

University of Canterbury

End-of-year Examinations 2009

Prescription Number(s): CHEM 272

Paper Title: Organic Chemistry

Time Allowed: Three hours

Number of pages: Eight

This paper is divided into **TWO** sections.

Section A: Answer **FIVE** questions (from a choice of **SIX**) in this section. Worth 40% of the total marks.

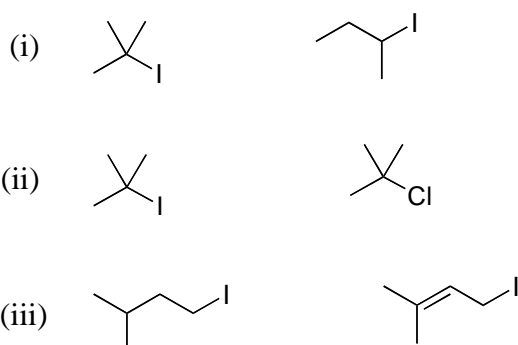
Section B: Answer **BOTH** questions in this section. Worth 60% of the total marks.

TURN OVER

SECTION A

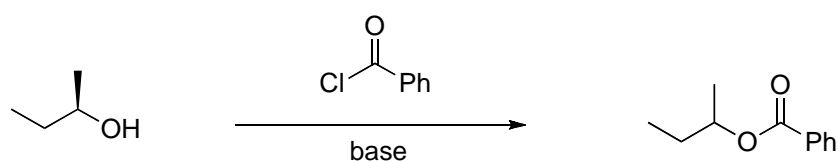
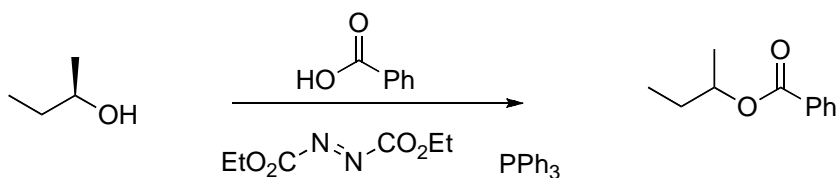
(Answer **FIVE** questions from this section. Worth 40% of the total marks.)

1. (8 marks)

(a) Outline the general features of an S_N1 reaction.(b) For the following pairs of compounds, rank the molecules in order of rate of reaction in the S_N1 reaction. Explain your reasoning:

2. (8 marks)

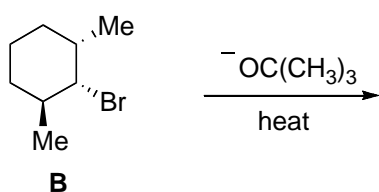
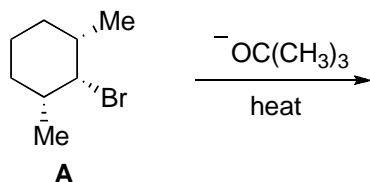
Describe the mechanisms of the following reactions. For each reaction draw the product in precise stereochemical detail.



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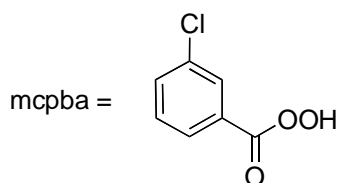
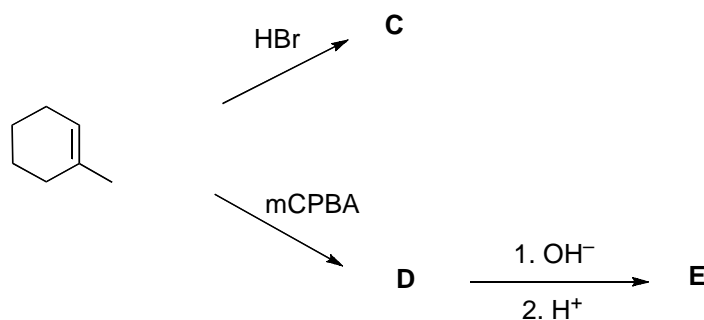
3. (8 marks)

When **A** is heated with *tert*-butoxide a single racemic product is formed. Under the same conditions **B** reacts to form a single enantiomer. Provide the structures of the products and give mechanisms to explain for the different reaction outcomes.



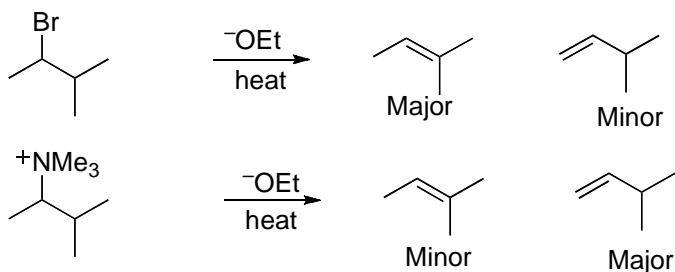
4. (8 marks)

(a) Show the structures of products (**C-E**) in the following scheme and provide the mechanisms for their formation. Clearly indicate the stereochemistry of each product and explain whether (**C-E**) are single compounds or mixtures of isomers.

