Autumn Examinations 2014

Exam Code(s) 4BS
Exam(s) 4th year Chemistry – CH401

Module Code(s) CH449
Module(s) Selectivity in Synthesis and Organometallic Chemistry

Paper No.

External Examiner(s) Prof. Tim Gallagher Prof. Duncan Wass
Internal Examiner(s) Prof. Paul V. Murphy Dr. Patrick O’Leary

Instructions: Answer 3 questions in total

Use a separate answer book for each question

Each question carries 100 marks distributed as shown where appropriate. Leave the first page of the answer book blank and list on it clearly the numbers of the questions attempted.

Duration 2 hours
No. of Pages 7 (incl. this front page)
Discipline(s) Chemistry

Requirements None
Q1. Answer all parts

(a) (i) Suggest syntheses of A-D where the alkene is formed in each case by a connective olefination step. Give the structures of the starting substrate(s) in each case as well as any other reagents that may be required.

(ii) Give a detailed explanation for the stereoselectivity observed in the formation of either A, B or C.

(b) (i) Give structures for E-G.

(ii) What kind of selectivity is observed in the formation of G? Explain the origin of this selectivity.

(iii) Write a mechanism using curly arrows for the reaction that gives E.
2. **Answer all parts**

(a) (i) Give the structure of H.

(ii) Write a mechanism for the reaction that gives H; \((\text{CH}_3)_2\text{S},\) CO and CO\(_2\) are by-products from the reaction.

![Chemical structure of H]

\[ \text{[25 marks]} \]

(b) (i) Give the products J and K, which arise from stereoselective reactions.

(ii) Explain why J is formed selectively.

![Chemical reactions for J and K]

\[ \text{[20 marks]} \]
(c)  (i) Give a chemical structure for M.

(ii) Discuss a detailed mechanism for the formation of M.

(iii) Compound M reacts with a nucleophile (sodium azide) to give N. Give a structure for N and explain the origin of two types of selectivity that are relevant in the formation of N.

(d) Showing examples, and reaction mechanism, discuss the basic aldol reaction and how diastereoselective aldol reactions are achieved.
When a metal co-ordinates to an alkene the alkene becomes non planar and the carbon carbon bond tends to lengthen. The level of deviation from planarity and the bond length of the alkene in three platinum complexes are shown above.

(a) Discuss the reasons behind the structure changes in the co-ordinated alkene. In addition discuss specifically the reasons for the variation seen in the three Pt complexes. [50 Marks]

(b) What is the product A of the reaction above. [10 Marks]

(c) Two routes are shown to the product B. What is B? [10 Marks]

(d) Synthetically which of the two routes to product B is preferable, explain your answer. [10 Marks]

(e) How would you prepare butyl lithium? [10 Marks]

(f) With butyl lithium in hand how would you prepare dibutyl lithium cuprate. [10 Marks]
4. **Answer all parts**

(a) Determine by means of electron counting whether the following complexes are stable or not. Explain your reasoning.

(b) Below is the mechanistic pathway of the Wacker oxidation reaction.

(i) What are the intermediates C and F and what is the eliminated product E?  

(ii) Show the mechanism by which \( \beta \)-hydride eliminates from D
(c) The diagram above shows a synthetic scheme.

(i) Suggest reagents and conditions \( G \) to carry out the first step. How might the key reagent be prepared? [10 Marks]

(ii) What reagents and conditions \( H \) are necessary for the second step? [15 Marks]

(iii) What reagents and conditions \( J \) are necessary for the third step? [15 Marks]

(iv) What is the final product \( K \)? [10 Marks]