UNIVERSITY OF VICTORIA

CHEMISTRY 335, S01

SYNTHETIC METHODS IN ORGANIC CHEMISTRY

MIDTERM EXAM #2 — MARCH 13, 2009

NAME:_____ **STUDENT ID:**_____

INSTRUCTOR: FRASER HOF

TOTAL MARKS = **40.5**

DURATION: **50 MINUTES**

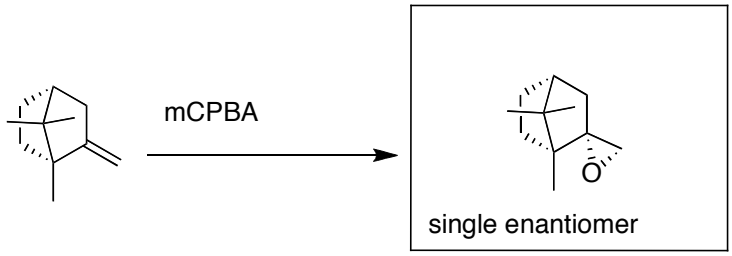
THIS EXAMINATION PAPER HAS **5** PAGES, INCLUDING THIS COVER PAGE. COUNT THE NUMBER OF PAGES IN THIS EXAMINATION PAPER BEFORE YOU START TO WRITE, AND REPORT ANY DISCREPANCY IMMEDIATELY TO THE INVIGILATOR.

QUESTIONS ARE TO BE ANSWERED IN THE SPACE PROVIDED ON THE EXAM FORM.

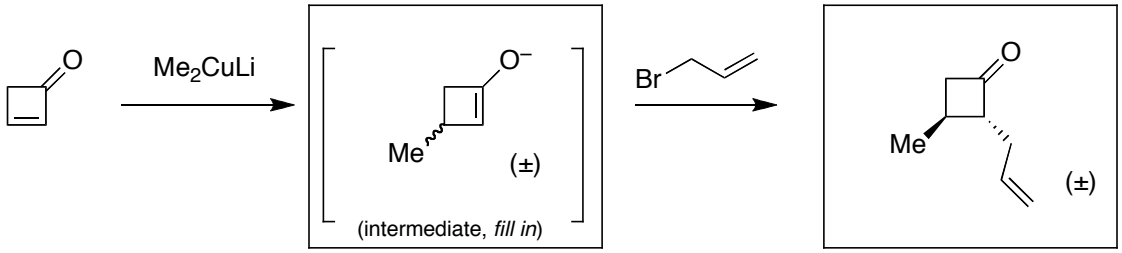
QUESTIONS ANSWERED IN PENCIL WILL NOT BE ELIGIBLE FOR RE-GRADING.

1. (10.5 marks) Fill in the boxes with the missing reagents or products **(1 mark each)**. Show only the MAJOR stereoisomer produced by the given reaction conditions. For all products that you fill in, indicate whether the compound is achiral, racemic, or a single enantiomer **(0.5 marks each)**.

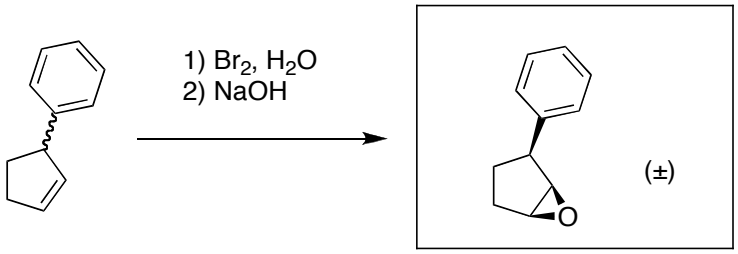
a)



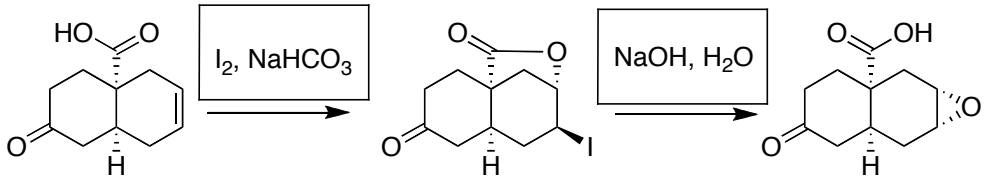
b)



