

University of Canterbury

End of Year Examinations 2005

Prescription Number(s):	CHEM 322 CHEM 362
Paper Title:	Organic Chemistry

Time Allowed: THREE HOURS

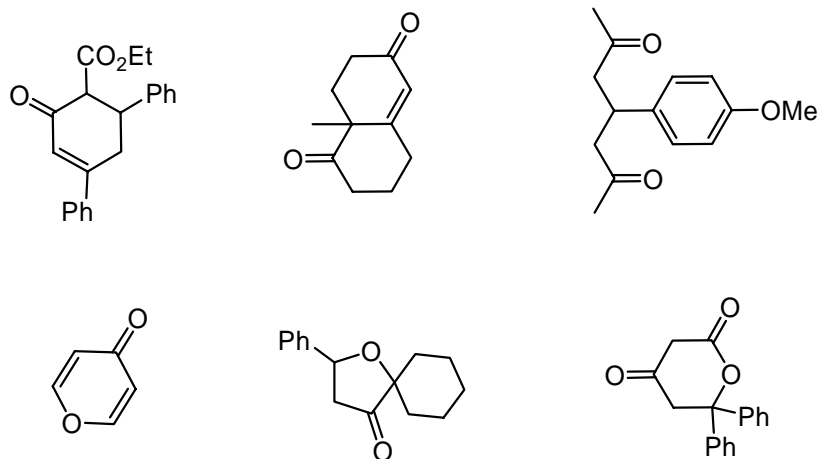
Number of pages: EIGHT

Answer **ALL** questions.

All questions are of equal value.

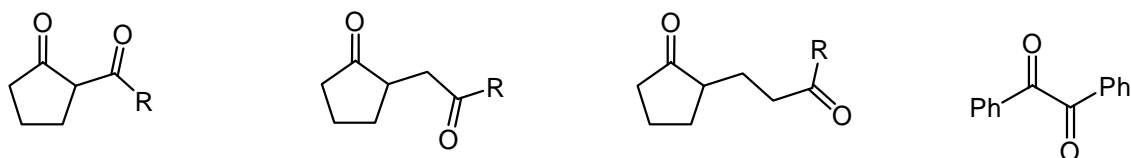
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1. Using retrosynthetic analysis show how **FIVE** of the following compounds could be made. Include all reagents required.



2. Show a synthesis for **THREE** of the following four diketones and show how the relationship between the two carbonyl functional groups influences your suggestions for each synthesis.

Show, by means of structural diagrams, a reaction mechanism for each step in your schemes.



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

IMPORTANT: In making a decision as to which of the questions below you answer, you should first consider the options available in Question 4 as your choice will restrict your options in that question.

EITHER

- (a) Write an account of the structure and chemistry of carbocations of various types. Your account should include some discussion of how their structure affects the reactions they undergo and the products of these reactions. Where possible your answer should be illustrated by suitable examples.

OR

- (b) The α hydrogens of ketones can be lost under strongly basic conditions to give resonance-stabilised carbanions. These carbanions can then be reacted with aldehydes, ketones, esters or, in some cases, alkyl halides to form C-C bonds. However, some ketones have more than one type of α -hydrogen. Butanone ($\text{CH}_3\text{CH}_2\text{COCH}_3$) is an example of one. Discuss some of the approaches that can be adopted to maximise the proportion of each of the two possible enolates derived from butanone.

OR

- (c) Reactions of carbon-centred free radicals are playing an increasing role in organic synthesis. While a number of methods are available for generating these, the most widely used involves the use of tributyltin hydride. Discuss some of the advantages and disadvantages of this reagent, and give examples of its use in (i) the reduction of alcohols or alkyl halides to hydrocarbons and (ii) the formation of 5-membered carbocyclic rings from acyclic precursors.

