IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – MAY 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 3

Tuesday 05th May 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.I3 – Advanced Transition Metal Chemistry

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

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

Draw the structures of **B**, **D** and **F** and identify gas **C** and water soluble solid **E**. Assume all equations are balanced. Would you expect compound **A** or benzene to react more rapidly with n-BuLi?
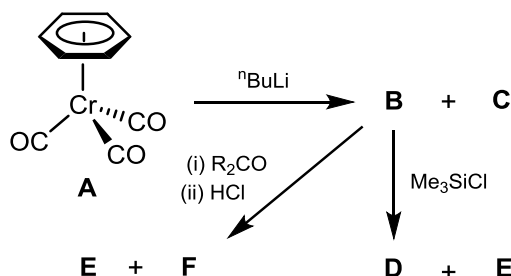
(7 marks)

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

The gold complexes shown below undergo two related H-elimination processes to form **G** and **I**, respectively. The ^1H NMR spectrum of **G** presents a singlet resonance at 5.0 ppm. In these reactions one equivalent of a hydrocarbon **H** is also formed.
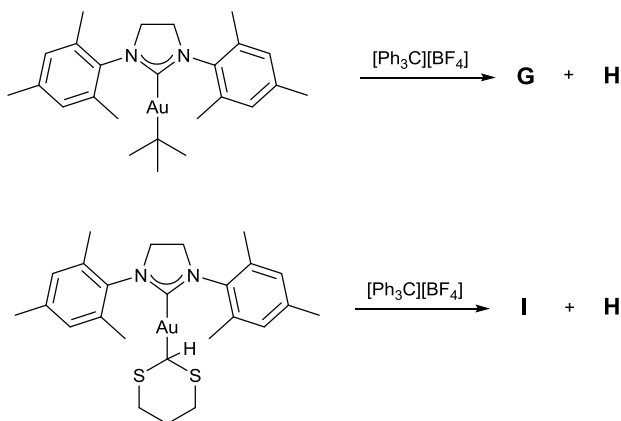

i) Draw the structures of **G**, and **I**, and name the reactions for their formation. Identify hydrocarbon **H**. At what chemical shift value would you expect the ^{13}C NMR signal due to the carbon between the sulfur atoms in compound **I**?

(4.5 marks)

QUESTION CONTINUED OVERLEAF

ii) The neopentyl-gold complex shown below forms **J** through the same elimination process that forms **I**. In this case, the elimination product **J** is not stable and rapidly undergoes a 1,2-methyl shift to give **K**. The ^{1}H NMR of **K** notably shows a quartet at 5.34 ppm ($^3J = 6.0$ Hz) that integrates for one hydrogen.
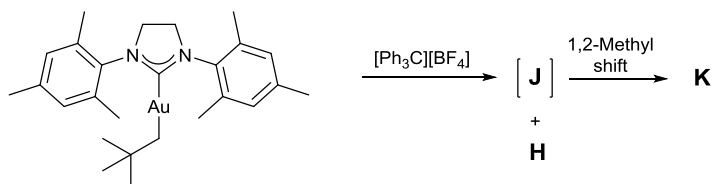

Draw the structures of **J** and **K** and explain the greater stability of **I** when compared to **J**.
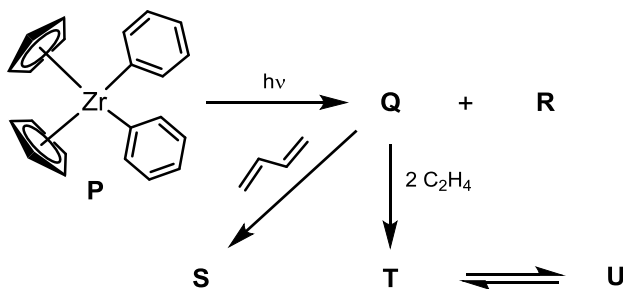
(3.5 marks)

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

i) What is the valence electron count of nickelocene (**L**)? Draw the structures of **M, N** and **O**. Only the equation to form **O** is balanced. Compounds **M** and **N** both show a singlet resonance around 4-5 ppm in the ^{1}H NMR spectrum integrating to 5 protons. Compound **O** shows absorptions in the infrared spectrum at around 1780 cm^{-1}.
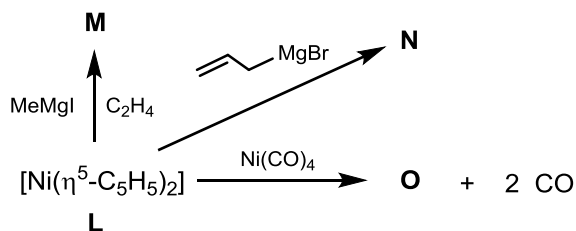
(5 marks)

ii) Draw the structures of **Q** - **U**. Assume all equations are balanced. **Q** is highly reactive and is formed alongside an organic solid **R**. Compound **T** is in equilibrium with metallacycle **U**.
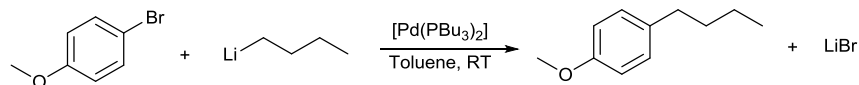

