

## Written Qualifying Examinations

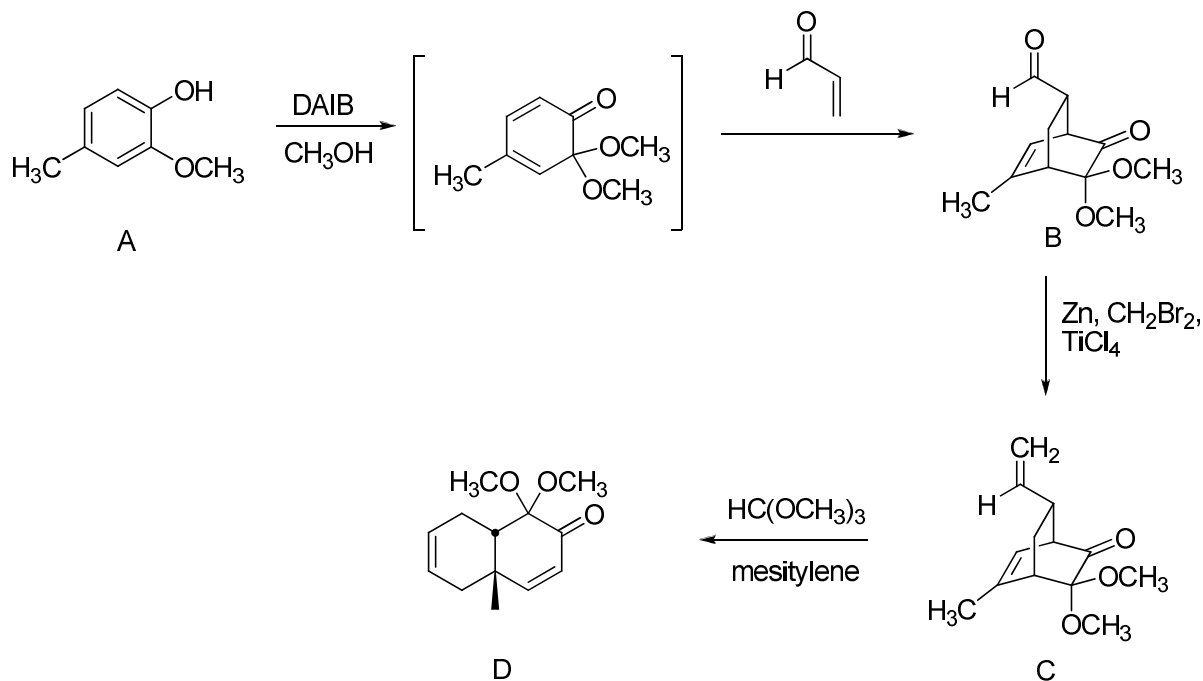
June 2008

### Organic Chemistry

These questions are based on the following article:

Liao, Chun-Chen et al. "Stereocontrolled Synthesis of Polyfunctionalized *cis*-Decalins from 2-Methoxyphenols". *J. Org. Chem.*, 73(7), 2554-2563, 2008.

- (1 point) Draw *cis*-decalin and *trans*-decalin (bond-line drawings, in 3D; i.e., use chair/boat conformations rather than a flat hexagon). Explicitly show the position of the hydrogens on the ring-fusion carbons.
- (4 points) The synthesis, as laid out in this paper, has three main steps, as illustrated below.



The first step (A → B) is a Diels-Alder cycloaddition. Provide a detailed molecular orbital argument for this reaction. Illustrate your answers appropriately.

- Is this reaction photochemically or thermally allowed?
- Is this a suprafacial or antarafacial addition?

- (2 points) The third stage in the synthesis (C → D) involves a Cope rearrangement. Propose a mechanism for this reaction, and explain why the *cis*-decalin is the final product.

4. (2 points) The stereochemistry of the *cis*-decalin products was confirmed by NOE spectroscopy.
  - a. What does NOE stand for?
  - b. Consider compound D in the illustration above. Propose two possible NOE experiments to verify its structure, and explain what you expect to observe in those experiments.
  
5. (1 point) Attached is the  $^1\text{H}$  NMR spectrum of compound B. Assign as many of the peaks as you can.

Green Chemistry Question (2 points):

The second stage in the synthesis ( $\text{B} \rightarrow \text{C}$ ) is an olefination. The authors use two different protocols to accomplish this transformation. One is a Wittig olefination ( $\text{CH}_3\text{PPh}_3\text{Br}$ , *n*-BuLi); the other utilizes Lombardo's reagent ( $\text{Zn}$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{TiCl}_4$ ). Compare and contrast these two methods from the perspective of green chemistry.

