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
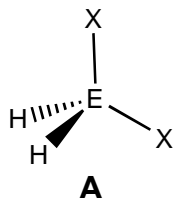
ADVANCED CHEMISTRY THEORY IIIB

Paper 2

Tuesday 10th May 2011, 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) of this question.

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

A

    i) Determine Γ_{vib} for the C_{2v} symmetry molecule EX_2H_2 (**A**). Show your working.

(7 marks)

    ii) Use the projection method to determine the equations for the **E-X stretching** vibrations. Show your working and draw a representative diagram for each of the vibrations.

(6 marks)

b) Answer any **TWO** of parts i), ii) or iii) of this question.

    i) **Describe** the Similarity Transformation. Use the fact that the identity symmetry operation e is self conjugate to **show** that $e=e^2$.

(6 marks)

    ii) **Derive** the first order correction to the energy $E^{(1)} = \int \psi_0^{(0)} H^{(1)} \psi_0^{(0)} d\tau$ using time independent perturbation theory.

Start from the expression:
$$H^{(0)}\psi^{(1)} + H^{(1)}\psi_0^{(0)} = E_0^{(0)}\psi^{(1)} + E^{(1)}\psi_0^{(0)}$$

$H^{(1)}$ = the first order perturbation to the Hamiltonian

$\psi^{(1)}$ = the first order perturbation to the wavefunction

$H^{(0)}\psi_0^{(0)} = E_0^{(0)}\psi_0^{(0)}$ is the unperturbed Schrödinger equation

(6 marks)

iii) **Write** the full reducible matrix for the $\sigma(xz)$ symmetry operation acting on H_2O (**B**). **Explain**, with reference to your matrix for $\sigma(xz)$, why the contributions to the reducible character are $+1$ per unshifted atom for a mirror plane.
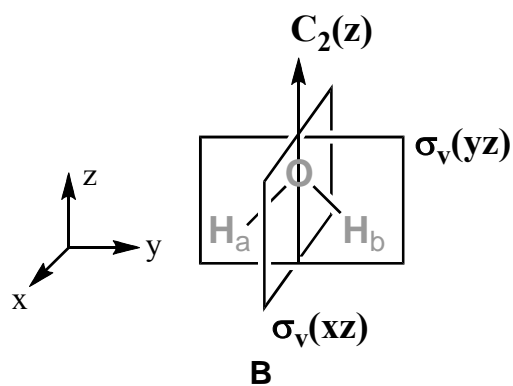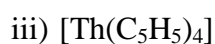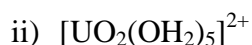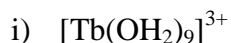

(6 marks)

3.I7 – Lanthanide and Actinide Chemistry

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

a)   Apply Hund's rules to determine the Russell-Saunders ground state term of the Ho^{3+} ion and the Gd^{3+} ion.
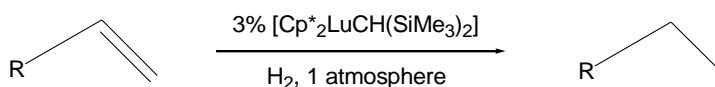
<div align="right">(6 marks)</div>

b)   Predict the shape of each of the following species, sketching the arrangement of the ligands around the metal centre.

    i) $[Tb(OH_2)_9]^{3+}$

    ii) $[UO_2(OH_2)_5]^{2+}$

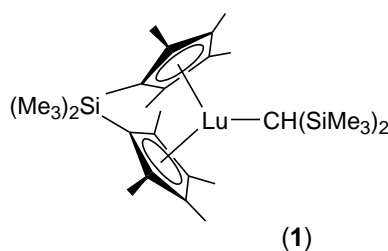   iii) $[Th(C_5H_5)_4]$

<div align="right">(6 marks)</div>

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

    i)   For the catalytic hydrogenation reaction shown below, illustrate a plausible reaction mechanism and describe the individual reaction steps involved.

<div align="right">(5 marks)</div>

    ii)   When the catalyst (**1**) shown below is used instead of $[Cp*_2LuCH(SiMe_3)_2]$ for the reaction above, the rate increases 75-fold. Explain this increase.


<div align="center">(**1**)</div>

<div align="right">(3 marks)</div>

d) Uranocene, $[U(\eta^8\text{-}C_8H_8)_2]$ is a stable, symmetric sandwich complex that has no direct counterpart in transition metal chemistry. Using a simple bonding picture discuss this statement.

<div align="right">(5 marks)</div>

e) Treatment of NdF_3 with F_2 gives no reaction, whereas treatment of UF_3 with F_2 gives UF_6. Explain this difference.

