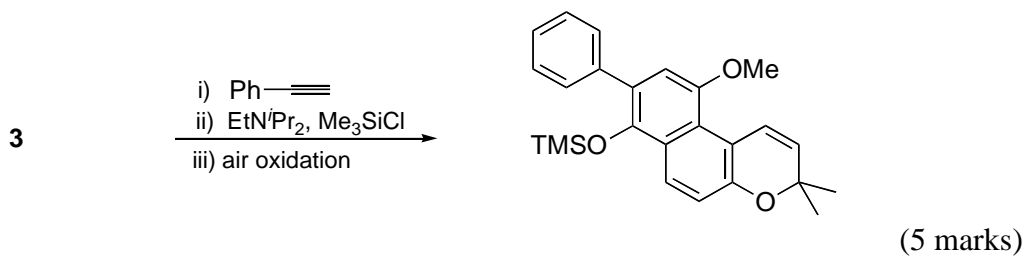$$\xrightarrow[\text{Cs}_2\text{CO}_3]{\begin{array}{c}\text{cat. [Pd(dppf)Cl}_2\text{]}\\ \text{cat. AsPh}_3\end{array}}$$
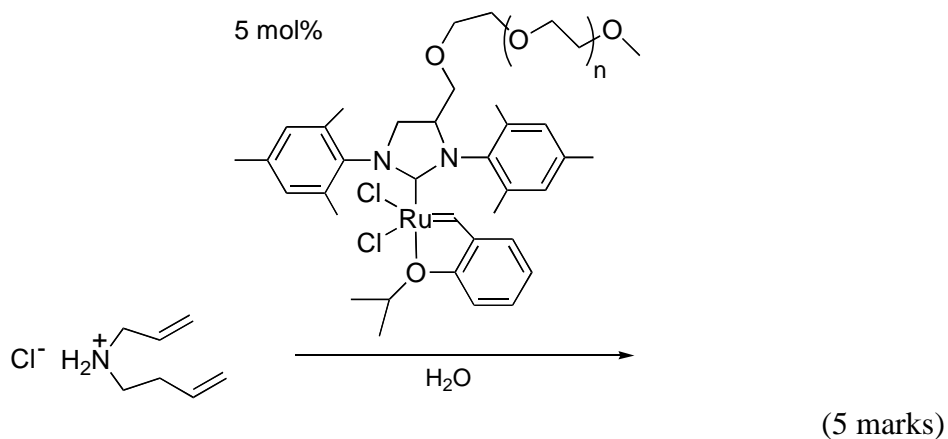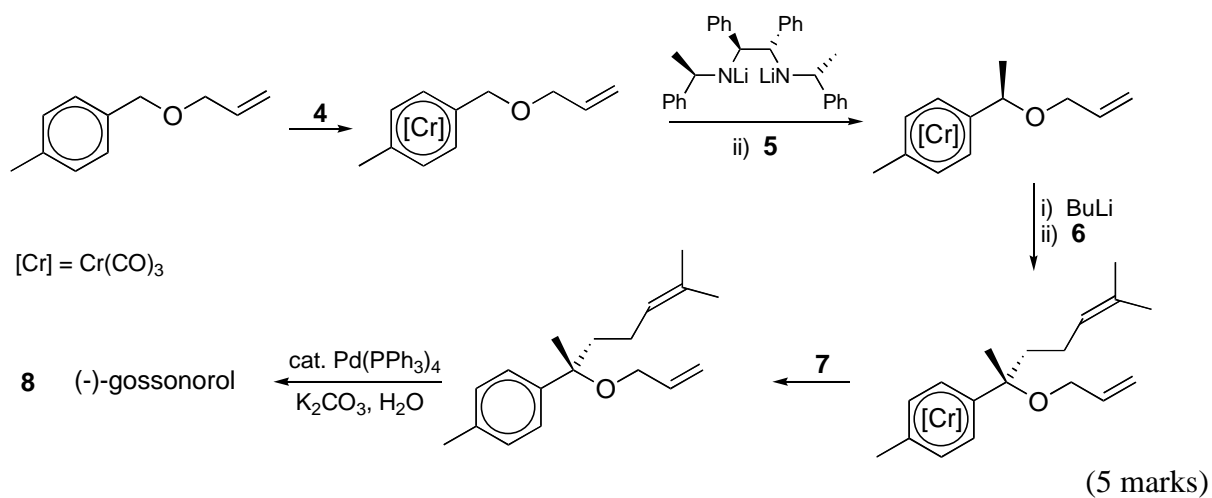
dppf = 1,1'-bis(diphenylphosphino)ferrocene

(5 marks)

d) Write down the structure of the chromium carbene **3** used as the substrate for the following reaction sequence.

3

i) Ph—≡
ii) EtN^{i}Pr$_2$, Me$_3$SiCl
iii) air oxidation

(5 marks)

e) Predict the two products of the following reaction. What was the purpose of incorporating the polyether chain into the catalyst?

5 mol%

Cl$^-$ H$_2$N$^+$

H$_2$O

(5 marks)

f) Write down the structures of reagents **4**-**7** and (-)-gossonorol **8**.

4

ii) **5**

i) BuLi
ii) **6**

[Cr] = Cr(CO)$_3$

cat. Pd(PPh$_3$)$_4$

K$_2$CO$_3$, H$_2$O

8   (-)-gossonorol

7

(5 marks)

3.O8 – Carbohydrate Chemistry

Answer part a) and **EITHER** part b) or c)

a) With full discussions of reagents, reaction conditions and stereochemistry, suggest methods to carry out the following three transformations. In each case, there may be more than one step in the overall process.