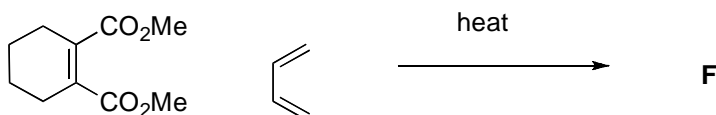


5. (8 marks)

(a) Give mechanisms to account for the difference in regiochemical outcomes of the following reactions:



(b) Show the structure of the product (**F**) in the following reaction and provide a mechanism for its formation. Clearly indicate the stereochemistry of the product.

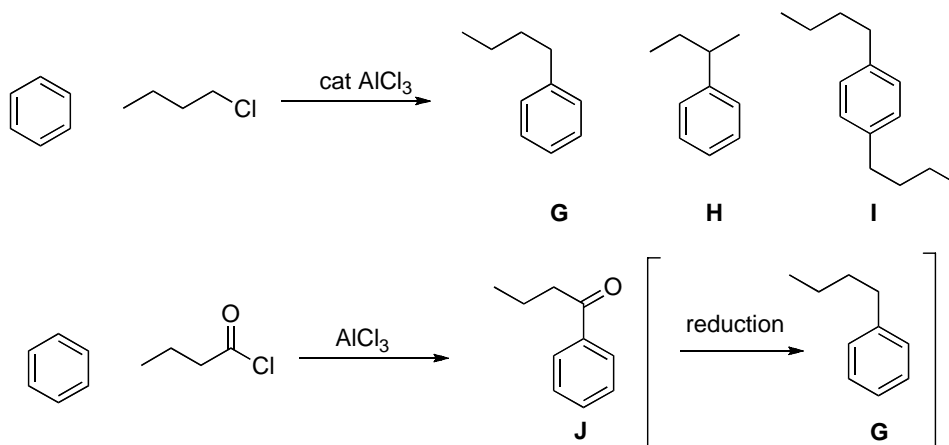


6. (8 marks)

An attempt to make 1-butylbenzene **G** using benzene and 1-chlorobutane (with catalytic amount of $AlCl_3$) results in the formation of the desired product, but also gives significant quantities of 1-*sec*-butylbenzene **H**, 1,4-dibutylbenzene **I** and other polyalkylated products.

In contrast, reaction of benzene with butanoyl chloride and stoichiometric quantities of $AlCl_3$ gives a high yield of 1-phenylbutan-1-one **J** (which can be readily converted to the desired 1-butylbenzene by reduction).

Give clear mechanistic explanations to account for these different observations.



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SECTION B

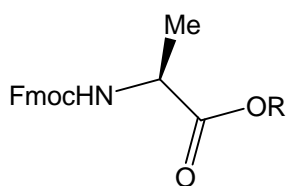
(Answer **BOTH** questions in this section. Worth 60% of the total marks.)

7. (30 marks)

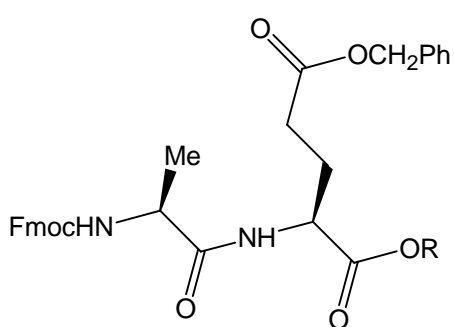
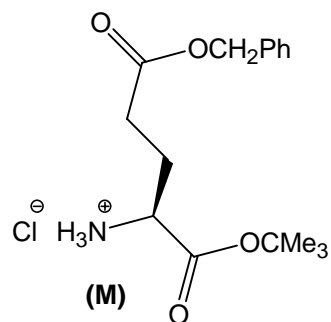
See the Peptide Synthesis **SCHEME** on the following page. Answer **TWO** of the following (a) – (c):