<div align="right">(5 marks)</div>

3.O1 – Organometallic Complexes in Organic Synthesis

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

a) Write down the structures of **A** and **B** paying particular attention to the regioselectivity of the reaction that generates **A** as revealed by the selected. NMR data provided for **B**.
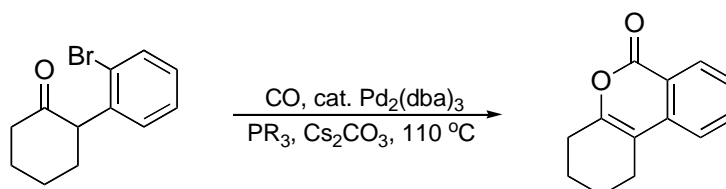

^{1}H NMR spectrum
of **B** between δ 7 and δ 8.5:
δ 7.25-7.47 (m, 6H),
8.11 (d, J = 8 Hz, 1H)
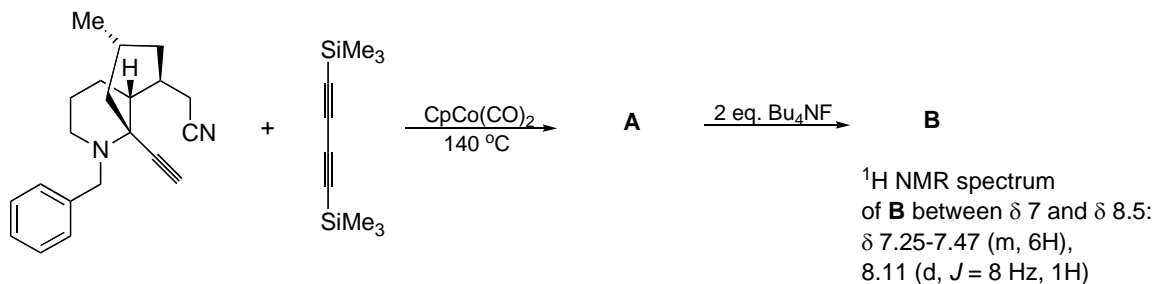
(5 marks)

b) Consider the scheme shown below. What is the role of the $Co_2(CO)_6$ in the first step? How many double bond equivalents are there in the hydrocarbon fragment of **C**? Write down the structure of **C**.

$[C_{12}H_8 \cdot Co_2(CO)_6]$
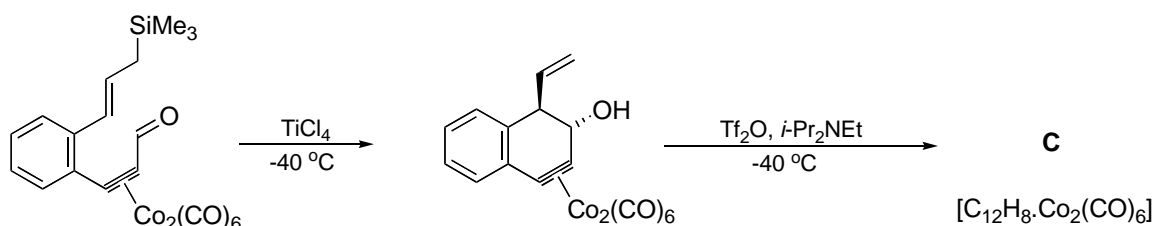
(5 marks)

c) Suggest a mechanism for the following transformation.

(5 marks)

QUESTION CONTINUED OVERLEAF

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d) Write down the structure of a pentacarbonyl chromium carbene that would undergo a Dötz reaction. Draw the structure of the product of the reaction between your carbene and diphenylethyne.
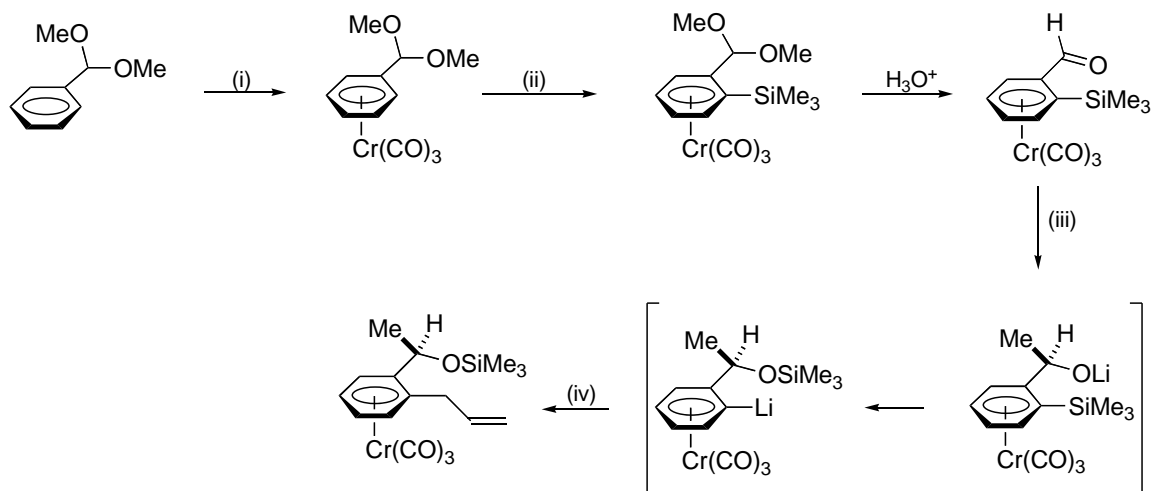
(5 marks)

e) Write down the bicyclic product of the following reaction. Overall the reaction may be viewed as an [x + y] cycloaddition. What are the values of x and y?

