

University of Canterbury

## End-of-year Examinations 2008

Prescription Number(s): CHEM 469

Paper Title: Special Topic

Time Allowed: Two hours

Number of pages: Seven

Answer **ALL** questions.

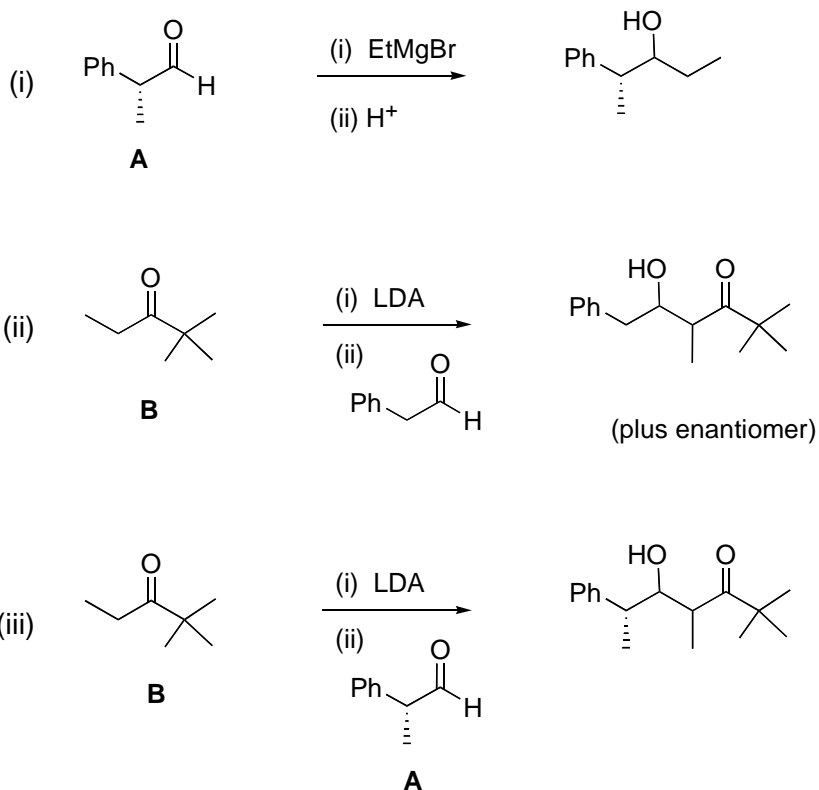
Total marks = 100

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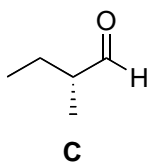


1. (20 marks)

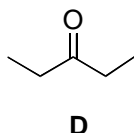
(a) Using clear mechanistic diagrams and explanations, predict the stereochemistry of the product in the following reactions:



(b) Explain what effect altering aldehyde A for aldehyde C below will have on the stereoselectivity of reactions (i) and (iii) in part (a) above.



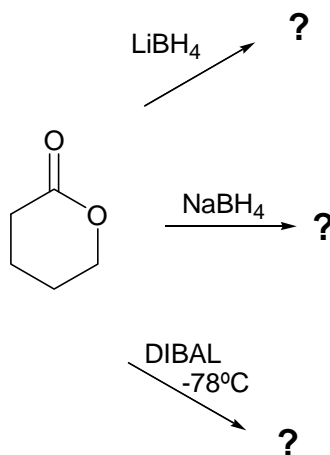
(c) Explain what effect altering ketone A for ketone B below will have on the stereoselectivity of reactions (ii) and (iii) in part (a) above.



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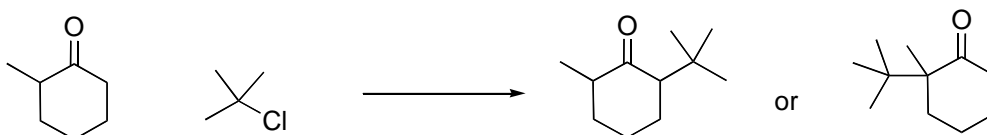
2. (10 marks)

Predict the outcome of the reaction of the lactone with each of the reducing agents shown. Provide an explanation for the different reaction outcomes and provide mechanisms for the reactions.



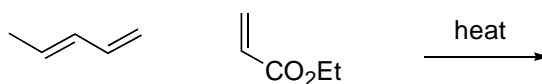
3. (10 marks)

In the following reaction, two products are possible. Provide specific reaction conditions that would lead to each product and explain why these reaction conditions give the required selectivity.