(5 marks)

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

Recently, a very efficient palladium-catalysed cross-coupling of alkyllithium reagents and aryl bromides has been reported (see Scheme below)

i) Draw the structure of the palladium complex used in this reaction and give its oxidation state and valence electron count.

(1 mark)

ii) Show the expected mechanism for this cross-coupling reaction, giving the oxidation state and geometry of all the proposed intermediates.

(4 marks)

iii) A remarkable feature of this system is the suppression of the undesired lithium-bromide exchange. Draw the by-product this exchange would produce and explain which features of the palladium catalyst favoured the cross-coupling over the exchange reaction.

(3 marks)

iv) What are the advantages and disadvantages of using organolithium compounds compared to the Suzuki-Miyaura cross-coupling that employs organoboron reagents (i.e. $R-B(OH)_2$) instead?

(2 marks)

3.O5 – Reactive Intermediates

Answer parts a) **OR** b) of this question.

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

    i)   Discuss the key requirements for successful intermolecular carbon-carbon bond formation in a radical chain reaction using an alkyl halide and an alkene.

            (10 marks)

    ii) Consider the conversion of **A** into **C** via **B**. Give reagents for the formation of **B** from **A** and provide a mechanism for the conversion of **B** into **C**, commenting on any aspects of reactivity, selectivity and stereochemistry where appropriate.

            (15 marks)
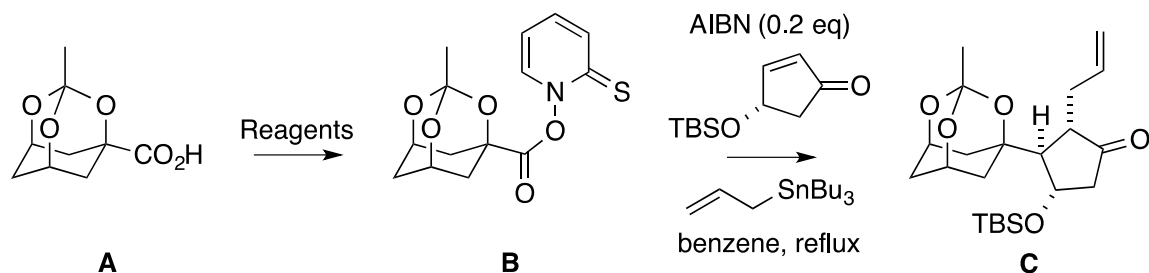
b) Answer **BOTH** parts of this question.

    i)   Discuss the possible intramolecular cyclisations modes of the 6-heptenyl radical. Include in your answer a comparison of the type of contrasting alkene that must be used for intermolecular carbon-carbon bond formation by radical addition. Discuss also any synthetic limitations to the intramolecular cyclisation of this radical.

            (10 marks)

