University of Canterbury

End of Year Examination 2006

Prescription Number(s):	CHEM 222 BCHM 206
Paper Title:	Organic Chemistry

Time Allowed:	TWO HOURS
Number of pages:	EIGHT

Answer all FOUR questions**.**

All questions are of equal value.

TURN OVER

1. Answer ***either*** **PART A** *or* **PART B**

PART A

. (a) Explain the mechanistic and stereochemical differences between S_N1 and S_N2 reactions. Include a reaction diagram of each process in your answer.

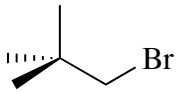
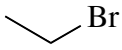
(b) Indicate briefly how the following factors may affect the rate of an S_N1 reaction:

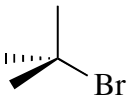
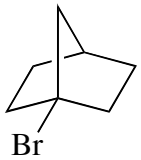
(i) Nature of the solvent.

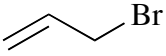
(ii) Nature of the nucleophile.

(iii) Nature of the leaving group.

(c) For each of the following pairs of substrates, explain which will react faster under the given reaction conditions. Include in your answer an explanation as to whether you expect the reaction to go by either an S_N1 or an S_N2 pathway in each case.

(i)  OR  with $PhS^- Na^+$ in DMF

(ii)  OR  with CH_3COOH

(iii)  OR  with CH_3COOH

Question 1 continued on next page

Question 1 continued

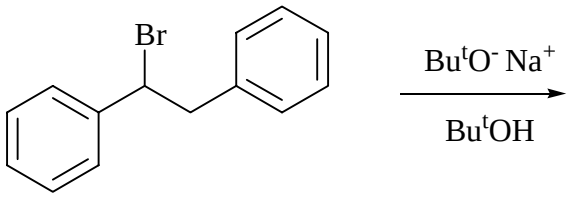
PART B

(a) Elimination reaction mechanisms are commonly divided into **THREE** types, called E1, E2 and $E1_{cb}$. Explain what is meant by each of these terms, and sketch reaction diagrams for each mechanism.

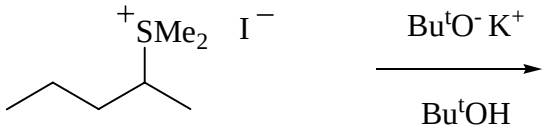
(b) Predict, with mechanistic reasoning, the major products from **three** of the following synthetic transformations.

(i)

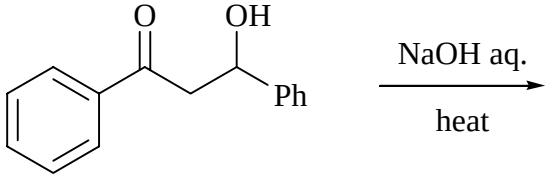
(ii)



(iii)

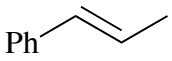


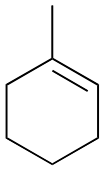
(iv)

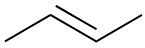


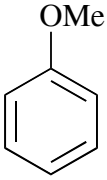
2. For **FIVE** of the following transformations below, predict the structure of the product and give mechanisms for the reaction sequences.

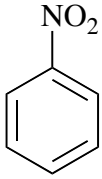
(i)  $\xrightarrow{Br_2}$

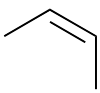
(ii)  $\xrightarrow{HBr}$

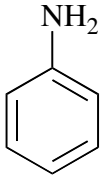
(iii)  $\xrightarrow[(ii)\ NaOH,\ H_2O_2]{(i)\ BH_3}$

(iv)  $\xrightarrow[(ii)\ H_3O^+]{(i)\ PhCO_3H}$

(v)  $\xrightarrow[AlCl_3]{PhCOCl}$

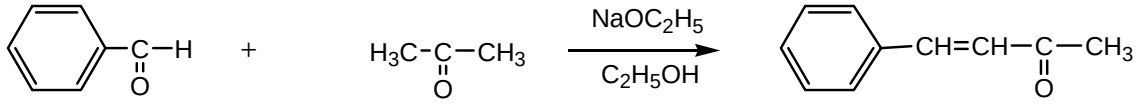
(vi)  $\xrightarrow[H_2SO_4]{HNO_3}$

(vii)  $\xrightarrow[(ii)\ NaOH]{(i)\ HOBr}$

(viii)  $\xrightarrow{Br_2}$

3. Answer (a) **OR** (b)

(a) When 1 mole of benzaldehyde and 1 mole of acetone are stirred together in ethanol in the presence of sodium ethoxide, the main product of the reaction is the α,β-unsaturated ketone 4-phenylbut-3-en-2-one.



