

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JUNE 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 IB

Organic Chemistry

Tuesday 16th June 2015, 09:30-11:45

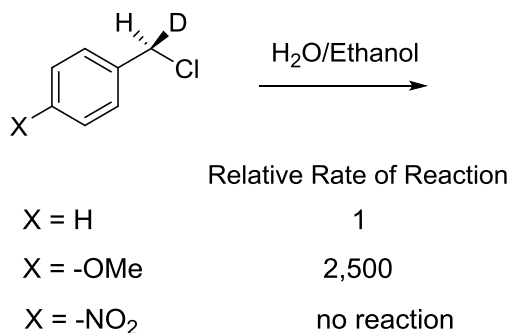
**PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT
THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING
OF ANY PRIOR CORE COURSE.**

**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 solvolysis reaction of a series of benzyl chlorides below.

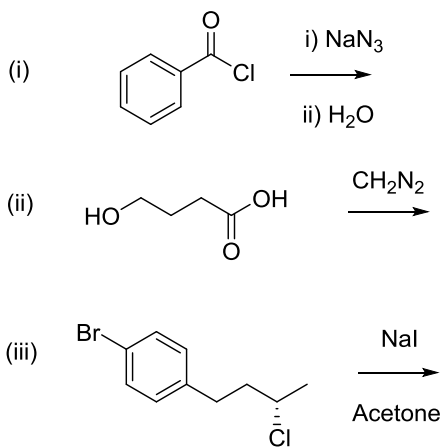


Based upon the information above, explain through the use of a detailed mechanism why the reaction proceeds more rapidly for the methoxy-substituted starting material and not at all for the nitro-substituted product. Paying particular attention to stereochemistry, show the structure of the product formed and define the reaction mechanism.

(7 marks)

b) Give the product for **TWO** of the following **THREE** reactions

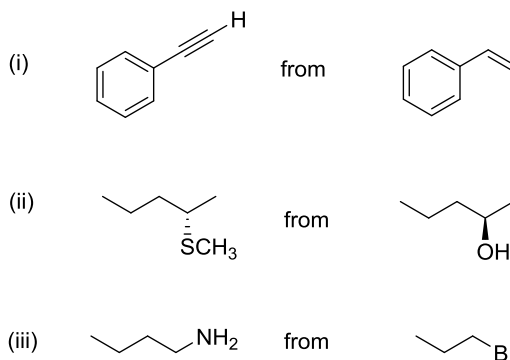
(4 marks)



QUESTION CONTINUED OVERLEAF

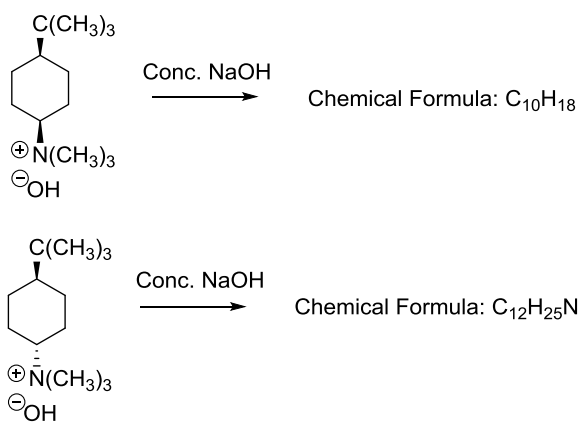
- c) Propose syntheses for **TWO** of the following **THREE** molecules from the indicated starting materials. Make use of any other reagents or solvents you need (**more than one synthetic step may be needed**). In case your reaction yields a mixture of products, you should specify reagents and conditions that will maximise the yield of the specified product.

(6 marks)



- d) Consider the reactions of the quaternary ammonium salts below when heated with a solution of concentrated NaOH. Identify the two products formed and provide a mechanism for their formation in each case.

(8 marks)

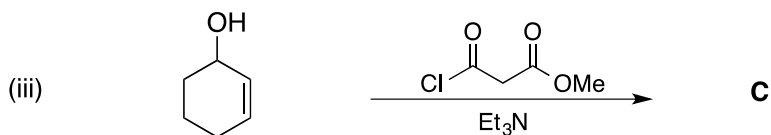


1.04 – Carbonyl and Carboxyl Groups

Answer **ALL** parts of this question.

