

Cumulative Examination  
Organic Chemistry

October 6, 2011

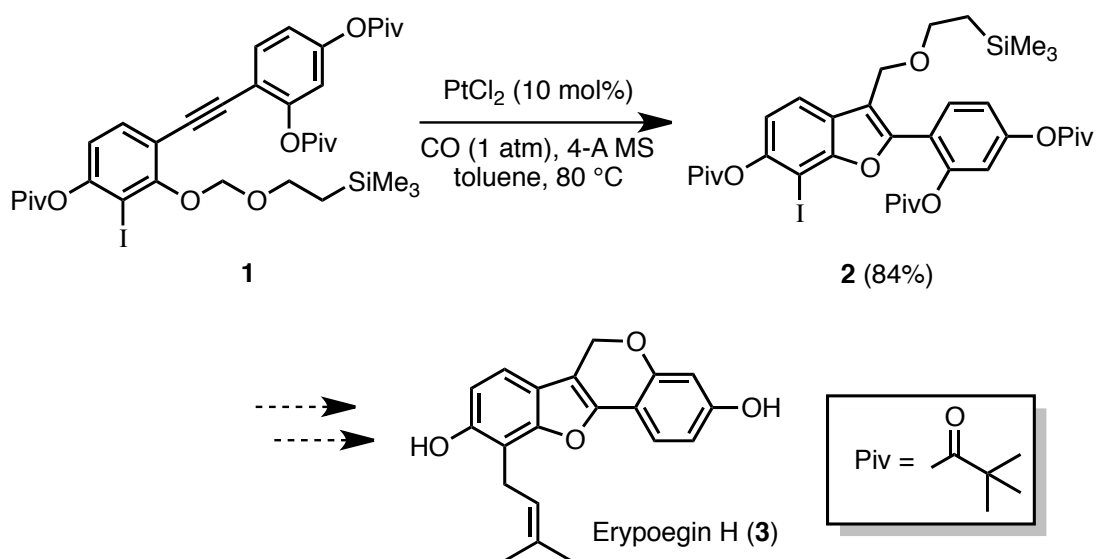
D. J. Wardrop

**Attempt All Questions (100 Total Points)**

**Question 1.**

In his recent departmental seminar, Professor Alois Fürstner of the Max-Planck-Institute für Kohlenforschung discussed a number of metal-mediated transformations and their employment in the total synthesis of complex natural products.

- (a) Draw a reasonable arrow-pushing mechanism for the following example of cycloisomerization, which was employed in the total synthesis of antibiotic Erypoegin H (**3**). Draw a reasonable arrow pushing mechanism for the conversion of **1** to **2**. Note that carbon monoxide is employed in this reaction as an accelerant and need not be presented in your answer.

**15 Points**

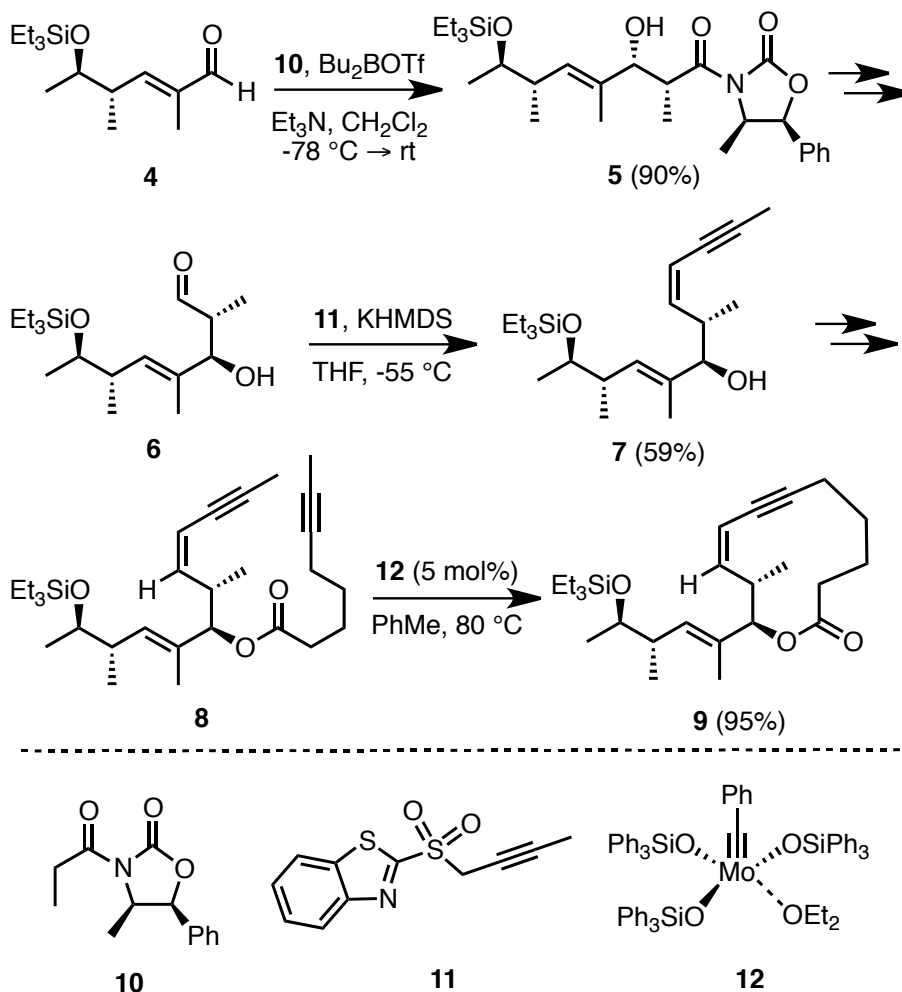
[Fürstner, A. *et al. Angew. Chem. Int. Ed.* **2007**, *46*, 4760-4763]

