University of Canterbury

End of Year Examination 2006

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

Time Allowed:	THREE HOURS
Number of pages:	NINE

Answer **ALL SIX** questions.

All questions are worth equal marks.

TURN OVER

1. Answer (a) **OR** (b) **OR** (c)

IMPORTANT: In making a decision as to which of the questions below you will answer, you should first consider the options available in question 2 since your choice here will limit your choices in question 2.

(a) Carbocations vary considerably in stability. Discuss how the presence of certain structural features can (i) stabilise or (ii) destabilise a carbocation. Illustrate your answer, where possible, with specific examples.

(b) The construction of C-C bonds plays a very important role in the total synthesis of natural products. One of the most commonly used methods for this purpose involves the reaction of a carbanion generated from one molecule with a carbonyl group of another. Discuss some of the reactions that can be used to perform this. If any of them have particular advantages or disadvantages, mention these.

(c) Reactions of carbon-centred free radicals are playing an increasing role in organic synthesis. Discuss some of the advantages and disadvantages of the use of such reactions for this purpose and illustrate your answer with suitable examples.

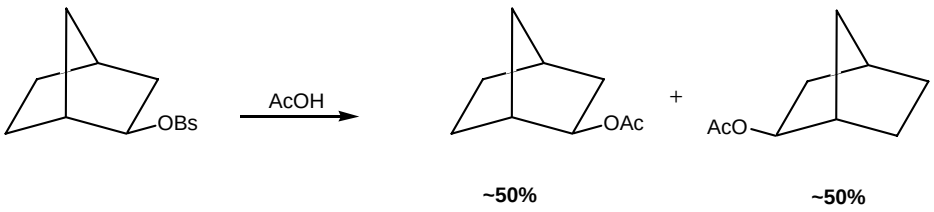
2. Answer **TWO** of the following:

IMPORTANT:

If you answered option (a) in the previous question you must answer (b) and (c).
If you answered option (b) in the previous question you must answer (a) and (c).
If you answered option (c) in the previous question you must answer (a) and (b).

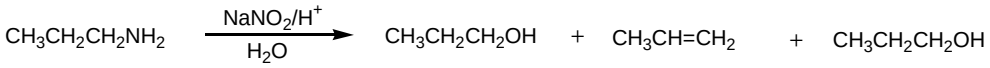
(a) Show how the product distributions obtained in reactions (i) and (ii) below can be accounted for on the basis on their mechanisms.

(i)



~50% **~50%**

(ii)

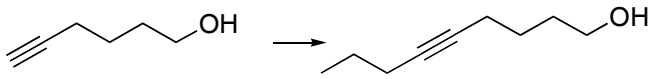


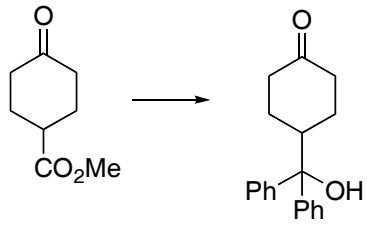
7% **28%** **32%**

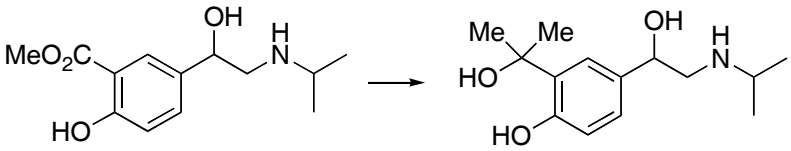
(b) Many ketones have more than one type of α-hydrogen. Explain how this can give rise to problems if you wish to carry out a crossed aldol reaction. Discuss possible approaches to overcoming these problems.

(c) In organic synthesis, one often obtains, at some point, a product with a carbon-halogen bond that one would like to replace by a C—H one. In the past, the approaches adopted were to either convert the halide to a Grignard reagent and add water, or to replace the halogen by H using $LiAlH_4$. Today, chemists often prefer to use tri-*n*-butyltin hydride as the reducing agent. Give the mechanism for the reduction of a halide by tri-*n*-butyltin hydride, discuss the driving forces for the reaction, and comment on any advantages/disadvantages it has over the older methods.

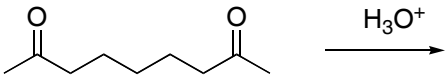
3. (a) Discuss ways to carry out the following **three** transformations. Indicate any possible problems, solutions to these problems, and also possible reagents and conditions.



