

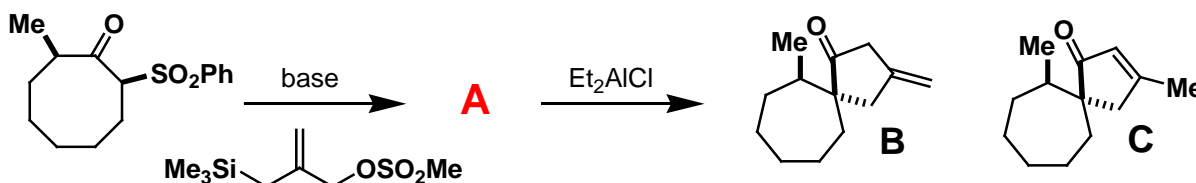


CHEM 8410_6410_4410 – Organic Synthesis

THE UNIVERSITY OF
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1872

Problem Set 4: This problem set is now available at (www.blackboard.utoledo.edu). It will be due in class 28 days (04/14/15) from today (03/19/15). Grades will be administered as follows: 5 (exceptional effort), 4 (complete), 3 (incomplete or inadequate effort), 2 (poor effort), 0 (nonexistent). **No late problem sets will be accepted.**

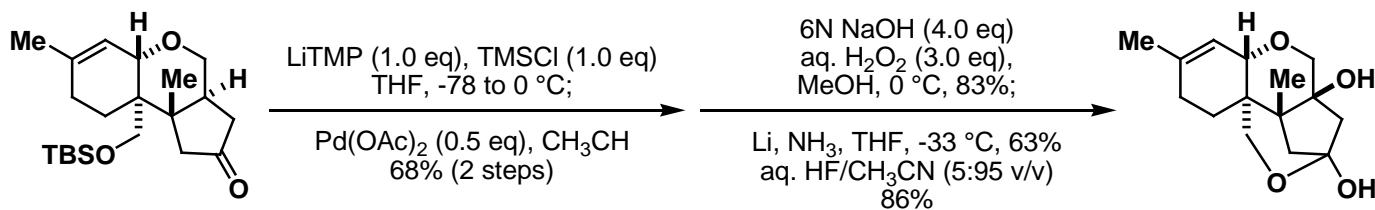
1. **Problem:** Trost and Adams have reported the interesting spiroannulation reaction sequence shown below (*JACS*, **1983**, *105*, 4849). In the first step the enolate alkylation produces a single diastereomeric adduct **A**. Rearrangement of **A** under Lewis acid conditions affords a mixture of **B** and **C**. As the reaction times are increased more **C** is produced by equilibration.



Part A: With independent readings regarding conformations of eight membered rings, predict the stereochemical outcome of the alkylation and identify the full stereostructure of **A**.

Part B: Provide a detailed mechanism for the transformation of **A** into **B**.

2. **Problem:** Please provide detailed mechanisms for the following transformations.



S. J. Danishefsky *et al.*, *Angew. Chem. Int. Ed.*, **2007**, *46*, 2199.



3. **Problem:** In conjunction with efforts to develop a general approach to the synthesis of the husubanan alkaloid Cepharamine, the following transformation was reported (*JACS*, **1972**, 2891). Provide a mechanism for this reaction. Clearly identify intermediates **A** and **B**.