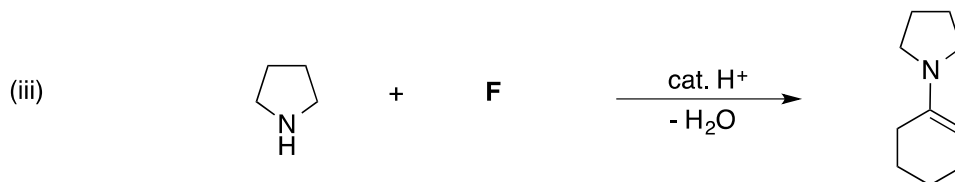
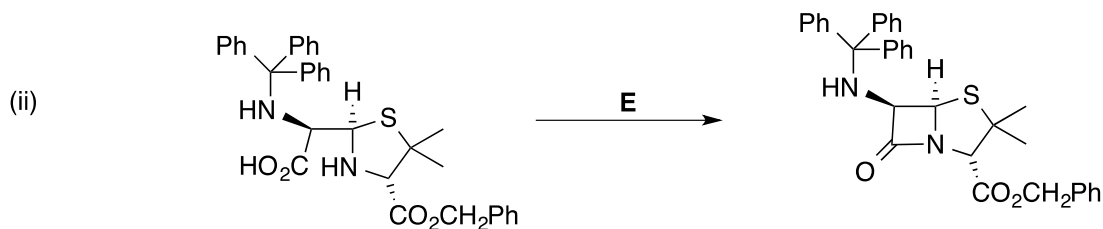
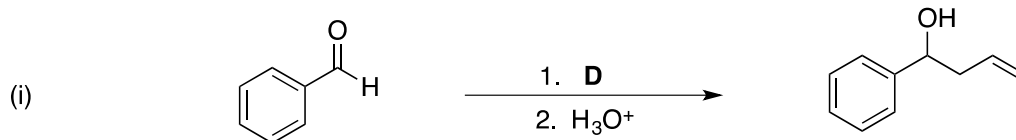
- a) Draw the structure of the product obtained from **TWO** out of the following **THREE** reactions.

(6 marks)



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

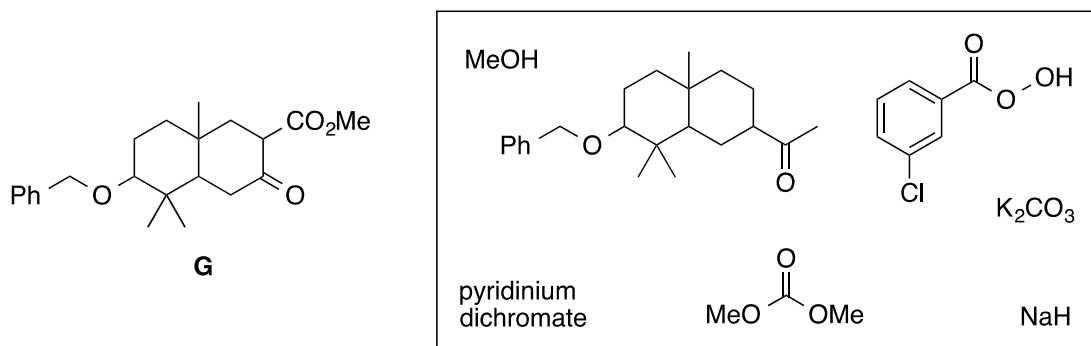
(6 marks)



QUESTION CONTINUED OVERLEAF

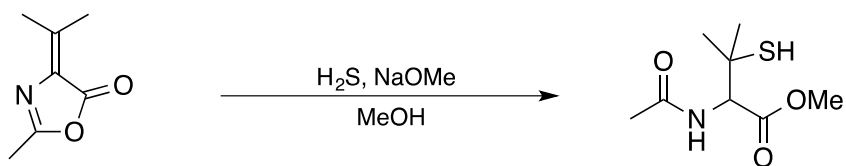
- c) Suggest a synthesis of **G**. Assume that you have access to the reagents in the box to the right of **G**.