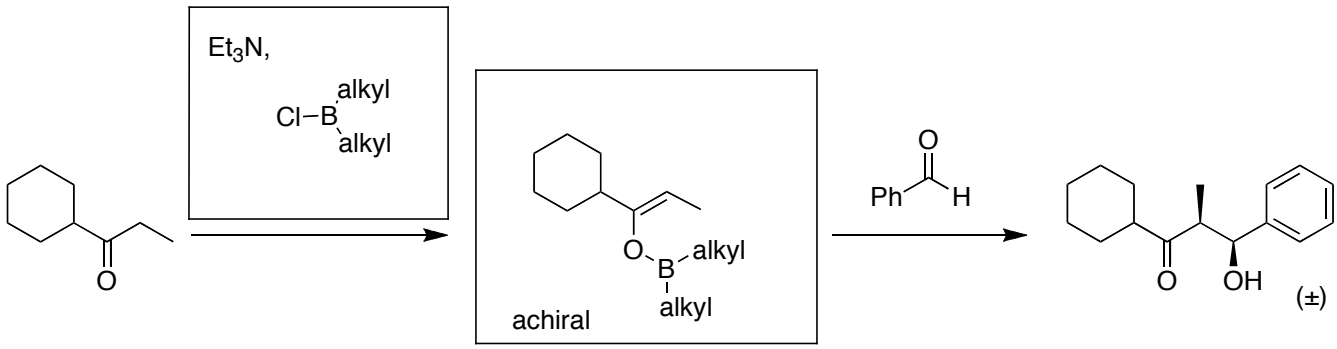
c)



d)

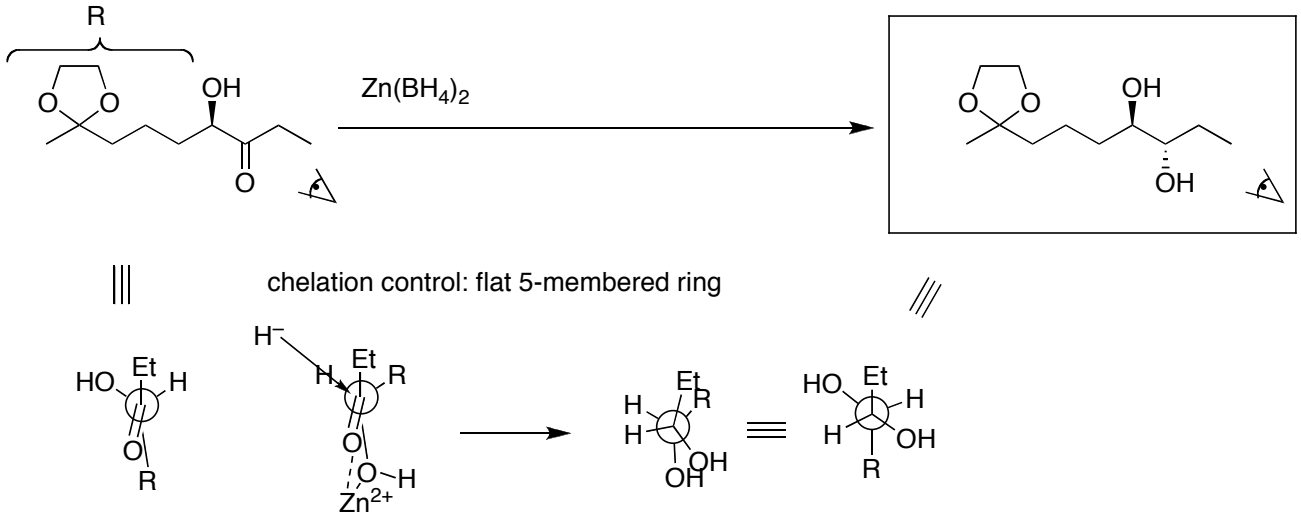


e)