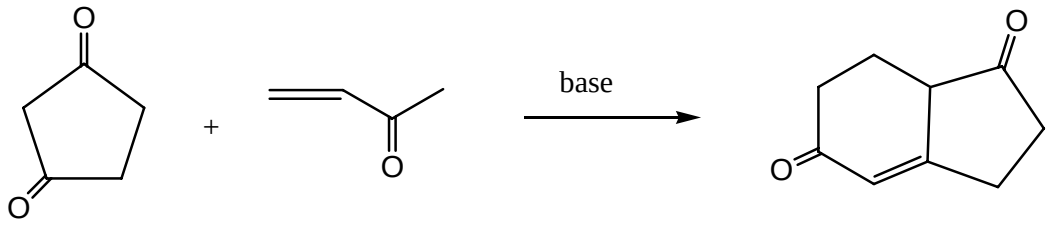
(i) Write the mechanism for this reaction.

(ii) Other products are formed in low yields. Give the structure(s) of at least one of these, and comment on why its yield is much lower.

(iii) What would be the <u>main</u> product if 1 mole of ethyl acetate ($CH_3CO_2C_2H_5$) was used instead of the benzaldehyde?

(iv) In (iii) the yield of product is low unless at least 1 mole of sodium ethoxide is used. Explain why this is so.

(b) In the multi-step reaction shown below, cyclopentane-1,3-dione reacts with butenone to give a product containing a 5-membered ring fused to a 6-membered one.



(i) Outline the mechanism for each step of this reaction and explain clearly what type of reaction it involves.

(ii) Briefly discuss why this type of annulation reaction is commercially important.

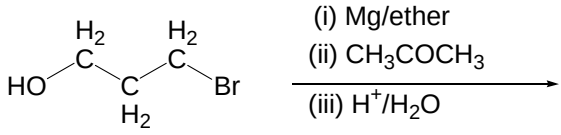
4. Answer **EITHER** (a) **OR** (b)

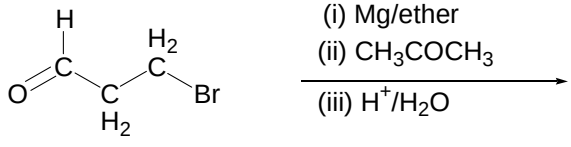
(a) The synthesis of organic compounds that contain more than one functional group is often complicated by the presence of functional groups that can interfere with the reaction one is trying to carry out, either by preventing it taking place altogether or by also reacting under the reaction conditions. The problem is commonly overcome by 'protecting' those groups that one does not wish to take part in the reaction, and subsequently 'deprotecting' them.

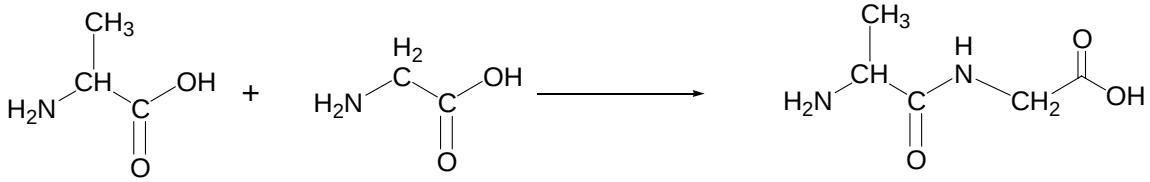
For **TWO** of the reactions below:

(i) Explain what the problems are in carrying out the scheme suggested.

(ii) Suggest a scheme by which the desired conversion can be achieved selectively.







Question 4 continued over the page

Question 4 continued

(b) The replacement of a diazonium (N_2^+) group on a benzene ring by another substituent is a very useful tool in the synthesis of benzene derivatives.

(i) Outline how you would prepare benzenediazonium chloride starting from benzene.

(ii) Many common substituents (e.g. $–NO_2$, –Cl, –COR, –R) can be introduced into the aromatic ring by electrophilic aromatic substitution using appropriate electrophiles. Three common ones, –OH, –F and –CN cannot. However, they can be introduced by replacement of the N_2^+ group of a diazonium salt. Explain how you could do replacements for **TWO** of these.

(iii) Sometimes a group that can be introduced into an aromatic ring directly (e.g. Cl, Br) is introduced indirectly via a diazonium salt. Why might this be useful?

(iv) Treatment of a diazonium salt with H_3PO_2 results in the $–N_2^+$ group being replaced by H. Why might one want to do this?

END OF PAPER