(6 marks)



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

(7 marks)



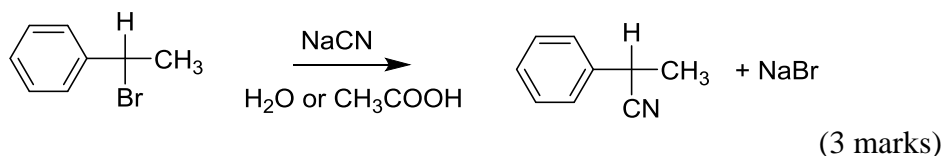
1.05 – Introduction to Physical Organic Chemistry

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

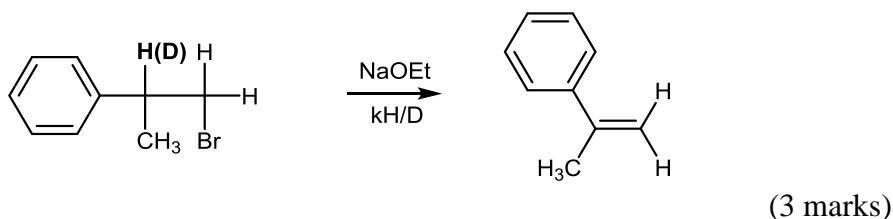
Answer part a) **AND EITHER** part b) **OR** part c) of this question.

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

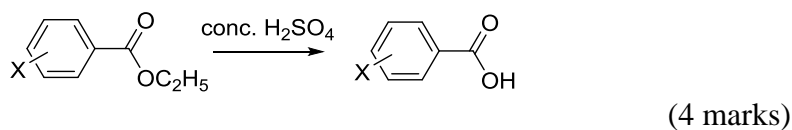
- i) The nucleophilic substitution reaction below can be carried out in either H_2O or CH_3COOH . The relative rate of reaction in H_2O was 150,000 that of CH_3COOH . Is this indicative of an $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ reaction? Why is the rate of reaction greater in H_2O ? Comment on the stereochemical outcome of the reaction when enantiomerically pure starting material is used.



- ii) Explain how the kinetic isotope effect from deuteration of the hydrogen (in bold) below can be used to determine the mechanism of the elimination reaction below.

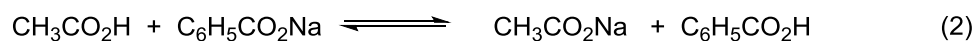


- iii) In the ester hydrolysis below, two different mechanisms can occur depending on whether the functional group X is strongly electron withdrawing or strongly electron donating. State which mechanism occurs in both cases, and explain why each mechanism is preferred.



QUESTION CONTINUED OVERLEAF

b) Explain, using the Hammond Postulate, why reaction 1 has an earlier transition state.

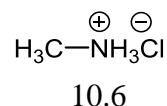
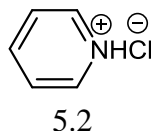


pKa H₂O = 15.7; pKa CH₃COOH = 4.8; pKa C₆H₅COOH = 4.2
(2.5 marks)

c) The conjugate acids of two bases are shown below, along with their respective pKa values. Write a balanced equation of the reaction between one of the bases and the conjugate acid of the other base, indicating which side of the equilibrium is favoured. Calculate the equilibrium constant.

(2.5 marks)

Conjugate acid
pKa

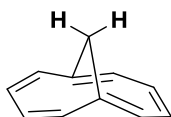


1.07 – Aromatic Chemistry

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

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

a) Consider the molecule, known as Vogel’s hydrocarbon, shown below.



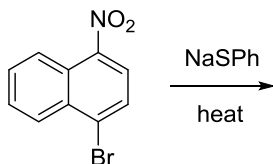
i) Is this molecule aromatic? Explain your reasoning with reference to Hückel’s rule.

(2 marks)

ii) Explain with the aid of a diagram, why the two indicated hydrogens resonate at $\delta = -0.7$ ppm. At approximately what chemical shift would you expect the other eight hydrogens in this molecule to resonate at?

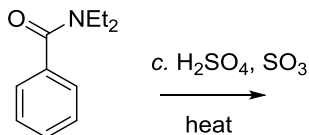
(4 marks)

b) Draw the expected major product of the following reaction and show a mechanism for its formation.



(6.5 marks)

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



(6.5 marks)