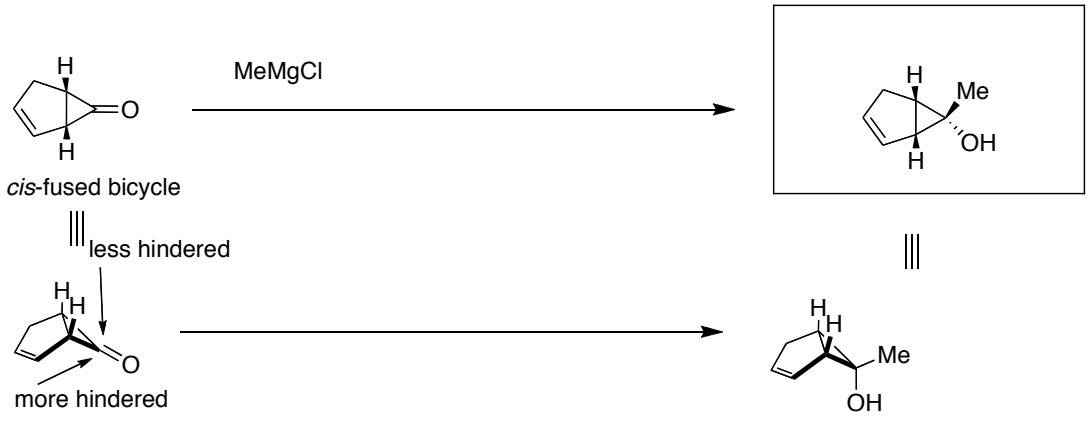
2. (12 marks) Give the product of the following reactions. In the space below each reaction, include stereochemical (3D) diagrams of starting materials and products, and explain the source of the observed stereoselectivity in words.

a)