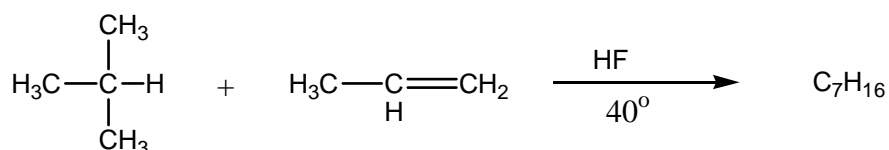
4. Answer **TWO** of the following:

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

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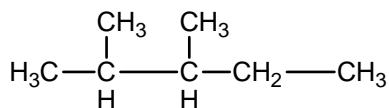
If you answered option (c) in the previous question you must answer (a) **and** (b).

- (a) In the alkylation process carried out in oil refineries, isobutane is reacted with propene in liquid hydrogen fluoride to form a mixture of heptanes.

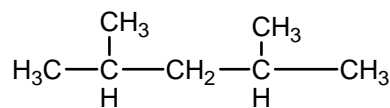


The first step in the reaction is believed to involve protonation of the propene to form the 2-propyl cation $(\text{CH}_3)_2\text{CH}^+$.

- (i) Suggest a mechanism by which a heptane might be formed.
- (ii) Explain why the main heptane products are 2,3-dimethylpentane and 2,4-dimethylpentane.



2,3-dimethylpentane



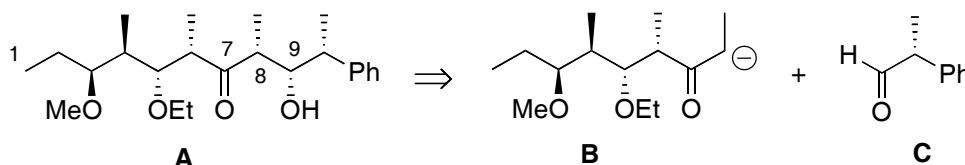
2,4-dimethylpentane

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Question 4 continued

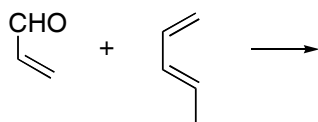
- (b) A common approach to the synthesis of natural products involves the construction of sub-units that are then linked together by C-C bonds. Such bonds often involve reactions of carbanions formed in one unit with suitable electrophilic centres in another. Among the reactions covered in your course that fall into this category are aldol additions, Claisen reactions, Michael additions and the Wittig reaction. Explain how each of these reactions can be used to achieve C-C bond formation.
- (c) Write a brief account of how free radicals can be generated, how they may be detected, and factors that affect their stability, giving relevant examples to support your account.

5. A key step in the synthesis of **A** (an intermediate in the synthesis of a natural antibiotic) involves the aldol reaction depicted in the following disconnection. Use this information to answer the following questions.



- (a) Assign each of the stereocentres in **A** as *R* or *S*, giving your reasons. Use this information to assign each pair of relative configurations of **A** as like (*l*) or unlike (*u*).
- (b) Predict, with reasons, the geometry of the enolate **B** and suggest how it might be formed.
- (c) Assign the relative configurations of **A** as erythro/threo and Cram/antiCram. Give your reasons.
- (d) Draw and discuss detailed cyclic transition states to explain your erythro/threo selectivity.
- (e) Draw and discuss detailed Felkin-Anh transition states to explain your Cram/antiCram selectivity.
- (f) What other factors might influence the stereochemical outcome of this aldol reaction?

6. (a) Give a detailed reaction mechanism for the following Diels Alder reaction and indicate the structure(s) of the products. Account for any stereoselectivity and regioselectivity associated with this reaction. Why is this reaction classified as a pericyclic reaction?



- (b) Draw the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for each reactant in part (a). Indicate the relative energies of the HOMO and LUMO in each case and suggest which combination will react in the Diels Alder reaction. Give your reasons.
- (c) How would the addition of a Lewis acid (e.g. AlCl_3) effect the Diels Alder reaction in part (a)? Explain your answer on the basis of HOMO / LUMO interactions.
- (d) Define the terms diastereoselectivity and enantioselectivity and use the example of a Diels Alder reaction, and other examples of your choice, to illustrate your answer in detail.

END OF PAPER

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