

**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JUNE 2016, 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 IB**

**Organic Chemistry**

**Thursday 16<sup>th</sup> June 2016, 09:30-11:45**

**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.**

### 1.03 – Haloalkanes, Alcohols and Amines

Answer **ALL** parts of this question.

a) Consider the reaction below:



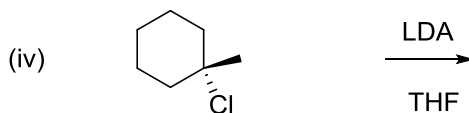
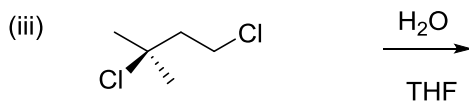
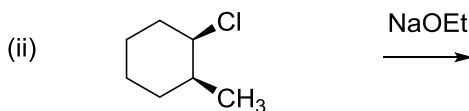
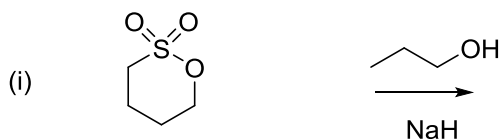
- i) Give the expected product of the reaction, and the rate equation that governs its formation (2 marks)
- ii) Explain, with reasoning, what you would expect to happen to the rate of reaction if:

- The substrate was changed to iodomethane
- The substrate was changed to 1-chloropropane
- The nucleophile was changed to  $\text{CH}_3\text{SNa}$
- The solvent was changed to DMSO

(8 marks)

b) Give the major product for **THREE** of the following **FOUR** reactions

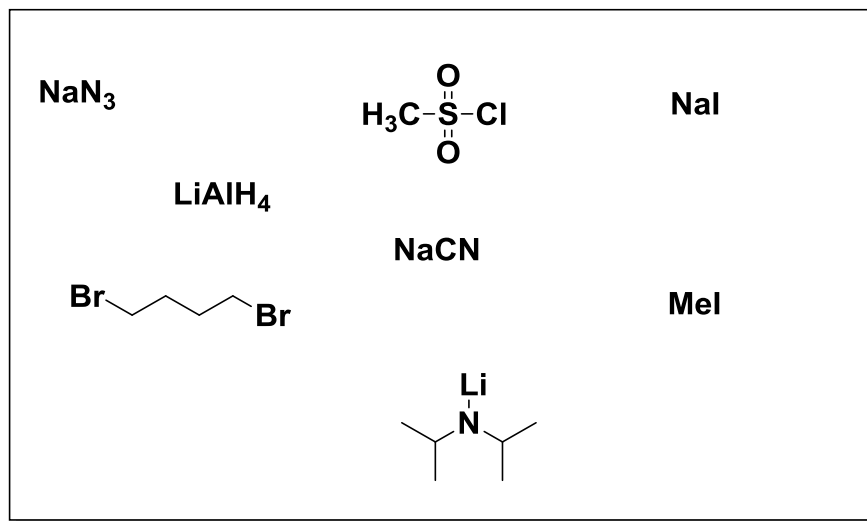
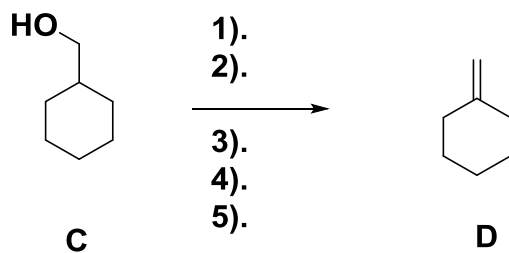
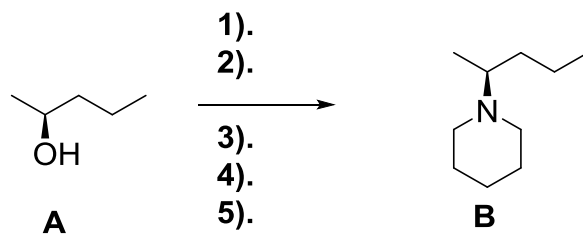
(6 marks)



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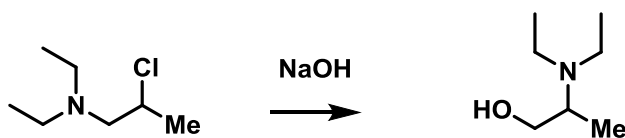
- c) Suggest a synthesis of **ONE** of molecule **B** or **D** using the reagents highlighted in the box. **Note** that you do **not** need to utilise all of reagents.

(5 marks)



- d) Give a curly arrow mechanism to explain the following reaction.

(4 marks)

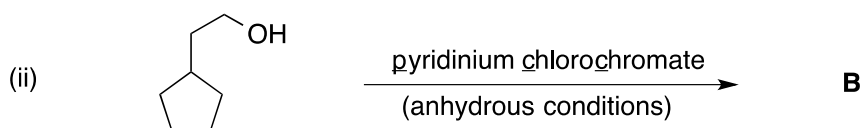


## 1.04 – Carbonyl and Carboxyl Groups

Answer **ALL** parts of this question.

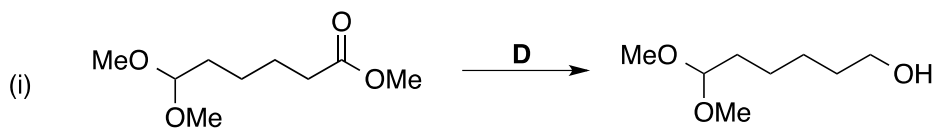
- a) Draw the structure of the product obtained for **TWO** out of the following **THREE** reactions.

(6 marks)



- b) Provide the missing reagents for **TWO** of the following **THREE** reactions.

