

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JUNE 2017, for Internal Students of the
Imperial College of Science, Technology and Medicine**

**This paper is also taken for the relevant examination for the
Associateship**

CHEM40002 ORGANIC CHEMISTRY 1

Monday 26th June 2017, 09:30-11:45

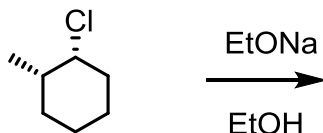
**PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT
THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING
OF ANY PRIOR CORE COURSE.**

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

Q1, Haloalkanes, Alcohols and Amines

Answer parts a), b), c) **AND** d) of this question.

a) Consider the reaction below:

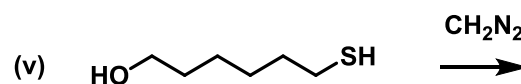
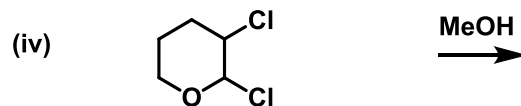
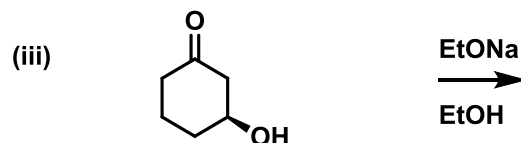
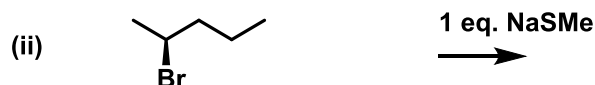
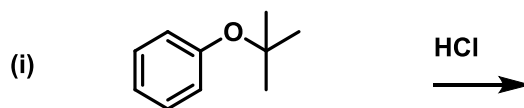


- i) Give the major product of the reaction, and the rate equation that governs its formation. (2 marks)
- ii) Explain with reasoning what would happen to the reaction rate if the bromide analogue was used instead? (1 mark)
- iii) Explain, with reasoning, what major product you would expect if:

- The stereochemistry of the starting chloride was inverted
- The base was changed to sodium *tert*-butoxide
- The base was changed to EtSNa

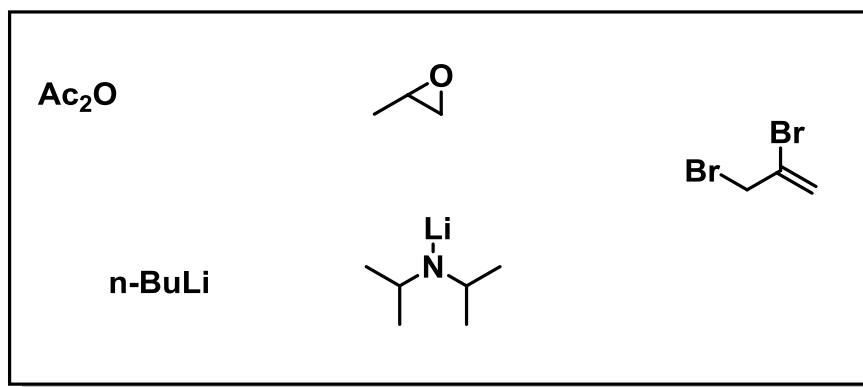
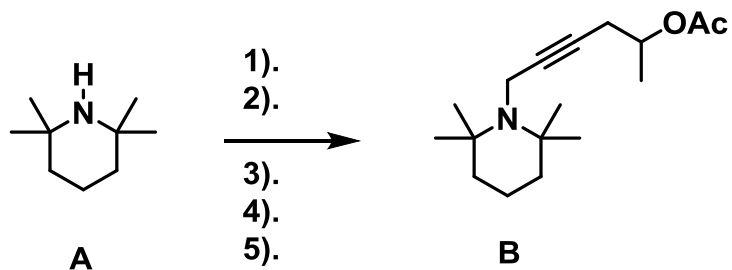
(6 marks)

b) Give the major organic product(s) for **THREE** of the following **FIVE** reactions (6 marks)