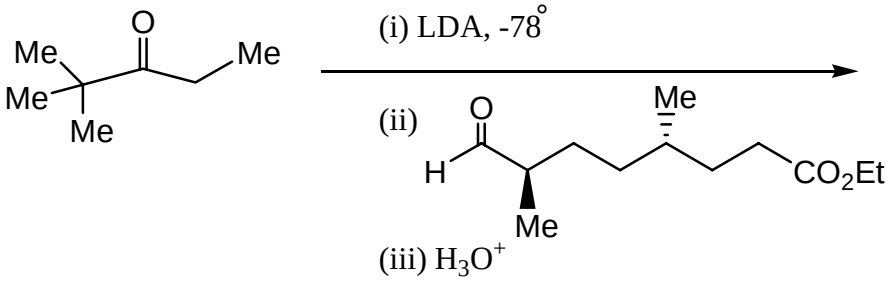


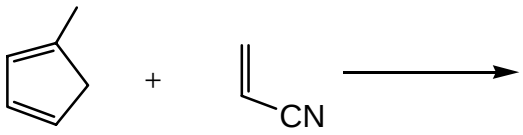


(b) Predict the product from the following reaction giving detailed reasons for your answer.



4. (a) Predict the outcome of the following **two** reactions, giving a **full and detailed mechanistic** analysis in each case to explain any stereochemical and regiochemical issues.





(b) For the first example, classify, with reasons, the relative topicity of the reaction and also the relative configuration of the product.

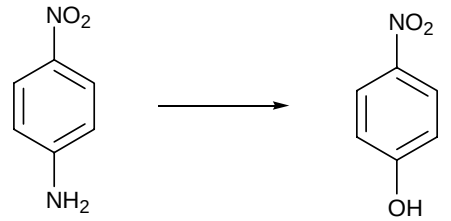
(c) For the second example, draw and discuss the reacting “frontier orbitals”. What could be added to this reaction in order to catalyze it? Explain your answer with reference to these “frontier orbitals”.

5. Answer **EITHER Part A OR Part B** of this question.

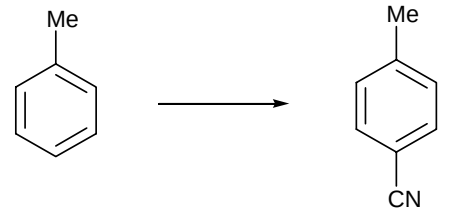
Part A

(a) Suggest reagents for **THREE** of the following synthetic transformations (all require more than one step).

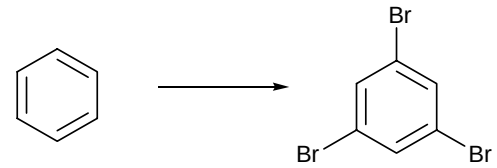
(i)



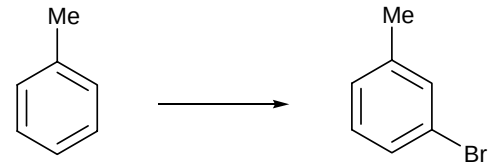
(ii)



(iii)

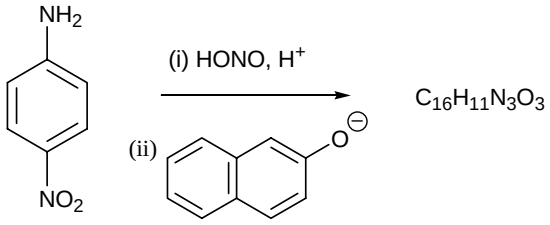


(iv)

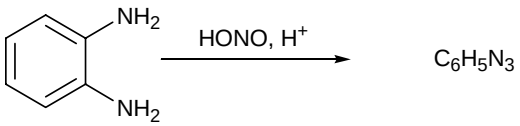


(b) For **both** the following synthetic sequences, predict the structures of the products and provide mechanisms for their formation.

(i)

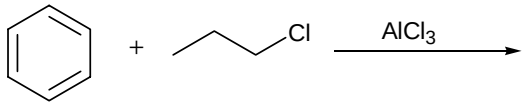


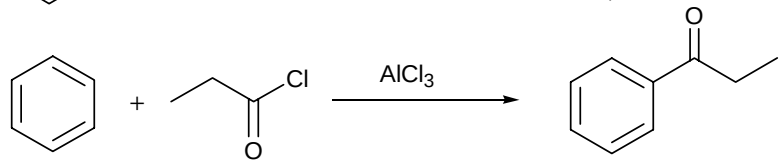
(ii)



Part B

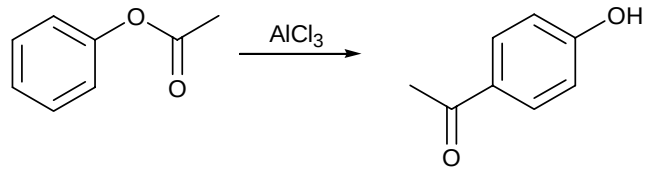
(a) Provide mechanistic explanations for the following reactions.

