

UNIVERSITY OF VICTORIA

CHEMISTRY 335, S01

SYNTHETIC METHODS IN ORGANIC CHEMISTRY

MIDTERM EXAM #2 — MARCH 12, 2010

NAME: _____

STUDENT ID: _____

INSTRUCTOR: FRASER HOF

TOTAL MARKS = **35**

DURATION: **50 MINUTES**

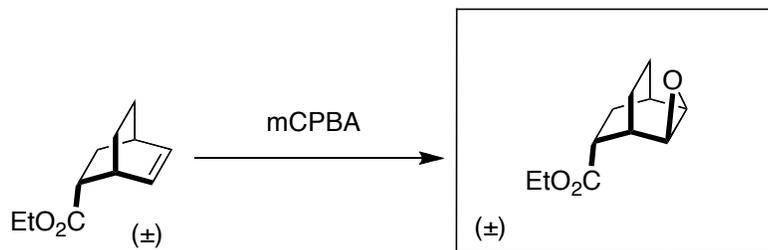
THIS EXAMINATION PAPER HAS **6** PAGES, INCLUDING THIS COVER PAGE. COUNT THE NUMBER OF PAGES IN THIS EXAMINATION PAPER BEFORE YOU START TO WRITE, AND REPORT ANY DISCREPANCY IMMEDIATELY TO THE INVIGILATOR.

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

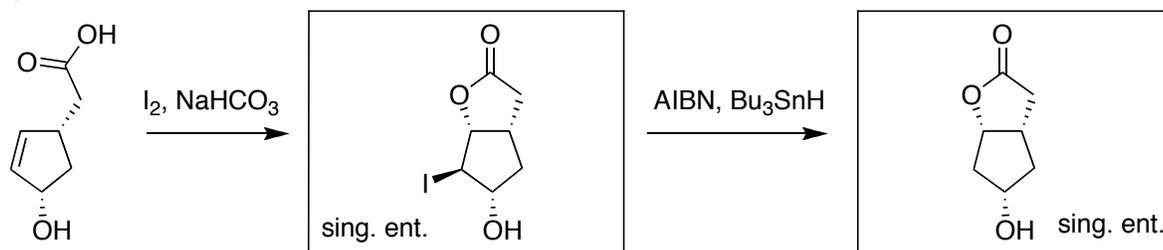
QUESTIONS ANSWERED IN PENCIL WILL NOT BE ELIGIBLE FOR RE-GRADING.

1. (continued)

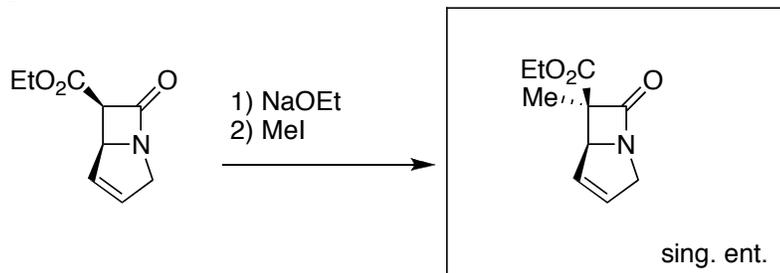
e)



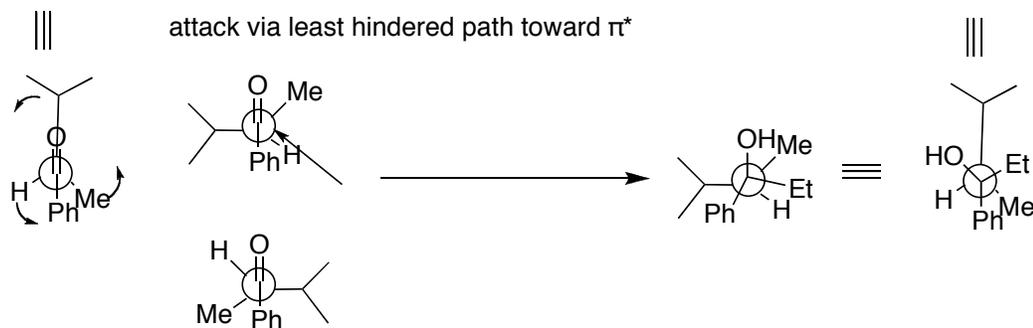
f)



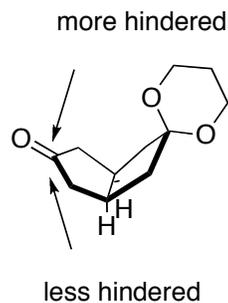
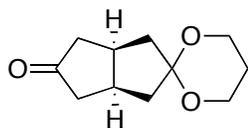
g)



