UNIVERSITY OF LONDON

BSc and MSci DEGREES – August 2003, for Internal Students of the Imperial College London

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

ORGANIC CHEMISTRY 1

RESIT

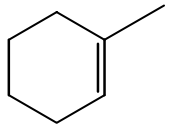
Wednesday 20th August 2003, 9.30 – 11.30

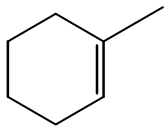
USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

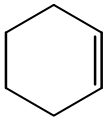
Q1 Alkanes, Alkenes, Alkynes & Aromatics

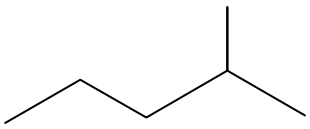
Answer **EITHER** Part (a**) OR** Part (b)

Part A: Give the mechanisms and products of the following reactions paying particular attention to the regiochemistry and stereochemistry where appropriate:

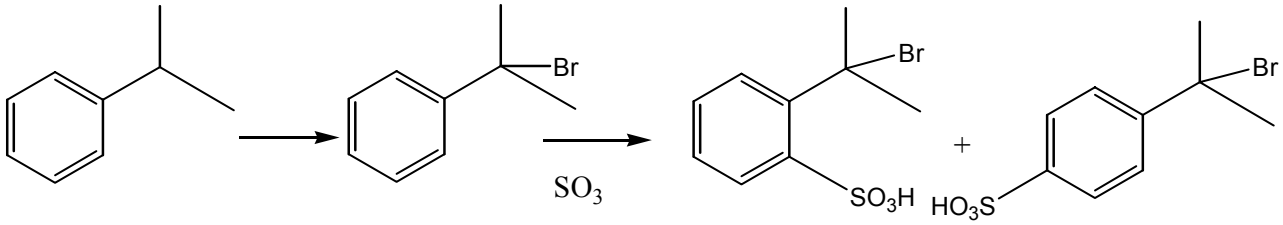
(a)  HBr → (**6 marks**)

(b)  HBr + ROOR, Δ → (**6 marks**)

(c)  OsO_4 → (**7 marks**)

(d)  Cl_2 → (consider only mono-chloro products)(**6 marks**)

Part B: Study the following reaction sequence and answer questions i - iv below.



A **B** **C** **D**

(i) What reagent may be used to convert **A** into **B**? (**5 marks**)

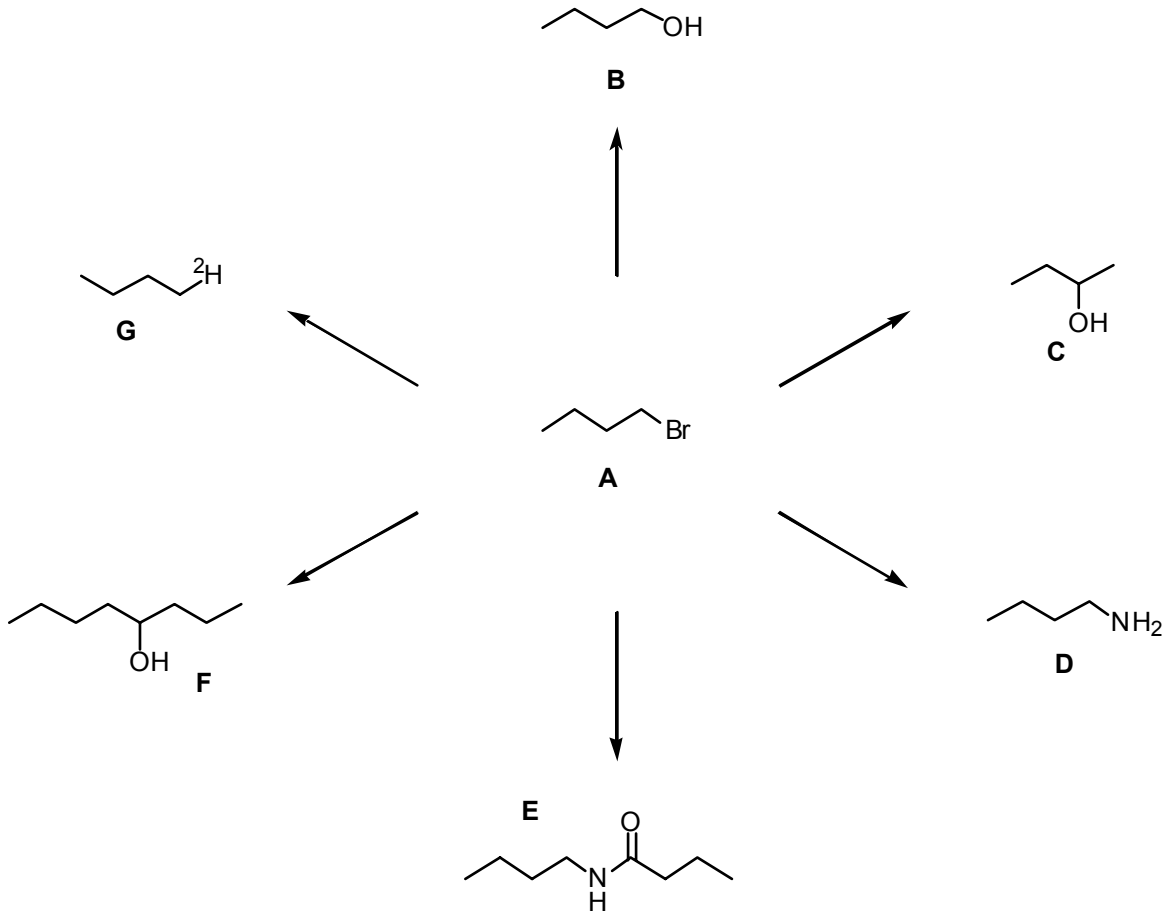
(ii) Give the mechanism for the conversion of **B** into **C** and **D**. (**8 marks**)