- (b) Suggest reagents and conditions that might be used to convert compound **2** to Erypoegin H (**3**). Use as many steps as you deem necessary.

**10 Points****25 Total Points**

## Question 2.

In the latter half of his seminar Professor Alois Fürstner discussed the development of the metathesis catalyst **12** and its application to natural product synthesis. The sequence of reactions show below form part of Fürstner's 2010 synthesis of the cell migration inhibitor Lactimidomycin (not shown).



[Fürstner, A. *J. Am. Chem. Soc.* **2010**, *132*, 14064-14066]

- (a) Draw a reasonable arrow-pushing mechanism for the conversion of **4** to **5** and rationalize *both* the enantio and diastereoselectivity of this process.

**15 Points**

- (a) Draw a reasonable arrow-pushing mechanism for the conversion of **6** to **7** and identify the named reaction taking place during this transformation.

**15 Points**

- (a) Draw a reasonable arrow-pushing mechanism for the conversion of **8** to **9** and identify the by-product of this reaction.

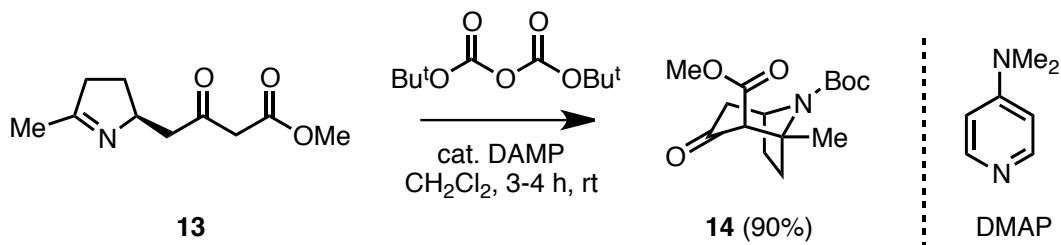
**15 Points**

**45 Total Points**

**Question 3.**

In his recent departmental seminar, Professor Franklin Davies of Temple University discussed the asymmetric synthesis tropane and indolizidine alkaloids using his signature sulfinimine chemistry.

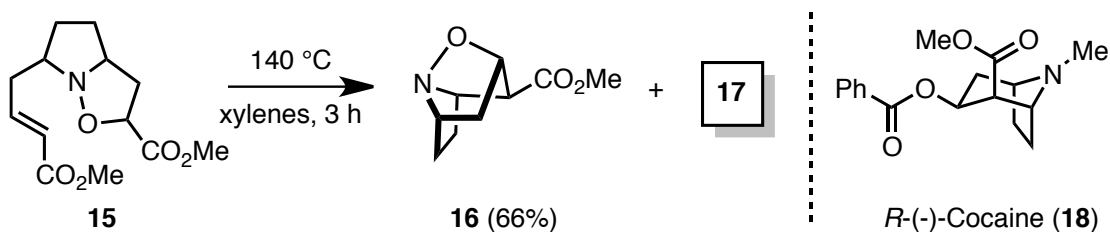
- (a) Draw a reasonable arrow-pushing mechanism for the conversion of imine **13** to substituted tropane **14**. Be careful to clearly show what role DMAP plays in this transformation. Assign descriptors of absolute stereochemistry (*R* or *S*) to all stereocenters in compound **14**.



[Davis, F. A. *et al. Org. Lett.* **2009**, *11*, 1647-1650]

**15 (10 + 5) Points**

- (b) During his talk, Professor Davies cited Tufariello's (*i.e.*, **15**→**16**) preparation of cocaine (**18**) as an important antecedent to his own synthesis of this alkaloid. Draw a reasonable arrow-pushing mechanism for the conversion isoxazolidine **15** to substituted tricyclic isoxazolidine **16**. Draw the structure of by-product **17**.



[Tufariello, J. J. *et al. J. Am. Chem. Soc.* **1979**, *101*, 2435-2442]

**15 (10 + 5) Points**

**30 Total Points**