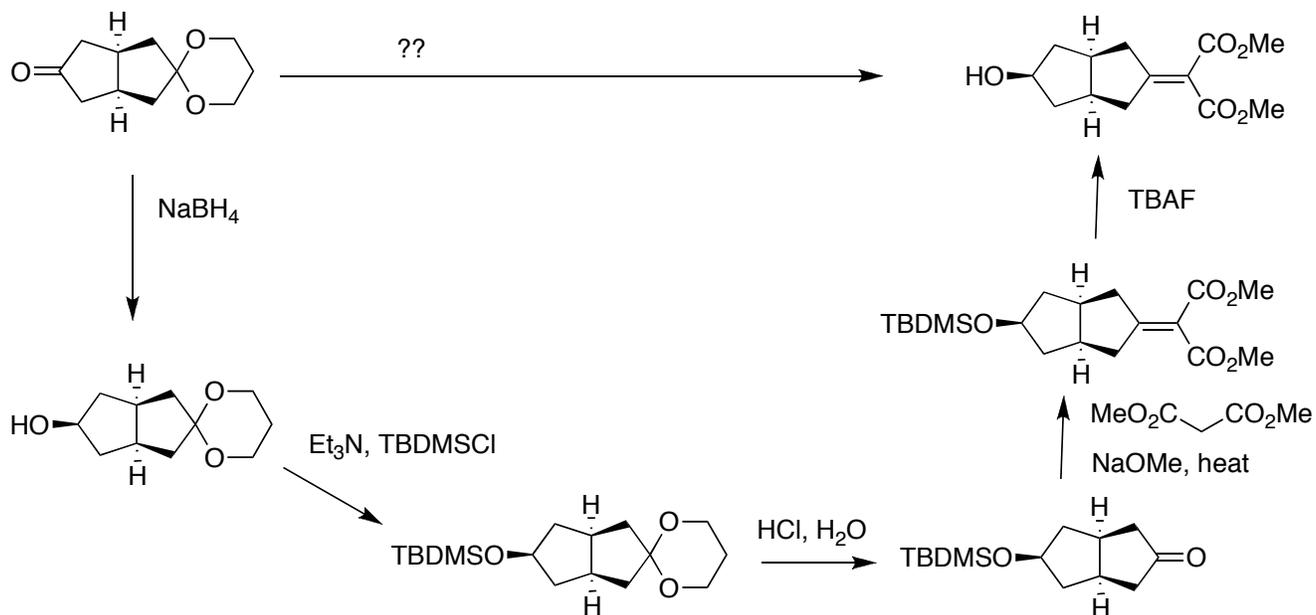
2. (4 marks) Give the product of the following reaction. In the space below the reaction, include stereochemical 3D diagrams of starting materials and products, and explain the source of the observed stereoselectivity in words.



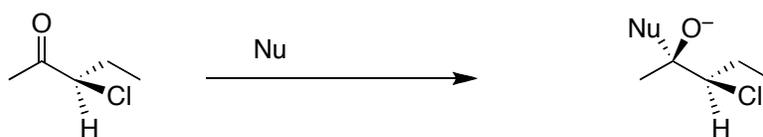
3a. (2 marks) Draw a 3-dimensional representation of the molecule shown below and indicate which of the two faces of the carbonyl is least hindered.