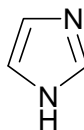
4. (10 marks)

Using clear mechanistic reasoning, predict the product of the following reaction. Account for the regio- and stereoselectivity of the reaction and describe how this reaction could be made enantioselective.



5. (a) (11 marks)

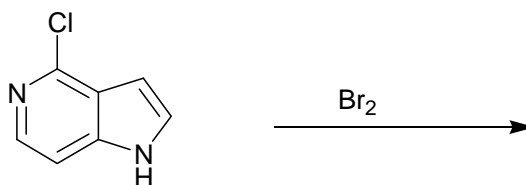
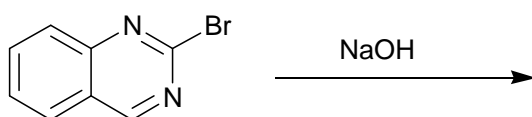
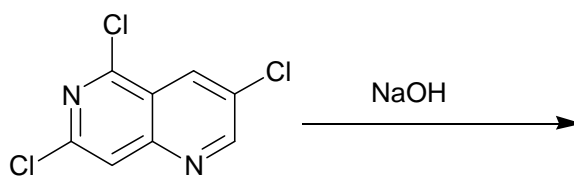
The structure of imidazole is shown below.



- (i) Predict the appearance of its  $^{13}\text{C}$  NMR spectrum.
- (ii) Explain why imidazole is both acidic and basic.
- (iii) How many isomers of dimethylimidazole exist?
- (iv) Show one method of synthesising an imidazole ring.

(b) (6 marks)

Predict the products of the following reactions, drawing the product in its most stable tautomeric form.



*Question 5 continued on following page*

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**Question 5 continued**

(c) (5 marks)

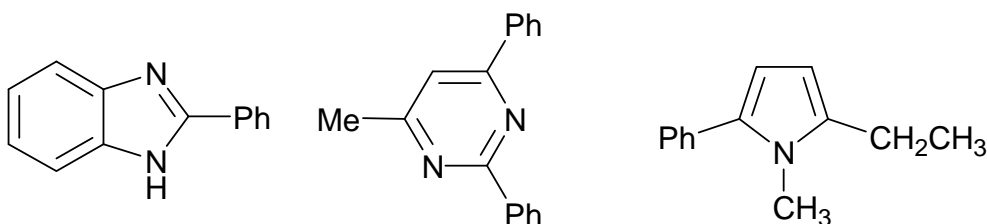
Pyridine is very unreactive towards electrophilic aromatic substitution. Outline TWO ways in which pyridines can be activated towards electrophilic substitution.

(d) (3 marks)

What types of heterocycles undergo Diels-Alder reactions?

6. (a) (6 marks)

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



(b) (6 marks)

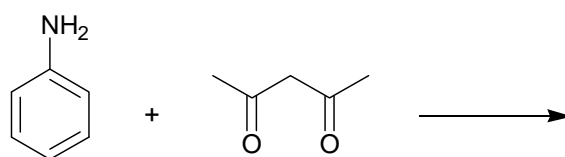
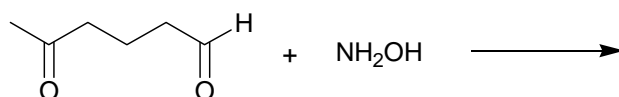
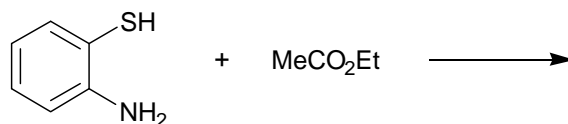
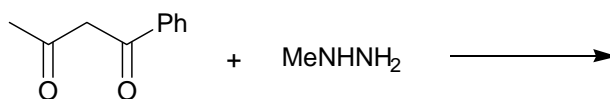
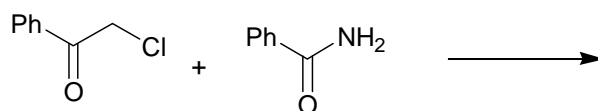
Briefly outline the problems associated with the use of reactants that contain both nucleophilic and electrophilic centres, as applied to the construction of heterocyclic rings.

*Question 6 continued on following page*

**Question 6 continued**

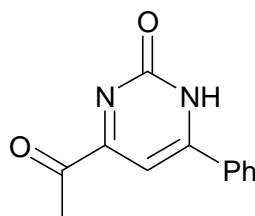
(c) (5 marks)

Predict the products of the following reactions.



(d) (8 marks)

Suggest a method of synthesis for the molecule shown below and draw three other tautomers for this compound, indicating their likely order of stability.

**END OF PAPER**