

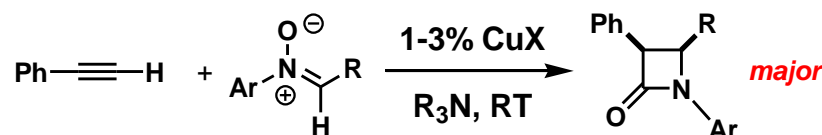


CHEM 8410_6410_4410 – Organic Synthesis

THE UNIVERSITY OF
TOLEDO
1872

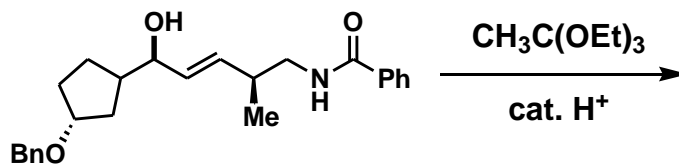
Problem Set 4: This problem set is now available at (www.blackboard.utdl.edu). It will be due in class 21 days (04/11/17) from today (03/21/17). Grades will be administered as follows: 10 (exceptional effort), 8 (complete), 5 (incomplete or inadequate effort), 2 (poor effort), 0 (nonexistent). **No late problem sets will be accepted.**

1. **Problem:** Provide a plausible mechanism for this transformation in the space below. In attacking this question, it is important that you are aware of the transformation that transpires when terminal acetylenes are treated with Cu(I) or Ag(I) in the presence of an amine base.



In 1995 Miura and co-workers reported the remarkable reaction illustrated above (*J. Org. Chem.* **1995**, 60, 4999). Recently, Fu has reported an enantioselective variant of this transformation (*J. Am. Chem. Soc.* **2002**, 124, 4572). In most instances, the *cis* adduct is formed in large excess (>90%). There is really no thoughtful mechanism in the literature for this transformation. You will be graded on "reasonability".

2. **Problem:** Give the product (with correct stereochemistry) and a detailed mechanism for the following reaction (you should have **more than 7 steps** in the overall mechanism which means you need to show what happens with the orthoester). What is the name of this reaction (include numbers)?





3. **Problem:** While I was a post-doc in the Schreiber Group, a great friend and colleague of mine from Japan, Hiroki Oguri (who is now a Research Associate in the Hiram Labs...equivalent to Associate Professor here in the USA) published a fascinating paper entitled "Skeletal diversity via a folding pathway: Synthesis of Indole alkaloid-like skeletons" Hiroki Oguri and Stuart L. Schreiber, *Org. Lett.*, **2005**, 7, 47-50. The key step in the synthesis of his work involved a carbene based strategic cyclization approach. Please provide the mechanism for this wonderful transformation. Rationalize the exclusive diastereoselectivity.