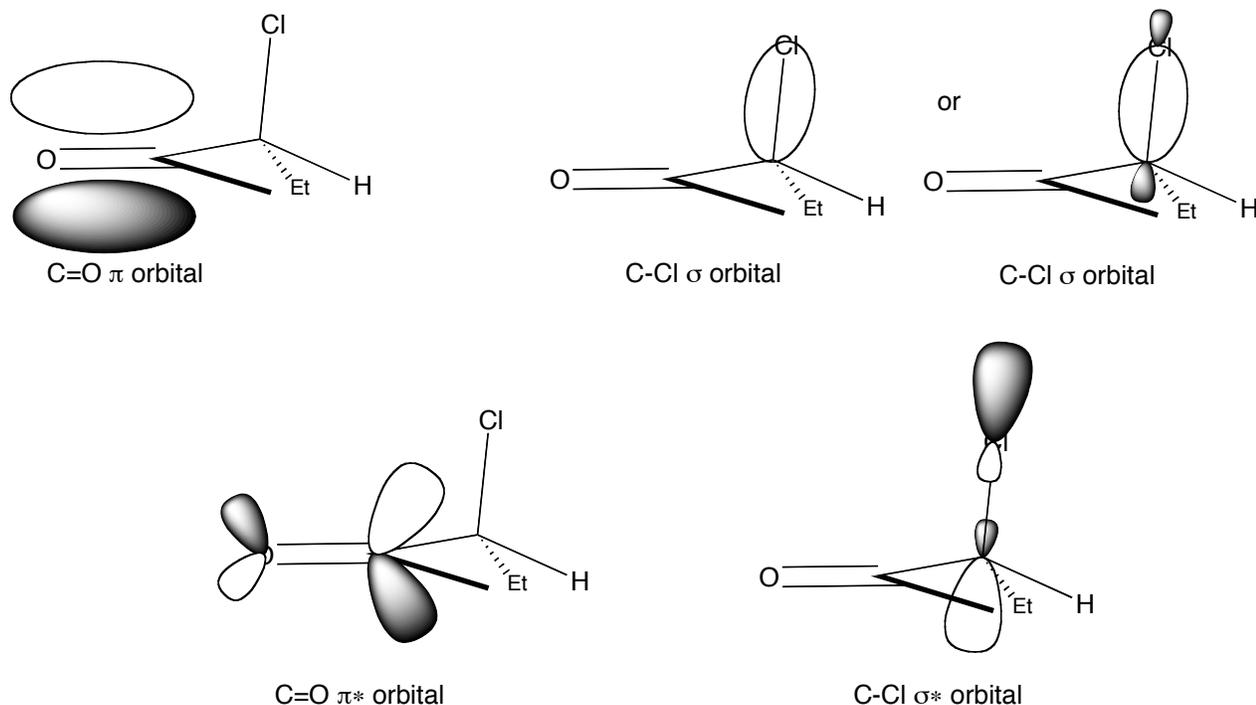
3b. (5 marks) Plan the synthesis shown below. Whether you go in the forward or reverse direction, show all intermediates, and include reagents and conditions for all reactions.



4. The chiral α -chloroketone shown below is represented in the conformation in which it is most likely to be attacked by a nucleophile.



4a. (4 marks) Draw the bonding/antibonding orbitals requested separately on each of the four side-view representations below.

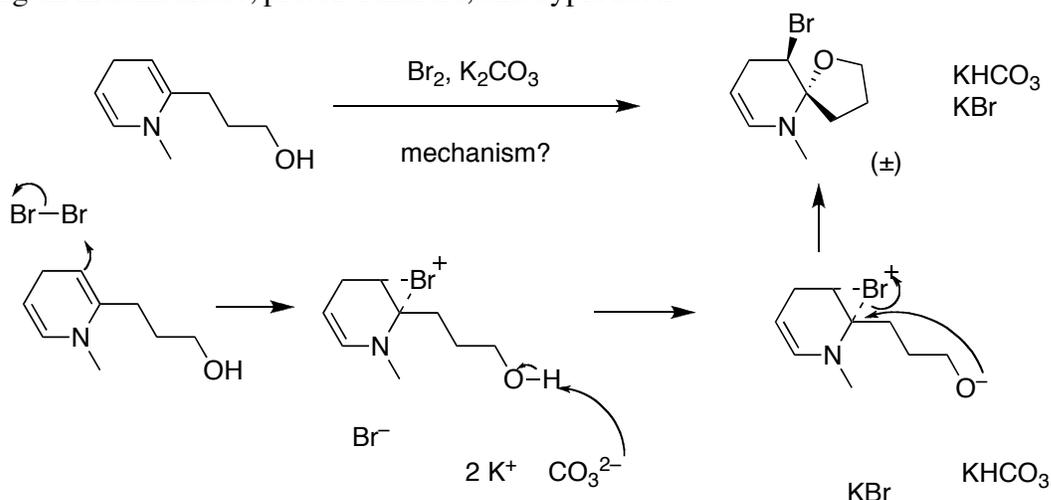


Key points: bonding orbitals have overlap between atoms... otherwise they don't make bonds. The Burgi-Dunitz angle *does* matter. Phases matter too.

4b. (2 marks) Explain why this is the conformation that will be attacked by the incoming nucleophile.

In this conformation, the σ^ orbital is aligned with the π^* orbital. This overlap stabilizes the π^* orbital and makes it easier to attack by incoming nucleophiles.*

5a. (3 marks) The reaction below, used in the synthesis of the natural product chlorofusin, is a close relative of iodolactonization called a bromoetherification. Give the detailed mechanism for this reaction, including all intermediates, proton transfers, and byproducts.



Note that in the first step, the arrow departing the alkene and making a new bond to bromine should be leaving from the actual pi electrons... a chemdraw glitch just won't let it come through that way on this printout.

5b. (2 marks) There are four alkene carbons in the starting material above. Explain why the oxygen atom attacks exclusively at the one indicated.

This is the only carbon atom that leads to the formation of a 5-membered ring. (Others would give 6, 7, and 8-membered rings.) 5-membered rings form more quickly than the others. (Baldwin's rules). It's because of the increased entropic penalty for forming any of the larger rings.

END