University of Canterbury

End of Year Examinations 2007

Prescription Number(s):	CHEM 322
Paper Title:	Organic Chemistry

Time Allowed:	TWO HOURS
Number of pages:	EIGHT

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

Section A: Answer **BOTH** questions;

Section B: Answer **TWO** questions out of THREE.

All questions are of equal value and you should allow approximately 30 minutes to answer each question.

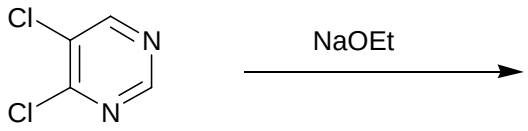
TURN OVER

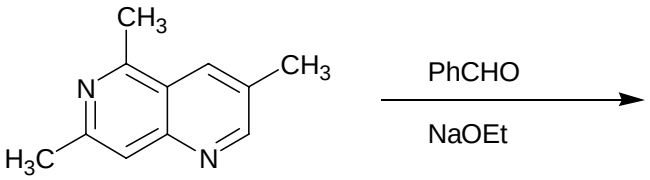
SECTION A

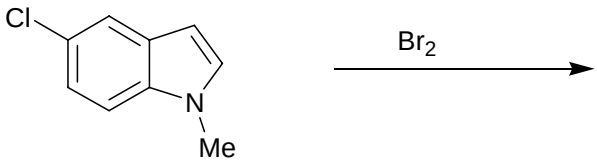
(Answer **BOTH** questions in this section.)

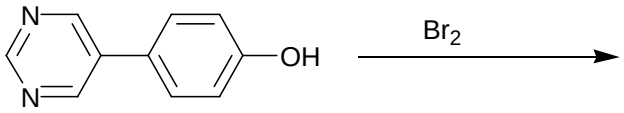
1. (a) (4 marks)

Predict the products of the following reactions.









(b) (4 marks)

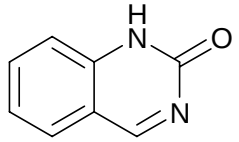
Pyridine is very unreactive towards electrophilic aromatic substitution. Outline **TWO** ways in which pyridines can be activated towards electrophilic substitution.

Question 1 continued on following page

Question 1 continued

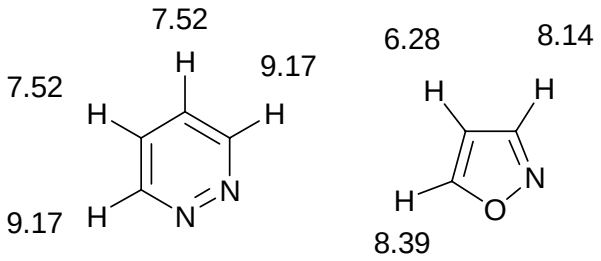
(c) (4 marks)

For the compound shown below draw two other tautomers and explain why each is less stable than the tautomer shown.



(d) (4 marks)

Explain the relative chemical shifts in the ^{1}H NMR spectra of each of the following compounds in terms of their polarisations.

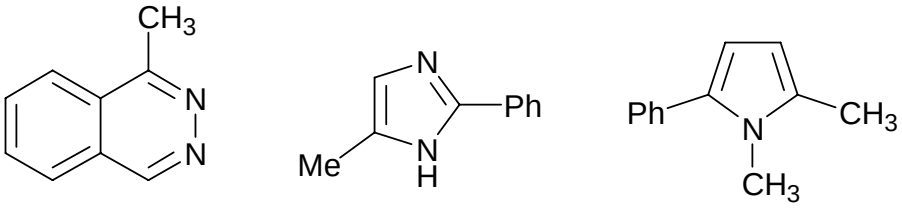


(e) (4 marks)

Briefly explain why pyridine is much more basic than pyrrole.

2. (a) (5 marks)

Show how each of the following compounds could be prepared by reaction between a binucleophile and a bielectrophile.



(b) (5 marks)

List the five most commonly employed reaction-types used for the construction of heterocyclic rings.

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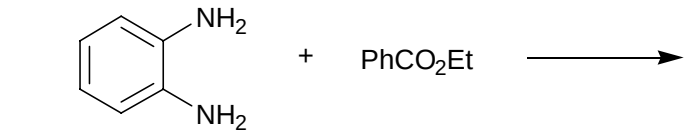
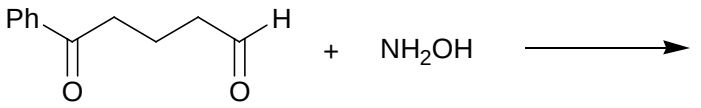
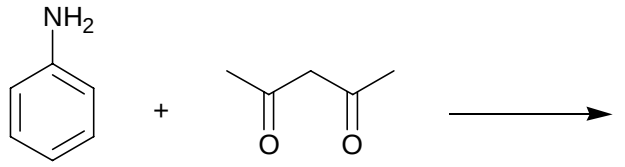
Question 2 continued

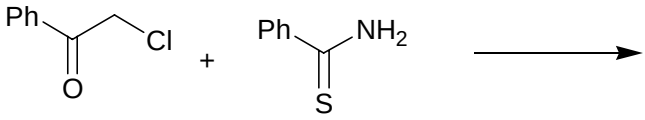
(c) (5 marks)

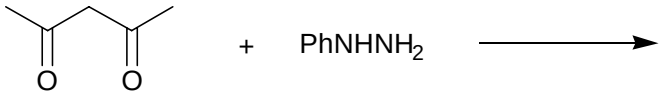
Predict the products of the following reactions.