(iii) Which of **C** or **D** predominates at room temperature? (**5 marks**)

(iv) Heating the mixture of **C** or **D** leads to only the more stable of the two compounds. Explain this result. (**7 marks**)

Q2 Haloalkanes, Alcohols & Amines

Propose, with plausible mechanisms, reactions by which 1-bromobutane **A** can be unambiguously converted into **FOUR** of **B-G**. Use 1-bromobutane **A** as your sole source of carbon in the products **B-G**. More than one step may be required in each case. [**6 marks each + 1 bonus**]



25 marks total

Q3 Carbonyl & Carboxyl Groups

Answer part (a) and **EITHER** part (b) **OR** part (c).

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

i) What is the most acidic proton for the molecule shown in Fig. 1. Explain your choice with the aid of resonance structures. (2 marks)

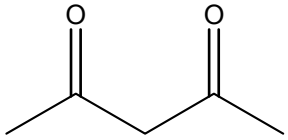
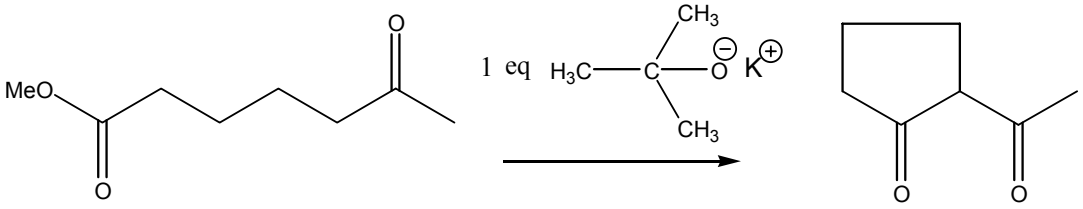


Fig. 1

ii) Give the mechanism for the reaction shown in Fig. 2.



eq = equivalent

Fig. 2 (4 marks)

iii) In the hydrolysis reaction shown in Fig. 3 only catalytic amounts of acid are needed. Explain this reactivity by drawing out the full mechanism for this reaction.