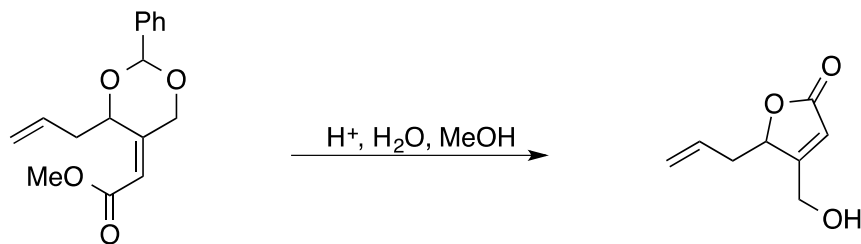
(6 marks)



QUESTION CONTINUED OVERLEAF

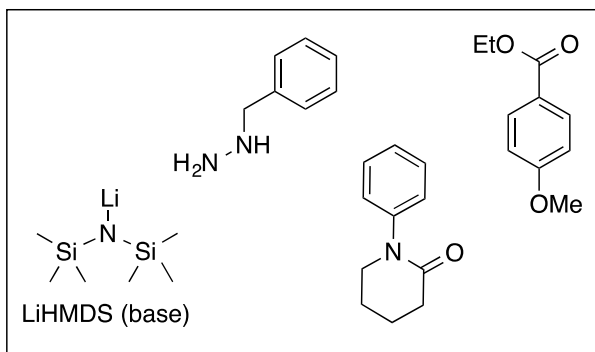
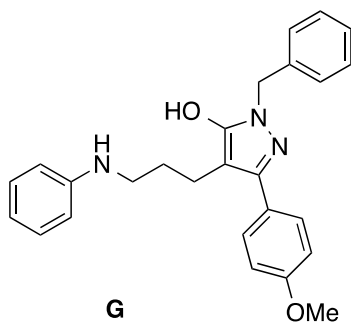
c) Suggest a curly arrow mechanism for the reaction shown below.

(8 marks)



d) Suggest a synthesis of **G**. Assume that you have access to the reagents in the box to the right of **G**.

(5 marks)



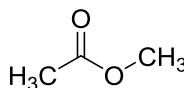
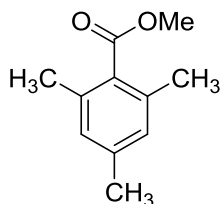
## 1.05 – Introduction to Physical Organic Chemistry

**NB. ‘Half a question’ (out of 12.5 marks)**

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

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

- i) Acid-catalysed hydrolysis of esters **1** and **2** below can occur by different mechanisms.



- A. How can the entropy of activation be used to differentiate between hydrolysis mechanisms?  
(1 mark)
- B. How does the molecular structure of the ester **1** influence the hydrolysis mechanism?  
(1 mark)
- C. Explain which mechanism is most likely for each ester, given that hydrolysis of ester **1** has a positive entropy of activation, and hydrolysis of ester **2** has a negative entropy of activation.  
(4 marks)
- ii) The sulfonation of benzene was observed to have a significant primary kinetic isotope effect (PKIE). Write a mechanism for the reaction, and explain the reason for the PKIE effect. Sketch the reaction energy profile for this reaction.  
(3.5 marks)
- b) Draw an energy diagram for the reaction of propene with HCl, and explain how the Hammond postulate can be used to rationalise the ratio of the two products.  
(3 marks)
- c) Would you expect 4-aminophenol to have a higher or lower  $pK_a$  than 4-bromophenol when measured in water? In what way would you expect the  $pK_a$  of 4-bromophenol to change when measured in  $CH_3CN$  and why?  
(3 marks)

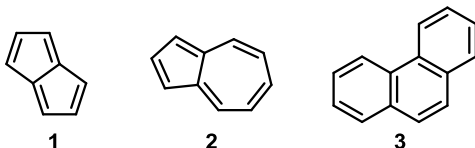
## 1.07 – Aromatic Chemistry

**NB. ‘Half a question’ (out of 12.5 marks)**

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

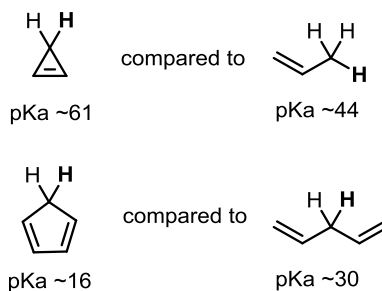
a) With reference to Hückel’s rule, answer the following:

i) Which of the following hydrocarbons are aromatic. Explain your reasoning.



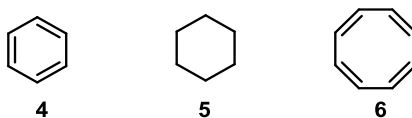
(2 marks)

ii) The pKa values of the indicated protons in two pairs of molecules are shown below. Rationalise the differences observed.



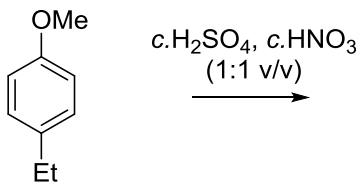
(2 marks)

iii) Which of the following compounds contains the longest carbon-carbon bonds and which one contains the shortest carbon-carbon bonds? Explain your reasoning.



(2 marks)

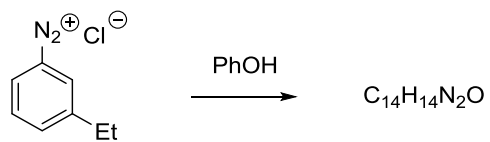
b) Draw the expected major product of the following reaction, draw a mechanism and briefly justify the regiochemical outcome.



(6.5 marks)

QUESTION CONTINUED OVERLEAF

- c) Draw the expected major product of the following reaction, draw a mechanism and briefly justify the regiochemical outcome.



(6.5 marks)