$$\text{0.5 mol\% RhCl(PPh}_3)_3$$
$$\text{0.5 mol\% AgOTf}$$
$$\text{toluene, 110 °C, 20 min}$$
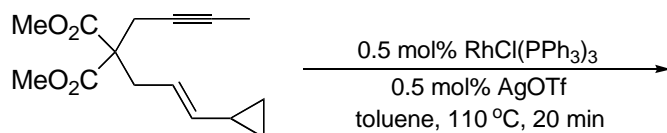
(5 marks)

f) Suggest reagents for steps (i)-(iv) and account for the stereochemical outcome of step (iii).
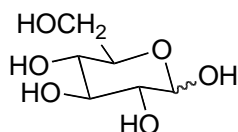

(5 marks)

3.O8 – Carbohydrate Chemistry

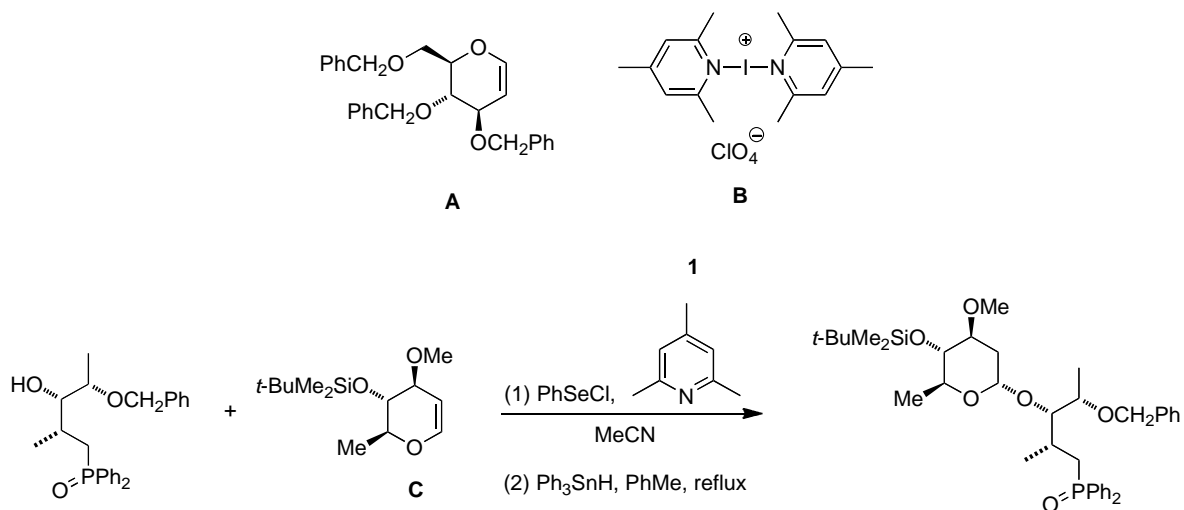Answer part a) **AND** part b) **OR** part a) **AND** part c) of this question.

a) With full discussions of reaction conditions and stereochemistry, compare and contrast two glycosidation reactions of derivatives of D-glucose using the following reagents in the key glycosidation steps (a) silver carbonate and tert-butyl alcohol and (b) tetraethylammonium bromide, tert-butyl alcohol and ethyl diisopropylamine in dichloromethane solution. Note in both of these glycosidation reactions, D-glucose will have to be first converted into a derivative for the glycosidation reaction and you are expected to provide reagents and reaction conditions for this step or these steps.


D-Glucopyranose (I)

(15 marks)

b) Give an example of a glycosidation reaction of the D-glucal derivative **A** using the iodine derivative **B** as one of the reagents.
Secondly, suggest a mechanism for the glycosidation reaction of glycal **C** as well as the deselenation reaction, as shown below.