D-Glucopyranose (I)   II

D-Galactopyranose (III)   IV

V   Boc = CO$_2$-*t*-Bu
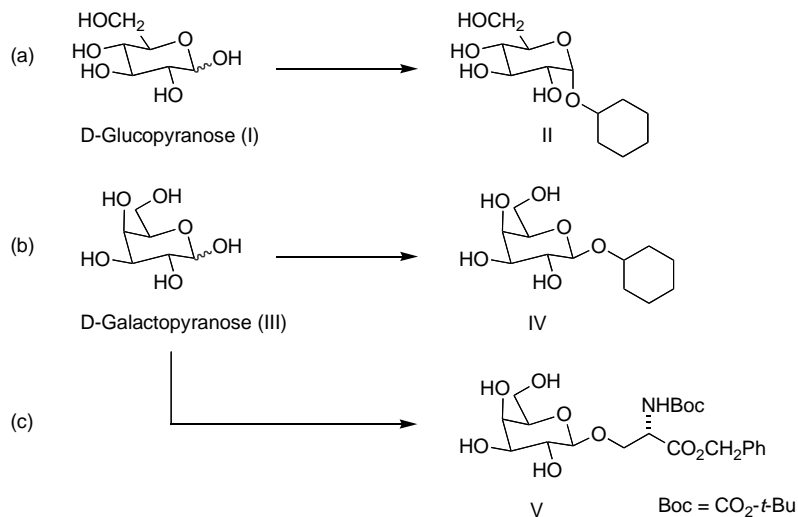
(5 marks each)

b) Starting from D-galactose, shown as D-galactopyranose (**III**) below, and *N*-acetyl-glucosamine, shown as the pyranose form **VI** below, suggest a method to synthesise the disaccharide **VII**. There are several steps in the overall process.

D-Galactopyranose (III)   VI   several steps   VII
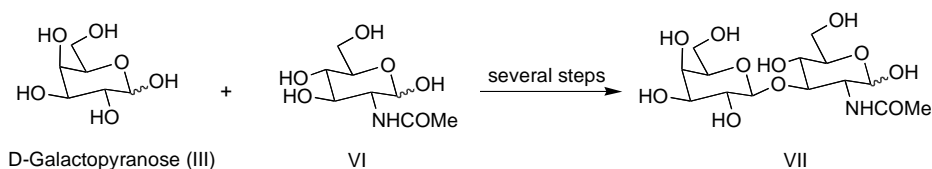
(10 marks)

c) In a total synthesis of a complex marine toxin, a key building block **X** was prepared from 2,3-*O*-isopropylidene D-glyceraldehyde (**VIII**). Suggest a method for the synthesis of **VIII** starting from D-mannose. (Hint D-mannose is epimeric with D-glucose at C-2). Secondly, suggest appropriate reagents and reaction conditions for the conversion of **VIII**, via **IX** into **X**.
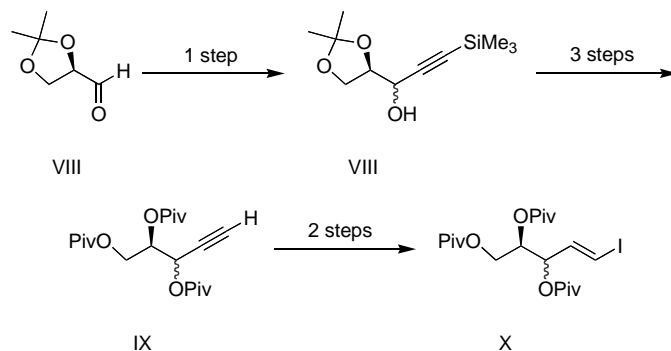
(10 marks)

3.P3 – Molecular Reaction Dynamics

Answer any **TWO** of the three parts a), b) and c)

There is an attached sheet of equations that you may find useful.

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

   i)   The distance between the electron acceptor embedded in a protein and the
        electron donor in a docking protein is 10Å. What is the rate of electron transfer
        between the donor and acceptor? Assume that the Franck-Condon factor is 1,
        and take the electron tunnelling coefficient to be 1.4 Å^{-1}.
        Carefully define each symbol used in your calculation.

        (6 marks)

   ii) Give an example of a chemical reaction in which the zero point energy of
        reactants and products needs to be taken into account. Explain how this may
        affect the rate of the reaction.

        (6.5 marks)

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

   i)   Discuss in terms of classical mechanics the observation that the reaction
        between F+HCl →Cl + HF is approximately five times as efficient when HCl is
        in its first vibrationally excited (v=1) state than when it is in its ground
        vibrational state (v=0) and the relative collision energy is increased by an
        amount equivalent to the difference $E_{v=1} - E_{v=0}$ (*i.e.* the total energy (vibrational
        and kinetic) is the same). Assuming that the interaction is collinear, draw two-
        dimensional potential energy surfaces to explain this observation.

        (9.5 marks)

   ii) Explain the Hammond Postulate.

        (3 marks)

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

   i)   Demonstrate that an observable calculated from an eigenstate does not vary with
        time even when the time-dependent part of the wavefunction is taken into
        account.

        (5 marks)

   ii) Demonstrate that an observable calculated from a linear superposition of two
        time dependent wavefunctions will show oscillations in its value as a function of
        time.

        (7.5 marks)