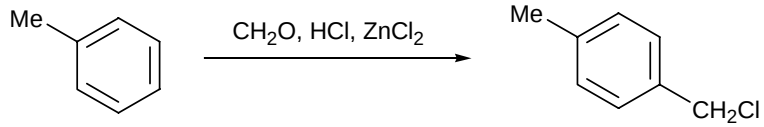
(i) 

(ii) 

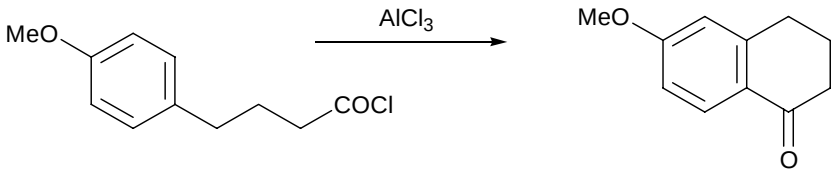
(b) Give **TWO** reasons why Friedel-Crafts acylation is synthetically a much more useful reaction than Friedel-Crafts alkylation.

(c) Give a mechanistic explanation for **ONE** of the following transformations.

(i) 

(ii) 

(d) Give a plausible mechanism for the following transformation.

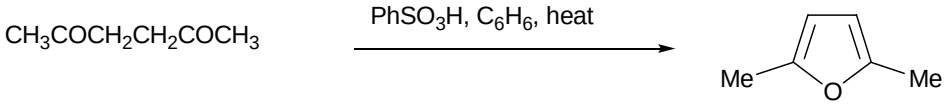


6. **ANSWER Part A AND EITHER Part B OR Part C**

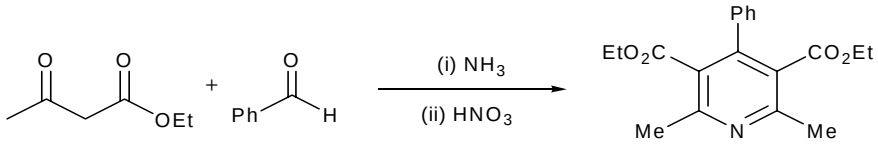
Part A

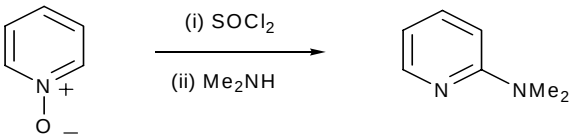
(a) Show how a retrosynthetic analysis of furans leads to 1,4-dicarbonyl compounds as starting materials.

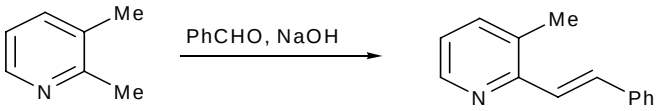
(b) Suggest a plausible mechanistic pathway for the following transformation.



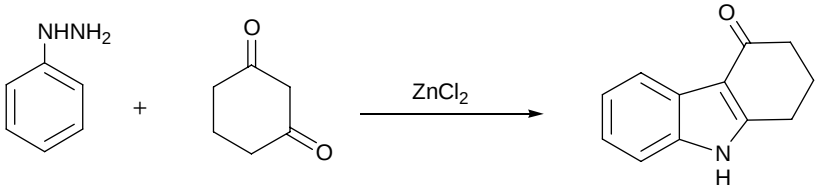
Part B Explain **two** of the following synthetic transformations:

(a)


(b)


(c)


Part C Explain **two** of the following synthetic transformations:

(a)


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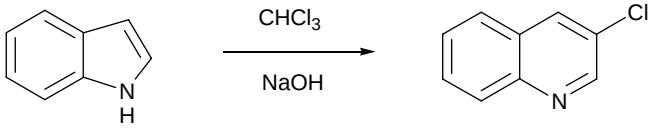

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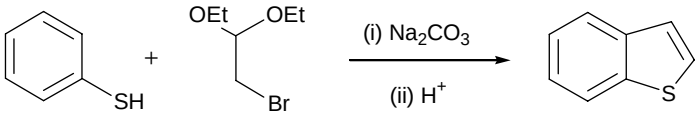

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