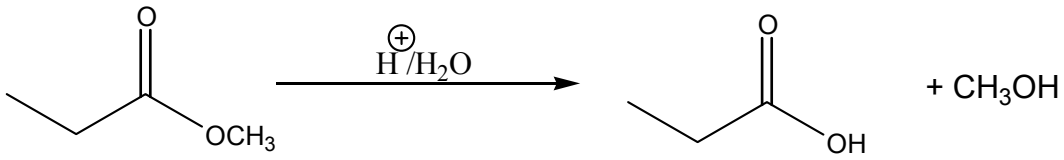
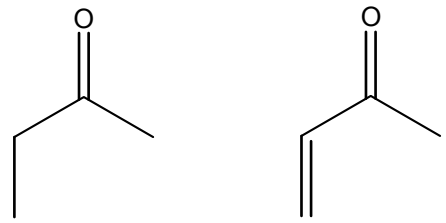


Fig. 3

(4 marks)

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

i) Briefly compare and contrast the reactivity of **A** and **B** (Fig. 4) towards soft and hard nucleophiles.



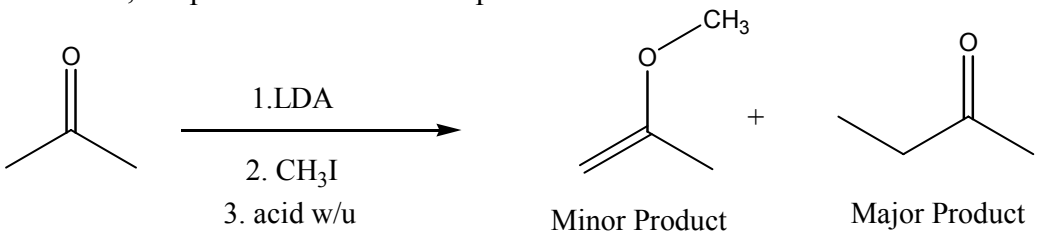
A **B**

(4 marks)

Fig. 4

ii) Give the mechanism for the synthesis of an ester from an acid chloride and include a full mechanism for this reaction. (3 marks)

iii) For the two step reaction shown in Fig. 5 draw the mechanism. Explain, including a full mechanism, the presence of the minor product shown.



LDA= lithium diisopropylamide; a strong hindered base

Fig. 5 (8 marks)

c)

i) Discuss the reason why the reaction shown in Fig. 6 does NOT occur.

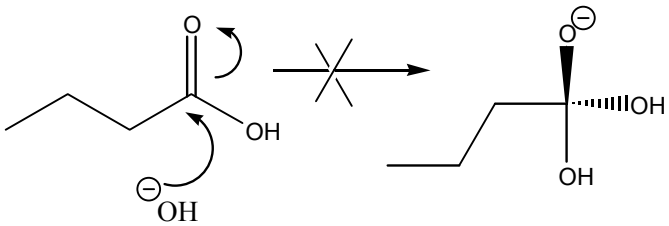
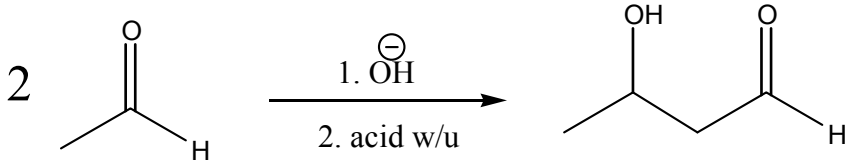


Fig. 6 (4 marks)

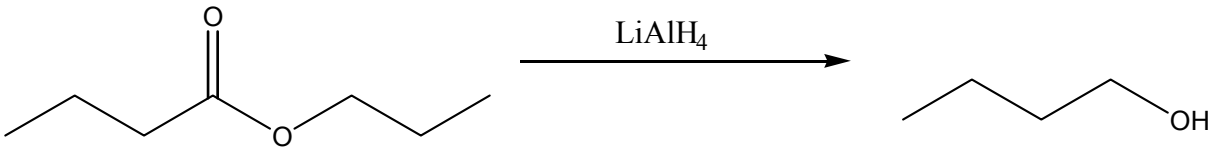
ii) Give the mechanism and product for the reaction shown in Fig. 7.



(3 marks)

Fig. 7

iii) Explain, giving products and a full mechanism, the reaction shown in Fig. 8. What happens if DIBALH is used (at low temperature) instead of $LiAlH_4$?



DIBALH = diisobutyl aluminium hydride; a reducing agent of lower reactivity

Fig. 8 (8 marks)