(d) (5 marks)

Either

(i) Briefly describe the different types of tautomerism that are important in heterocyclic chemistry

Or

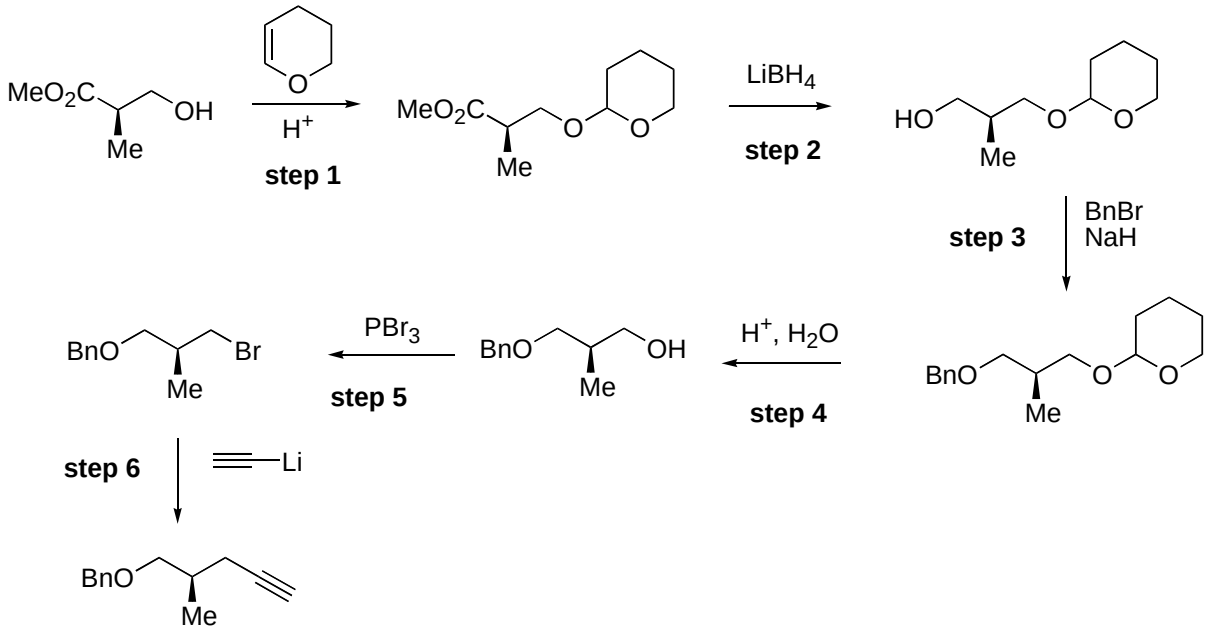
(ii) Explain the terms π-deficient and π-excessive as applied to nitrogen heterocycles.

SECTION B

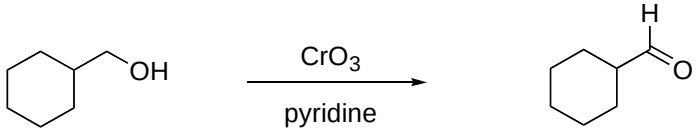
(Answer **TWO** questions out of THREE.)

3. (a) Protection of the hydroxyl group is important for the success of many syntheses, such as in the scheme given below. Discuss the choices of protecting groups used in this scheme, provide mechanisms for the protection and deprotection steps (steps 1,3 & 4), and indicate why protecting groups are required in this synthetic scheme.

Explain why $LiBH_4$ is a suitable reducing agent for step 2, whereas $NaBH_4$ is not.



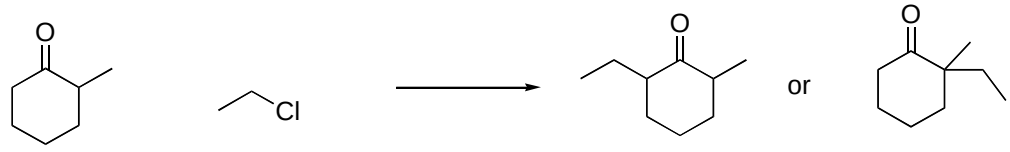
(b) For the following oxidation reaction give the reaction mechanism and explain why it is necessary to exclude water from the reaction.