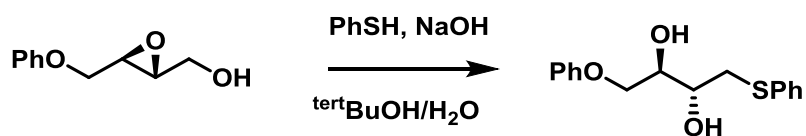


QUESTION CONTINUED OVERLEAF

- c) Suggest a synthesis of molecule **B** using the reagents highlighted in the box. (5 marks)



- d) Give a curly arrow mechanism to explain the following reaction. (5 marks)

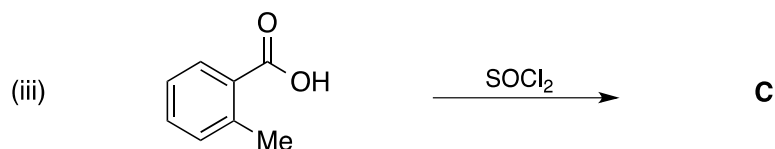
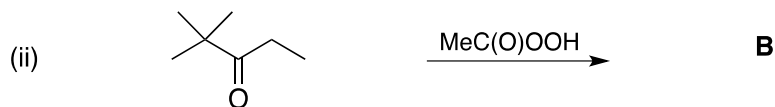


Q2, Carbonyl and Carboxyl Groups

Answer parts a), b), c) **AND** d) of this question.

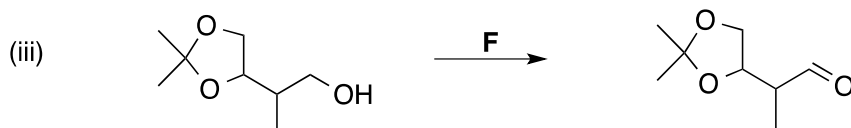
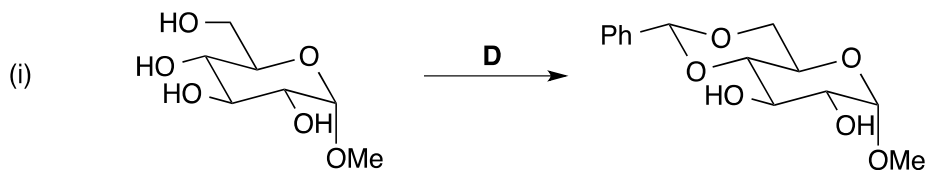
- a) Draw the structure of the product obtained from **TWO** out of the following **THREE** reactions.

(6 marks)



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

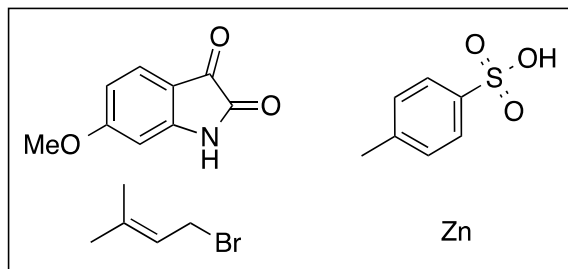
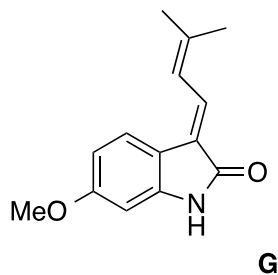
(6 marks)



QUESTION CONTINUED OVERLEAF

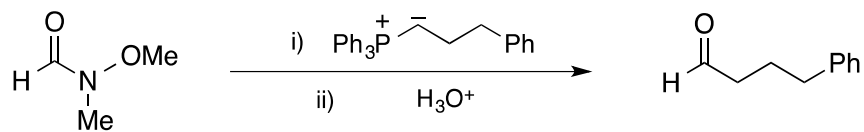
- c) Suggest a synthesis of **G**. Assume that you have access to the reagents in the box to the right of **G**.

