

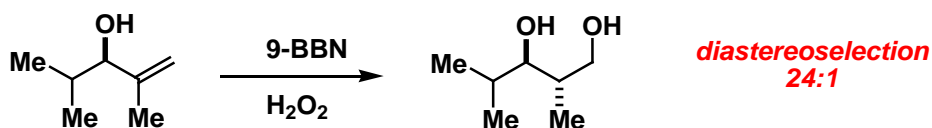


CHEM 8410_6410_4410 – Organic Synthesis

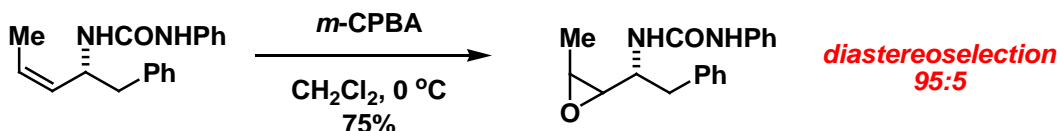
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Problem Set 1: This problem set is now available at (www.blackboard.utoledo.edu). It will be due in class 18 days (02/10/15) from today (01/23/15) in class. Grades will be administered as follows: 10 (exceptional effort), 8 (complete), 5 (incomplete or inadequate effort), 2 (poor effort), 0 (nonexistent) per question (3 questions total). **No late problem sets will be accepted.**

1. **Problem:** Rationalize the stereochemical outcome of these 2 reactions.

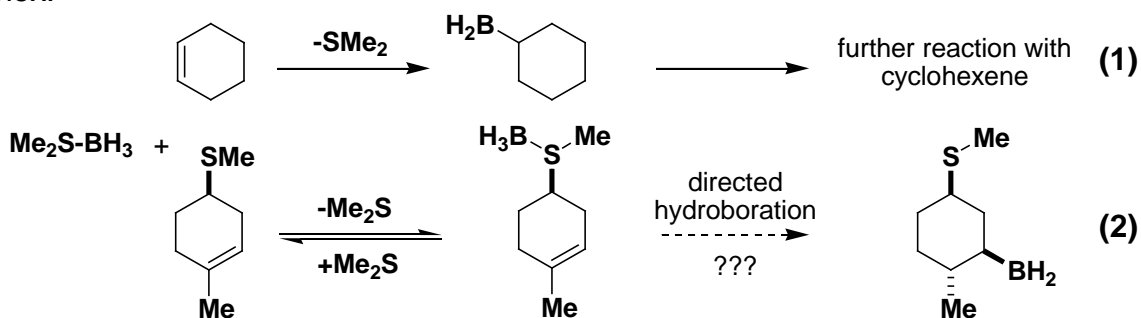


W.C. Still & J. C. Barrish *J. Am. Chem. Soc.* **1983**, 105, 2487.



W. Roush *J. Org. Chem.* **1987**, 52, 5127.

2. **Problem:** The following was an idea that was proposed to us by a former UT graduate student who is now employed at a major pharmaceutical company. The proposal is based on the fact that borane-methyl sulfide complex is an effective hydroboration reagent (**eq. 1**). It is proposed that homoallylic sulfides such as that illustrated below should be capable of “directing” the hydroboration process from this substituent through the borane-substrate complex.



Part A. In order to begin your critique, you must possess a good working knowledge of the details of the hydroboration of olefins with borane-methyl sulfide. Provide a clear depiction of the transition state for the hydroboration process using ethylene as the olefinic substrate and borane-methyl sulfide as the hydroborating agent.

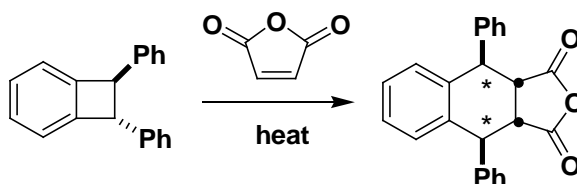


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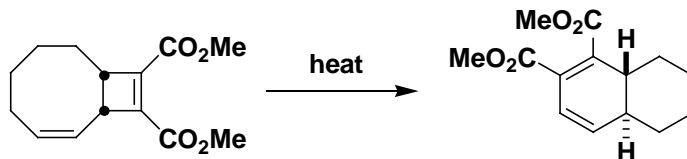
Part B. Now based on your knowledge of the hydroboration reaction and the principles learned thus far in CHM 7200, critique the idea proposed in (eq. 2). You should concisely state the logic upon which you based your assessment. Remember the old saying “**A picture is worth a thousand words**”.

3. **Problem:** A) Predict the stereochemical outcome of this reaction.

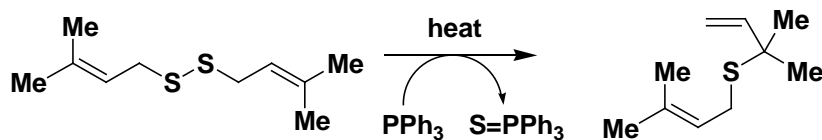


Huisgen, *TL*, 1964, 3381.

B) Suggest a mechanism for the following reactions.



Bloomfield, *TL*, 1969, 3719.



For a study on this [2,3] rearrangement, see Baldwin *J. Am. Chem. Soc.* 1971, 93, 6307.