    ii) Consider the conversion of **D** into **F** via **E**. Give reagents for the formation of **E** from **D** and provide a mechanism for the conversion of **E** into **F**, commenting on any aspects of reactivity, selectivity and stereochemistry where appropriate.
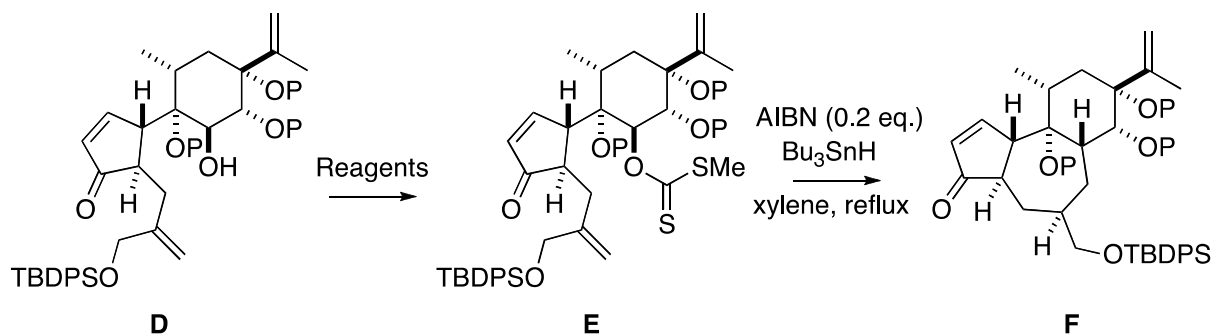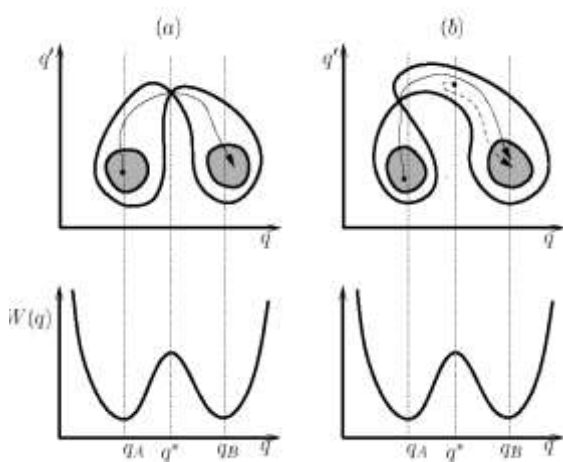

            (15 marks)

3.P3 – Reaction Dynamics

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

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

   i) Below are two illustrative potential energies V(q,q') with their corresponding free energy functions W(q) . Explain using mathematical arguments based on transition state theory and its generalisations, which of the two cases below (a) or (b) is an appropriate reaction coordinate for the system.


(8.5 marks)

   ii) State and explain the Hammond postulate

(4 marks)

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

   i) Contour maps of potential energy surfaces for two collinear A+BC → AB+C reactions are shown below. The dashed lines represent reaction paths. For each of the two reactions, plot the potential energy profile, i.e. the potential along the reaction path that corresponds to each contour map. Label all axes and points of interest. Explicitly identify and name the points indicated by the tips of the two the arrows in diagrams a) and b).

(a)

(b)
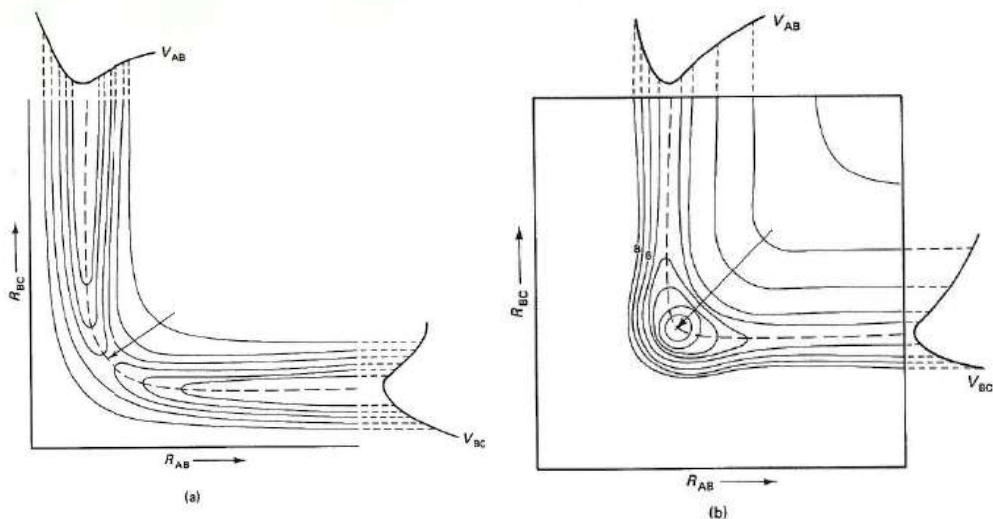
(8 marks)

ii) A diatomic molecule has a vibration with wavenumber 3000cm^{-1}. Estimate the duration of an optical pulse that would be required to create a vibrational wave-packet.

(3 marks)

iii) How many moles of photons does a laser with an intensity of 0.1watt at 560 nm produce in one hour?

(1.5 marks)

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

i) The rate of electron transfer in a donor-acceptor molecular wire is measured to be 8.74×10^6 s^{-1}. The edge-to-edge distance between donor and acceptor is 1.23 nm. Assuming activationless electron transfer, estimate the electron tunnelling coefficient of the wire environment. Define each symbol used and explain any approximations made.

(6 marks)

ii) Define the Franck-Condon factor and show how to calculate it in a model of two one-dimensional identical harmonic potential surfaces that are horizontally shifted with respect to each other. Define all symbols used in your equations.

(6.5 marks)