- (a) Treatment of protected alanine derivative (**J**) with piperidine in DMF leads to a selective deprotection reaction. Draw the structure of the product and explain the mechanistic basis of the selectivity of this reaction. If (**J**) is treated with 3M aq. HCl a different selective deprotection occurs. Draw the structure of the product of this reaction and give a mechanism for the acid-catalysed process. For each reaction clearly explain why one protecting group is unaffected by the conditions.
- (b) A chemist proposes to synthesize the protected dipeptide (**N**) by neutralizing the glutamic acid derivative (**M**) and reacting the resulting amine immediately with one of the alanine derivatives (**J**), (**K**) or (**L**). Explain the different reactivity of (**J**), (**K**) and (**L**) in this peptide-forming reaction. Which would be the best and worst choices for the alanine component of this reaction? Why is it important to use the salt (**M**) and neutralise it just before the peptide-forming reaction, rather than to store (**M**) in the free amine form and use it directly? Explain your reasoning and provide structures for potential side-products where appropriate.
- (c) A chemist attempts two synthetic routes to the protected tripeptide (**Q**). In the first synthesis (**J**) is *N*-deprotected and then coupled with (**O**) in the presence of a base. In the second synthesis (**P**) is *N*-deprotected and then coupled with (**L**) in the presence of a base. Draw the mechanisms for these two coupling reactions. Although both of these processes provide (**Q**), the first route also produces a significant amount of a stereoisomer of (**Q**). Explain the mechanistic basis for the formation of this stereoisomeric side-product and comment on the implications of this finding for the synthesis of longer peptides.

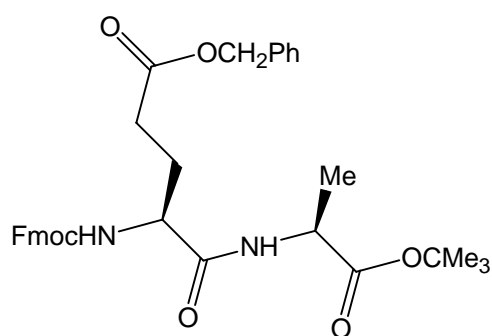
PEPTIDE SYNTHESIS SCHEME



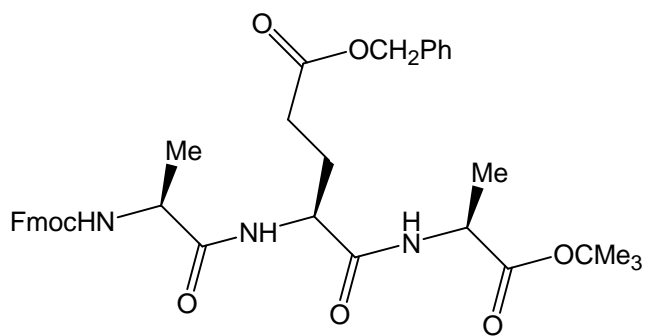
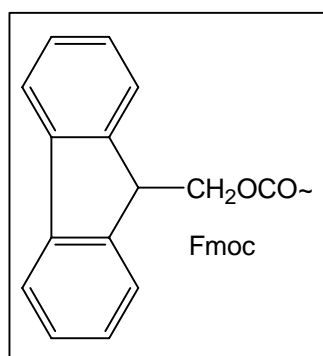
(J): R = CMe₃;
 (K): R = C₆H₅;
 (L): R = C₆F₅



(N): R = CMe₃;
 (O): R = C₆F₅



(P)



(Q)

8. (30 marks)

Answer **TWO** of the following (a) – (c):

Ethene ($\text{CH}_2=\text{CH}_2$), 1,3-butadiene ($\text{CH}_2=\text{CHCH}=\text{CH}_2$), and methyl methacrylate ($\text{CH}_2=\text{CMeCO}_2\text{Me}$) are all important monomers for the industrial production of synthetic polymers.

- (a) Give a brief critical analysis of the enthalpy and entropy changes for the free radical polymerization of these three monomers at 25°C as given in the Table below:

TABLE

Ethene	1,3-Butadiene	Methyl methacrylate
$\Delta H = -109 \text{ kJmol}^{-1}$	$\Delta H = -78 \text{ kJmol}^{-1}$	$\Delta H = -65 \text{ kJmol}^{-1}$
$\Delta S = -155 \text{ JK}^{-1}\text{mol}^{-1}$	$\Delta S = -89 \text{ JK}^{-1}\text{mol}^{-1}$	$\Delta S = -117 \text{ JK}^{-1}\text{mol}^{-1}$

- (b) 1,3-Butadiene can be polymerized by treatment with a trace of *n*-butyl lithium. Write a mechanism for this polymerization reaction. Briefly comment on the regiochemistry and stereochemistry of addition to 1,3 butadiene in polymerisation reactions.
- (c) Methyl methacrylate and ethene can both be polymerized by heating in the presence of a trace of AIBN ($\text{NCCMe}_2\text{N}=\text{NCMe}_2\text{CN}$). Write a mechanism for each of these polymerisation reactions. Poly(methyl methacrylate) produced in this way is a linear (unbranched polymer), but the poly(ethene) produced in this way contains a significant number of butyl groups branching from the main polymer chain. Explain how the branching of poly(ethene) occurs and why this is not a problem for poly(methyl methacrylate) synthesis.

END OF PAPER