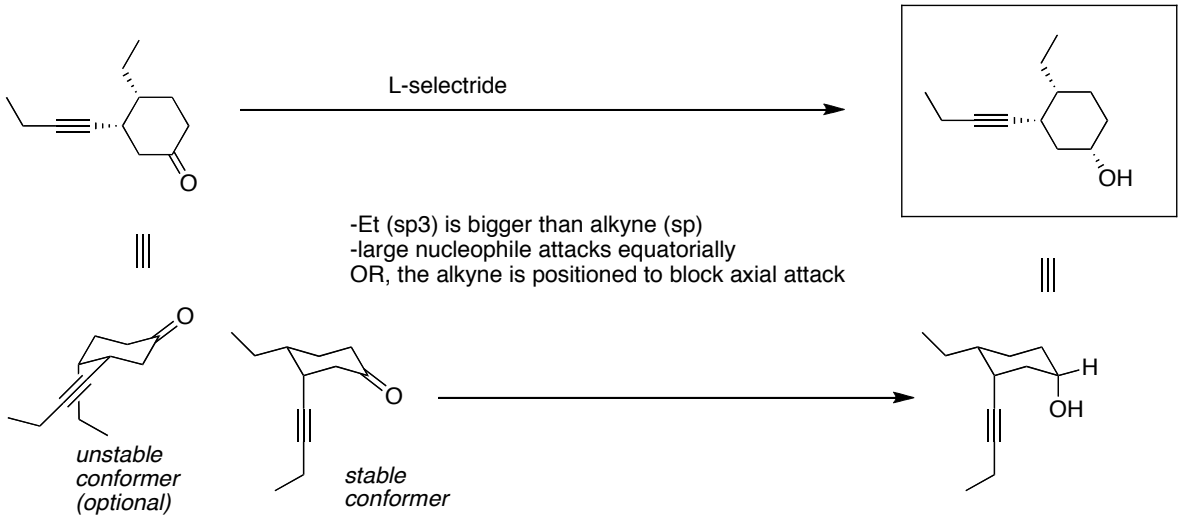


attack via least hindered path toward π*

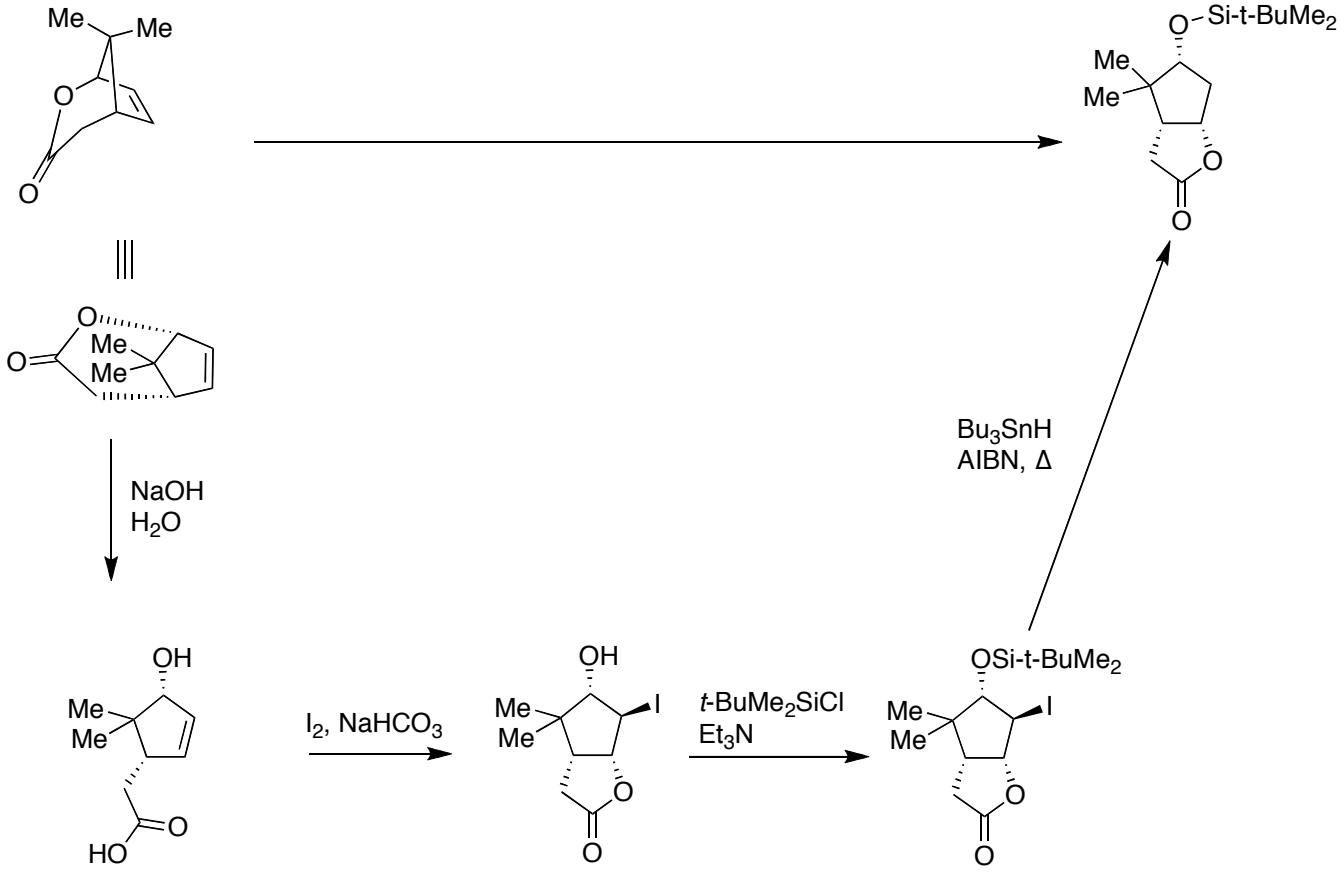
b)



