Mechanisms Club

Princeton University
http://www.princeton.edu/~orggroup/mechclubindex.html
Frick Laboratory, Room 124
Friday, February 9, 2007
12:00-1:30 pm

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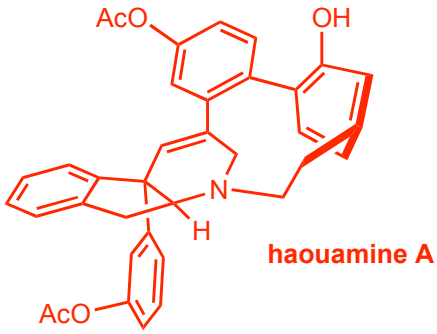
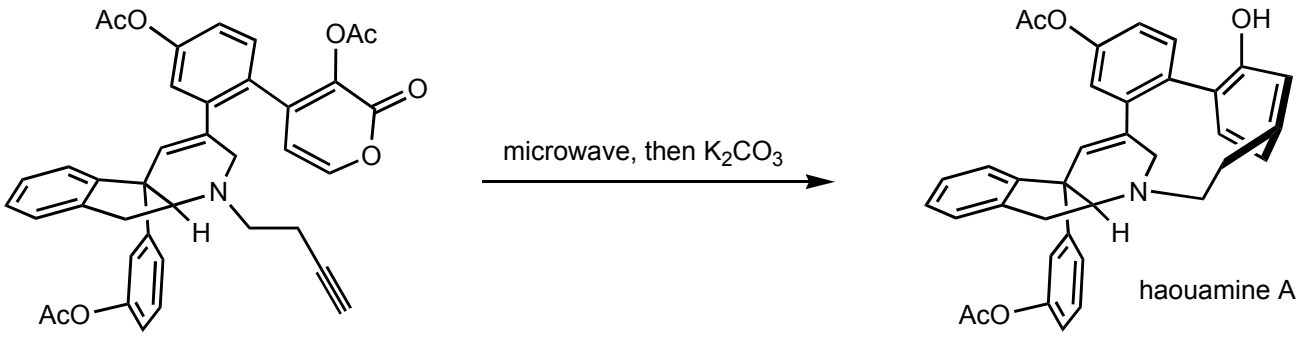
Problem #1
Baran and co-workers recently reported an eight step total synthesis of haouamine A (*JACS* **2006**, 128, 3908-9). The final step in their synthesis establishes the bent aromatic ring functionality. Indicate the mechanism by which this occurs.

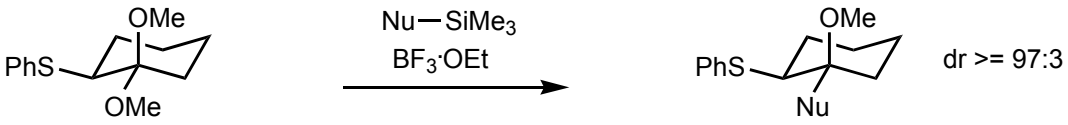


haouamine A



haouamine A

Problem #2
Woerpel and Billings (*JOC*, **2006**, *71*, 5171) recently reported high levels of diastereoselectivity associated with nucleophilic substitution reactions of sulfur-substituted acetals. Please provide a mechanism and a Newman projection to explain these high levels of selectivity.



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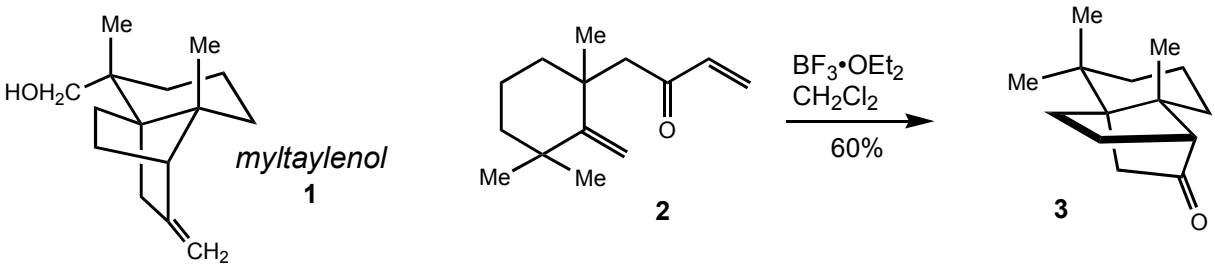
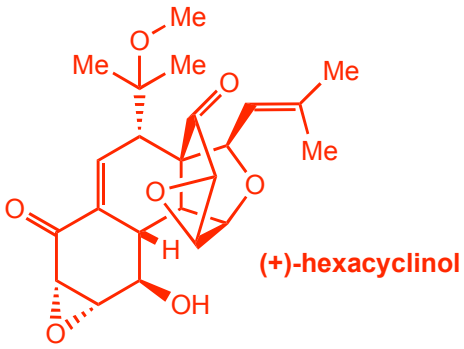
Problem #3

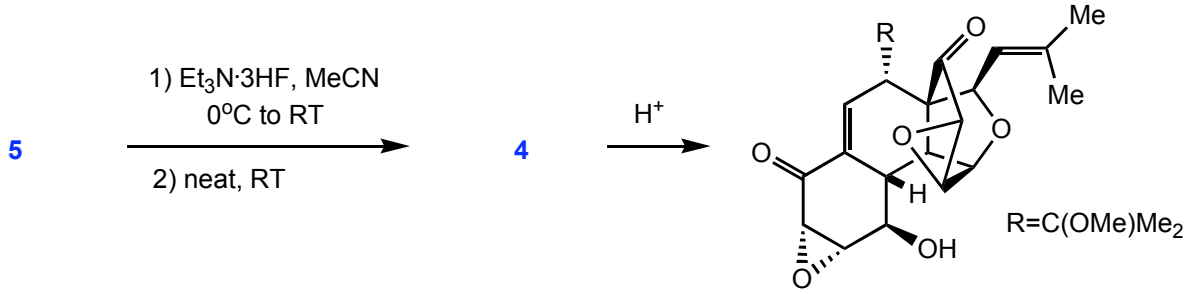
The recently isolated irregular sesquiterpene myltaylenol (**1**) stimulated Srikrishna and co-workers (*Chem Commun*. **1994**, 2259) to study the biogenetically modeled acid-promoted rearrangement of **2** which leads to the desired terpenoid skeleton in good yield. In the space below provide a detailed mechanism for the transformation of **2** to **3**.



Problem #4

Porco and Rychnovsky recently published a synthesis of the revised structure of (+)-hexacyclinol (*ACIEE*, **2006**, *45*, 1-4). **5** dimerizes to form "pre-hexacyclinol" (**4**), which upon treatment with acidic conditions (K10 clay), affords **2**. Please provide mechanisms for the two transformations and identify **4** and **5**.





Problem #5

Please provide a mechanism for the following transformation. (*Org. Biomol. Chem.* **2007**, *5*, 58.)
Provided by Tom Graham.