(10 marks)

c) Suggest a mechanism for the glycosidation reaction shown below and clearly indicate the stereochemistry of the glycoside formed. What is the structure of the side product **D** (C_5H_9IO)? Hint scandium triflate [$Sc(OSO_2CF_3)_3$] is a Lewis acid.
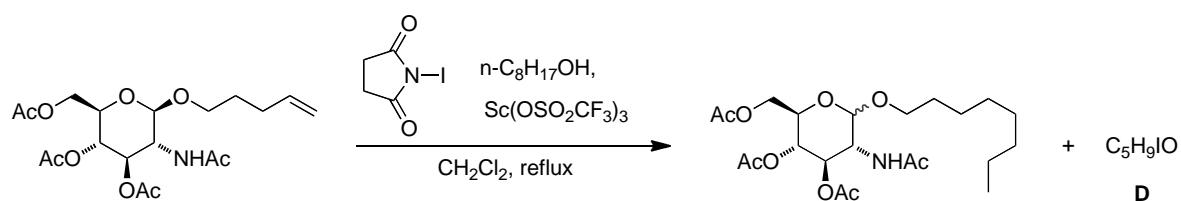
(10 marks)

3.P1 – Modern Analytical Chemistry

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

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

   i) What is a virtual state in Raman spectroscopy?

   (1 mark)

   ii) Why does the ratio of anti-Stokes to Stokes intensities increase with sample temperature? (hint: using a Jablonski diagram might be helpful)

   (2 marks)

   iii) At what wavelengths in nanometers would the Stokes and anti-Stokes Raman lines for carbon tetrachloride ($\Delta v = 218$ cm^{-1}) appear if the source were 1) a Helium-Neon laser (632.8 nm) and 2) an Argon ion laser (488 nm).

   (4 marks)

   iv) Assume both excitation sources in iii) have the same power, compare the relative intensities of the CCl_4 Raman line when each of the two excitation sources are used. Which will give a stronger signal?

   (4 marks)

   v) For temperatures of 20 and 40 $^{\circ}$C, calculate the ratios of intensities of the Stokes and anti-Stokes lines for CCl_4 at 218 cm^{-1}.
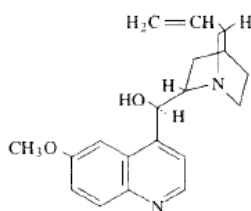
   (4 marks)

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

    i) Which compounds in each of the pairs below would you expect to have a greater fluorescence quantum yield? Explain your answer.

Phenolphthalein

Fluorescein

2,2′-Dihydroxyazobenzene

bis(hydroxyphenyl)hydrazine
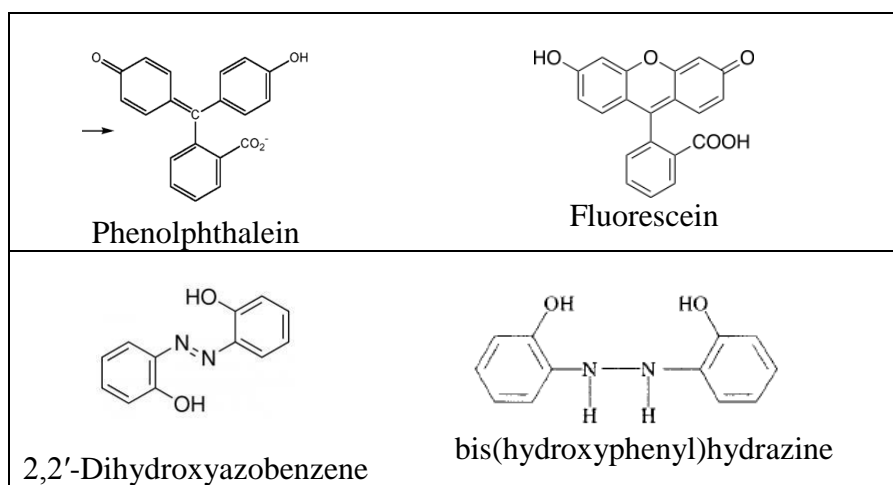
(3 marks)

    ii) Quinine is one of the best-known fluorescent molecules. The structure of quinine is given below. Which part of the molecule is most likely to behave as the fluorescent centre? Explain your reasoning.

(2 marks)

    iii) State an equation describing the fluorescence radiant power in terms of quantum efficiency and incident excitation power. Using this equation derive the relationship between fluorescent radiant power and fluorescence lifetime assuming a dilute sample.

(5 marks)

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

i) In single molecule fluorescence spectroscopy justify why it is important to work with either a small detection volume or low concentrations. Use diagrams as necessary.

(3 marks)

ii) In single molecule spectroscopy, why is it advantageous to use high numerical aperture objectives? Use both an equation and diagram to explain your answer.

(3 marks)

iii) Autocorrelation curves of two differently sized particles are shown below. Experiments were performed at 20 ^{o}C and the detection probe volume was 250 nm in radius. Using these curves: 1) estimate the number of particles in the detection probe volume; 2) Determine the particle size for each curve.

(4 marks)

Water Viscosity = 1.002 x 10^{-3} N s m^{-2} at 20 ^{o}C.
Hint: The following equation might be useful, $D = kT/(6\pi\eta R)$