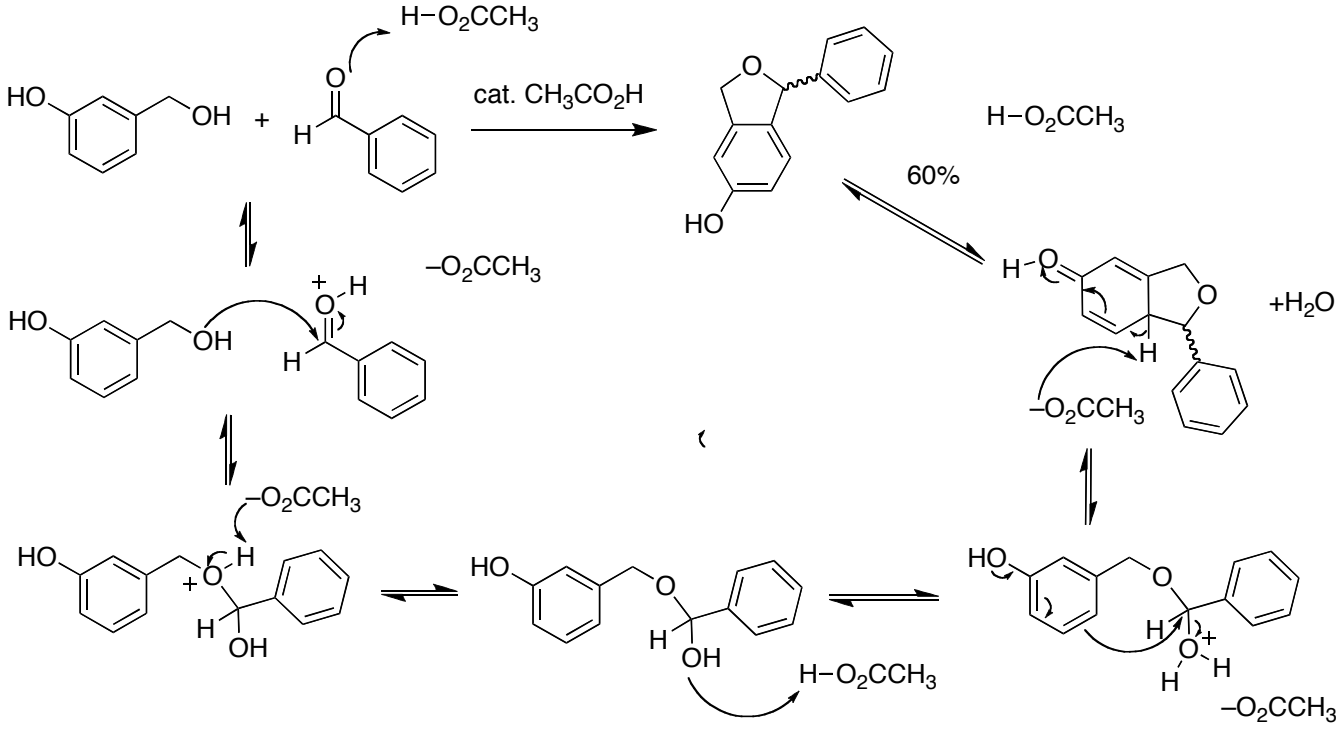
c)



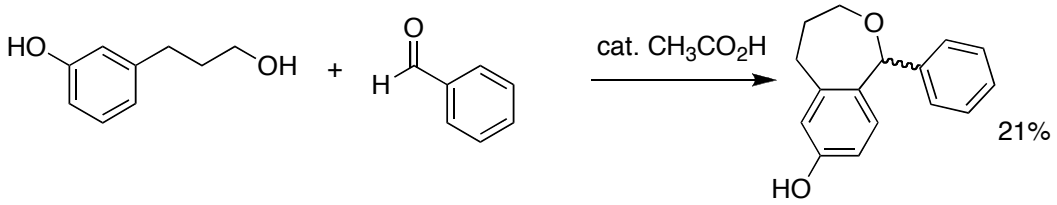
3. (8 marks) Plan the synthesis shown below. You can go in the forward or reverse direction. Indicate which reagents and conditions are required for each step. Do not show mechanisms.



4. a) **(8 marks)** The following synthesis of the heterocycle "isophthalan" was reported in 2008. The authors refer to this key step as an "oxa-Pictet-Spengler" reaction. Propose a detailed mechanism reaction, explicitly showing all intermediates, proton transfers, and byproducts.



b) **(2 marks)** The same team reported that the reaction below proceeds in much lower yield than the reaction in part a) above. Explain why, making specific reference to kinetics and/or thermodynamics.



-the formation of a seven-membered ring is kinetically slow due to unfavourable chain entropy (more rotational degrees of freedom with each rotatable bond).

OR

-the formation of a seven membered ring is thermodynamically unfavorable because the 7-membered ring has some internal ring strain (non-ideal bond angles) relative to 6-membered and 5-membered rings.

END