

University of Canterbury

End of Year Examinations 2005

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

Time Allowed: TWO HOURS

Number of pages: SEVEN

Answer **ALL** questions

All questions are of equal value

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

EITHER

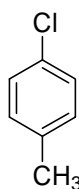
- (a) (i) By means of structural diagrams, illustrate each of the S_N1 and S_N2 mechanisms for substitution of an alkyl halide.
- (ii) Show the appropriate structures of the alkyl groups (i.e. primary, secondary or tertiary) and the types of nucleophiles that might be expected to undergo reactions by each of these mechanisms.
- (iii) For each of these mechanisms, draw a reaction-coordinate diagram and give the structure of any intermediate(s) or transition state(s) that are important.
- (iv) For each mechanism, indicate if the rate will vary significantly with change in the concentration of the nucleophile.

OR

- (b) (i) By means of structural diagrams, illustrate each of the E1 and E2 mechanisms for elimination of HBr from an alkyl bromide.
- (ii) Suggest the appropriate structures of the alkyl groups (i.e. primary, secondary or tertiary) and the types of bases that might be expected to undergo reactions by each of these mechanisms.
- (iii) For each of these mechanisms, draw a reaction-coordinate diagram and give the structure of any intermediate(s) or transition state(s) that are important.
- (iv) For each mechanism, indicate if the rate will vary significantly with change in the concentration of base.

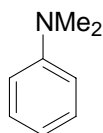
2. Answer **THREE** of the following (a) – (e):

- (a) Write the mechanism for Friedel-Craft alkylation of benzene with methyl chloride and aluminium chloride. Draw a reaction coordinate diagram for the substitution reaction and show on it the structure of any intermediate(s) or transition state(s) that are important.
- (b) By means of structural diagrams, show how you could prepare 4-chlorotoluene from benzene:



4-chlorotoluene

- (c) Explain why nitration of *N,N*-dimethylaniline gives mainly the *m*-nitro derivative when concentrated nitric and sulfuric acids are used, but mainly the *o*- and *p*-nitro derivatives in less acidic conditions.



N,N-dimethylaniline

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Question 2 continued

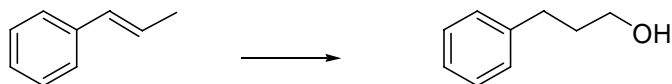
- (d) Below are some data on the relative rates of addition of bromine and of HBr to alkenes.

Relative rate of addition reactions of alkenes

with bromine				
	$\text{CH}_2=\text{CH}_2$	$\text{CH}_3\text{CH}=\text{CH}_2$	$(\text{CH}_3)_2\text{C}=\text{CH}_2$ $\text{CH}_3\text{CH}=\text{CHCH}_3$	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$
$k_{\text{relative ca.}}$	1	10^2	10^4	10^6
with HBr				
	$\text{CH}_2=\text{CH}_2$	$\text{CH}_3\text{CH}=\text{CH}_2$ $\text{CH}_3\text{CH}=\text{CHCH}_3$	$(\text{CH}_3)_2\text{C}=\text{CH}_2$ $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	
$k_{\text{relative ca.}}$	1	10^5	10^9	

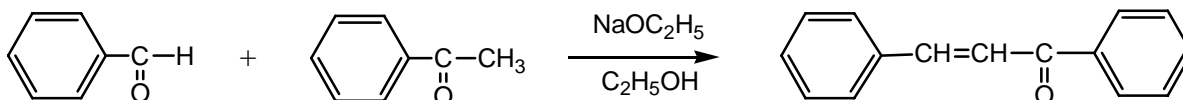
What do the data tell you about the mechanism of the addition of these two reagents and the structure of any intermediates or transition states involved? Give reasons for your conclusions.

- (e) Show how the following transformation might be effected by means of boron chemistry.



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

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



- (i) Write the mechanism for this reaction.
- (ii) A second product, also an α,β -unsaturated ketone, is formed in low yield. Give the structure of this compound, and comment on why the yield of this is much lower.
- (iii) What would the **main** product be if 1 mole of ethyl benzoate (C₆H₅CO₂C₂H₅) 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) The formation of cyclic compounds from acyclic starting materials is an important process in organic synthesis, since the most readily obtained raw material for organic compounds is petroleum, which consists largely of straight chain hydrocarbons. Some of the most useful methods are based on reactions of diethyl malonate (CH₂(CO₂C₂H₅)₂).

By means of suitably chosen examples, show how you could, using such reactions, synthesise cycloalkane derivatives containing 3-, 4-, 5-, and 6-membered rings. Briefly comment on the specific experimental conditions required in each case.

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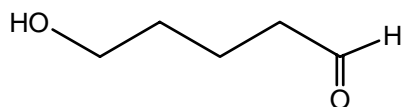
4. Answer **TWO** of the following (a) – (c).

(a) The formation of C—C bonds is an important reaction in the synthesis of natural products.

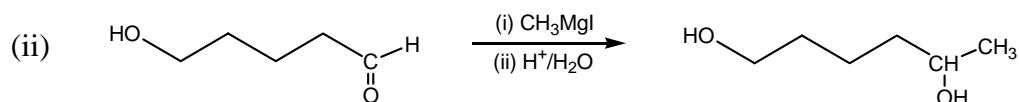
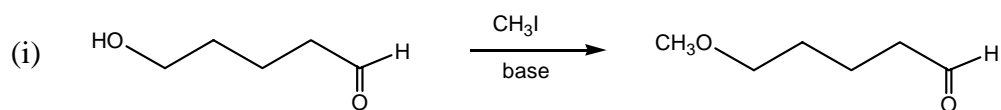
(i) Why is this? Discuss, in general terms, the sorts of situations where C—C bond formation is important.

(ii) Give **THREE** examples of reactions that can be used to form C—C bonds, and comment on any particular advantages each one has.

(b) Like C—C bond formation, functional group interconversion also plays a very important part in organic synthesis. Such interconversions may be complicated by the presence of more than one type of functional group in the molecule. The molecule below contains both a hydroxyl group and an aldehyde group.



Explain what the problems are in achieving the conversions below, and how you could overcome them:



(c) Discuss some of the problems that can be encountered in introducing substituents into an aromatic nucleus, and explain how these may be overcome.

END OF PAPER