Question 3 continued on following page

Question 3 continued

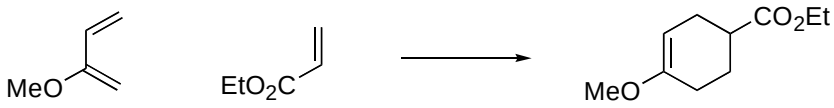
(c) For the following enolate alkylation reaction two products are possible. Provide specific reaction conditions that would lead to each product shown, and, using diagrams, clearly explain why the conditions you have chosen favour predominantly one product.



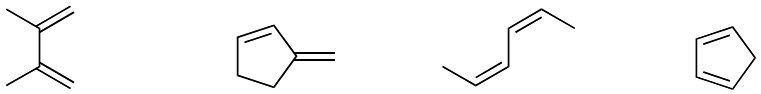
4. (a) What is a pericyclic reaction?

(b) Use frontier orbital theory to explain why Diels-Alder reactions are thermally allowed, whereas [2+2] cycloaddition reactions are thermally disallowed.

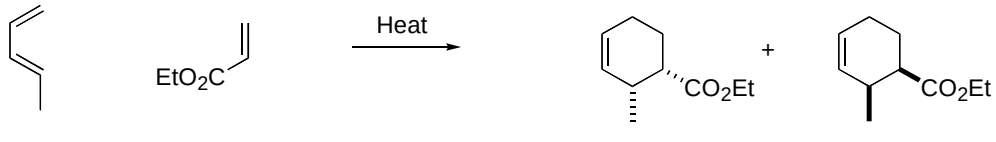
(c) Use frontier molecular orbital theory to account for the regioselectivity of the following Diels-Alder reaction.

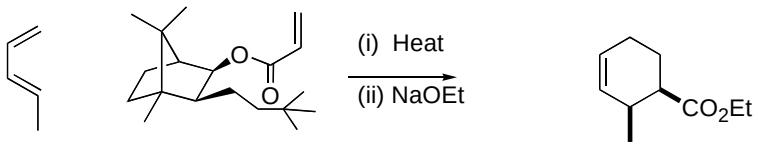


(d) List the following dienes in order of decreasing activity in a Diels-Alder reaction. Explain your reasoning.

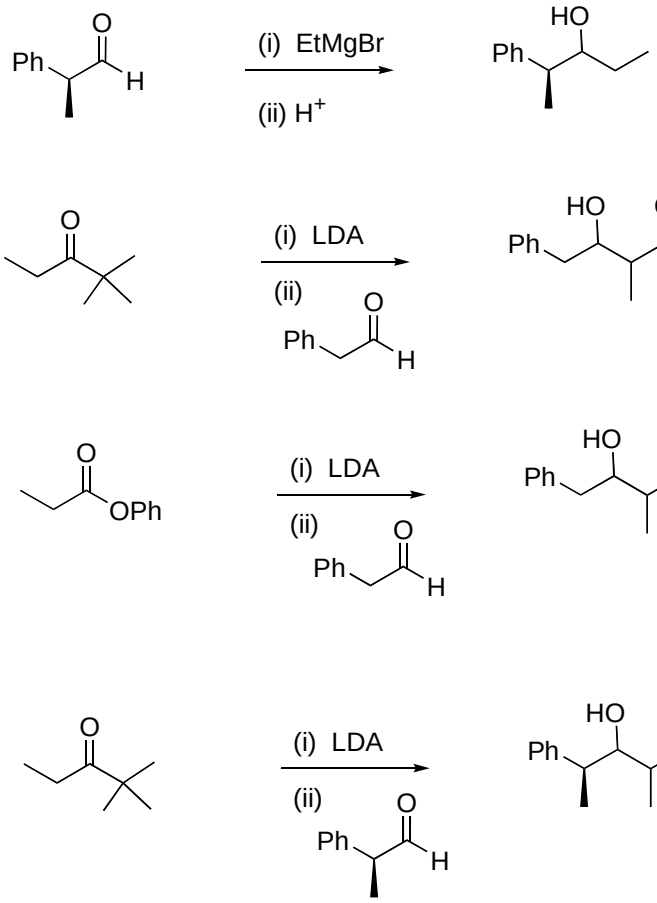


(e) Explain the stereoselectivity observed in the following Diels-Alder reactions:

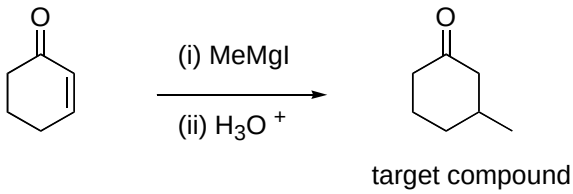




5. (a) Using clear diagrams to show your reasoning, predict the stereochemical outcomes of the following reactions.



(b) The following reaction did not produce the required target compound. Suggest a more likely outcome of the reaction and provide an explanation for its formation. Show a way in which the target compound could be made from this starting material.



target compound

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