(6 marks)



- d) Provide a curly arrow mechanism for the reaction shown below.

(7 marks)



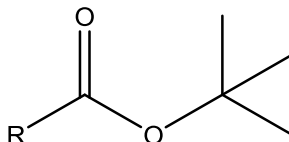
Q3, Introduction to Physical Organic Chemistry

NB. 'Half a question' (out of 12.5 marks)

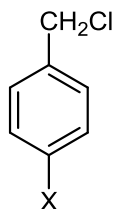
Answer part a) **AND** either part b) **OR** part c) of this question.

- a) How can radiolabelling of the alkyl oxygen atom of the ester below or the oxygen atom of water be used to identify the mechanism of acid-catalysed hydrolysis?

(4 marks)



The rate of hydrolysis of the substituted aryl chloride below was observed to depend strongly on the electron-withdrawing and electron-donating nature of the substituent.



- i) What is the mechanistic reason for the rate dependence?

(2 marks)

- ii) How could the entropy of activation measurements of the reactions be used to differentiate between the two potential reaction mechanisms for the hydrolysis above?

(1 mark)

- iii) How can the choice of solvent play a role in the rate of hydrolysis?

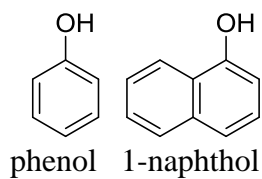
(1.5 marks)

Suggest an appropriate solvent to maximise the rate of reaction when X is OMe and when X is NO₂.

(2 marks)

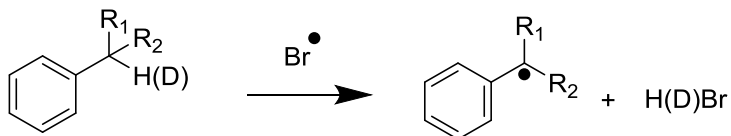
QUESTION CONTINUED OVERLEAF

- b) Write a balanced equation for the reaction of phenol and the sodium salt of 1-naphthol, indicating which side of the reaction the equilibrium is favoured.



(2 marks)

- c) Consider the KIE data for the following reaction



R ₁	R ₂	k _H /k _D
H	H	4.9
CH ₃	H	2.7
CH ₃	CH ₃	1.8

Discuss the symmetry of the transition state for the three molecules in the table.

(2 marks)

Q4, 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) Answer **BOTH** parts of this question.

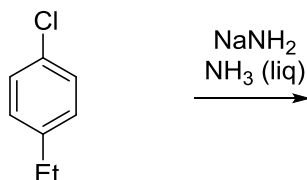
- i) Draw a curly arrow mechanism and sketch an energy profile diagram for the reaction of benzene with a chlorine cation (Cl^+) giving chlorobenzene *via* an $\text{S}_{\text{E}}\text{Ar}$ pathway. Clearly indicate the relative energies of the starting material, transition state(s), intermediate(s) and product in your diagram.

(4 marks)

- ii) Using the reaction of chlorobenzene with fuming concentrated sulfuric acid (*i.e.* $\text{c. H}_2\text{SO}_4 + \text{SO}_3$, oleum) as an example, explain the directing effect of the chlorine substituent on this $\text{S}_{\text{E}}\text{Ar}$ reaction. Refer to Hammond's postulate and the structure of the Wheland intermediate in your answer. Also explain why only mono-substitution occurs.

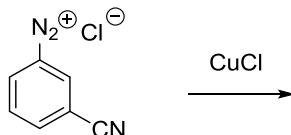
(4 marks)

- b) Draw a curly arrow mechanism for the following reaction. Clearly indicate the expected product(s) and briefly explain the regiochemistry of the product(s).



(4.5 marks)

- c) Draw the expected major product of the following reaction, draw a curly arrow mechanism and justify the regiochemical outcome. What alternative reagent apart from CuCl could be used to achieve this transformation?



(4.5 marks)