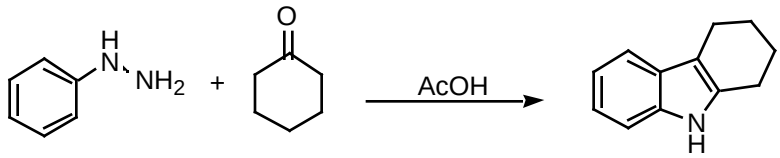
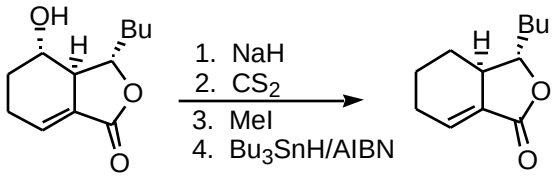
Organic Cumulative
September 12, 1998
9:00 AM to Noon
125 Chemistry Conference Room
Mechanisms

1. a) (15 points) Provide a complete arrow pushing mechanism for the following transformation:



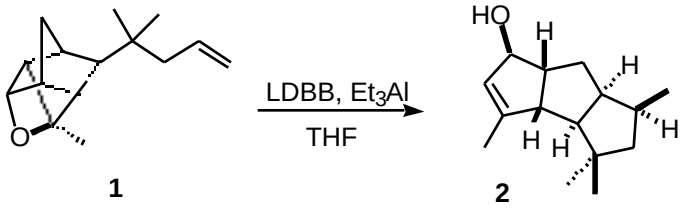
b) (5 points) What in the name of the reaction shown in part a?

2. a) (15 points) Provide a complete arrow pushing mechanism for the following transformation:



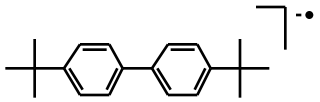
b) (5 points) What in the name of the reaction shown in part a?

3. a) (15 points) For the following triquinane synthesis provide a mechanism for the conversion of **1** to **2**. Be complete and address the observed stereochemistry in **2**.



1 **2**

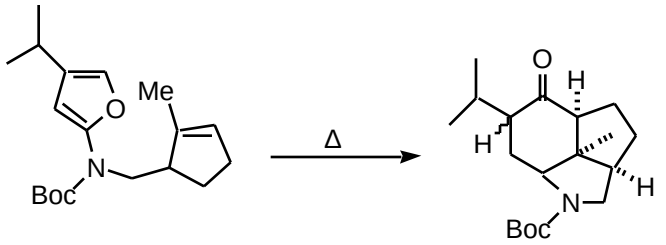
LDBB: lithium di-*tert*-butylbiphenylide



Dvorak, C.A.; Dufour, C.; Iwasa, S.; Rawal, V.H. *J. Org. Chem.* **1998**, *63*, 5302-5303.

b) (5 points) What is the name of the four membered ring ether functionality present in **1**.

4. (20 points) In a recent set of lectures (Organic Day 1998) Professor Albert Padwa of Emory University described the importance of the hetero Diels-Alder reaction in the synthesis of complex heterocycles. Knowing this provide a mechanism and explain the observed stereochemistry for the following reaction.



74% 2:1 mixture of diastereomers

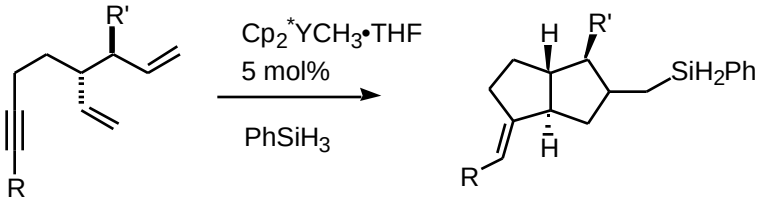
Padwa, A.; Brodney, M.A.; Dimitroff, M. *J. Org. Chem.* **1998**, *63*, 5304-5305.

5. Metal catalyzed tandem reactions are becoming very important to organic synthesis. One of the most important of these is the tandem polyene cyclization. A recent example of a tandem polycyclization involves the use of $Cp_2^*YCH_3$•THF with $PhSiH_3$. The following is overall a olefin hydrosilylation reaction:

a) (2.5 points) What does Cp^* stand for?

b) (2.5 points) What metal does Y stand for?

c) (15 points) Provide a mechanism for the following catalytic reaction:



Hint: $Cp_2^*YCH_3$•THF + $PhSiH_3$ ⟶ "Cp_2^*YH"

Metal Hydride

Start with a hydrosilylation reaction

Molander, G.A.; Retsch, W.H. *J. Org. Chem.* **1998**, *63*, 5507-5516

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