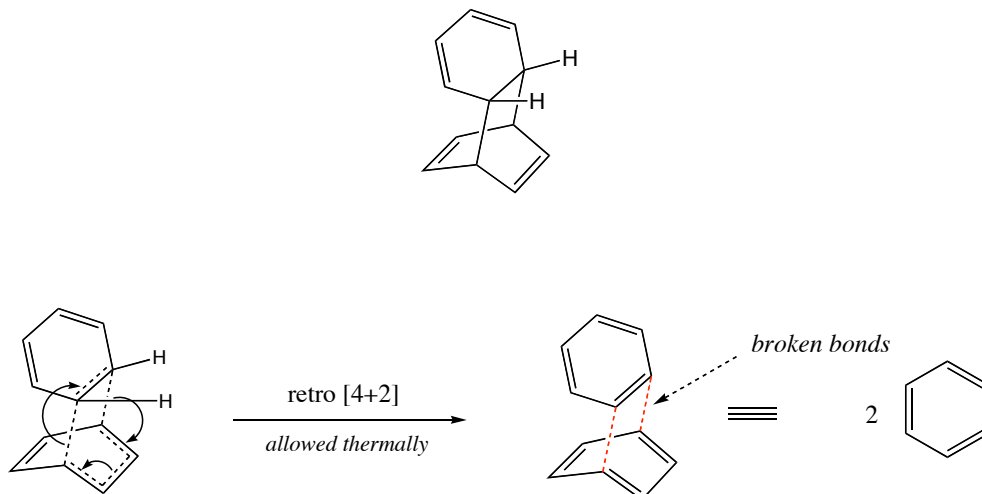
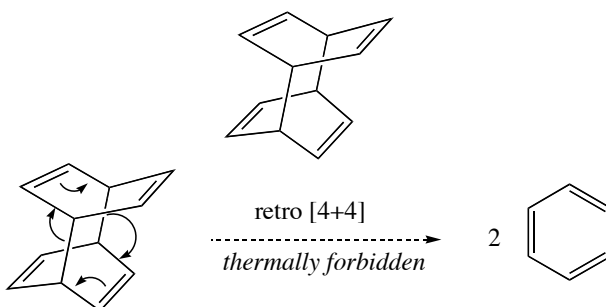


Answers to Problem Set #4

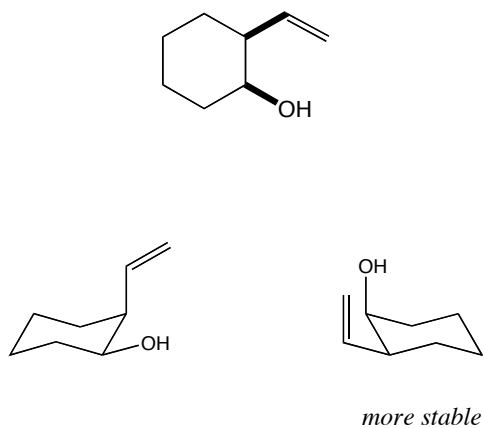
Question 1. a) The following compound is not stable. Provide a mechanism for its decomposition and identify the product(s) produced.



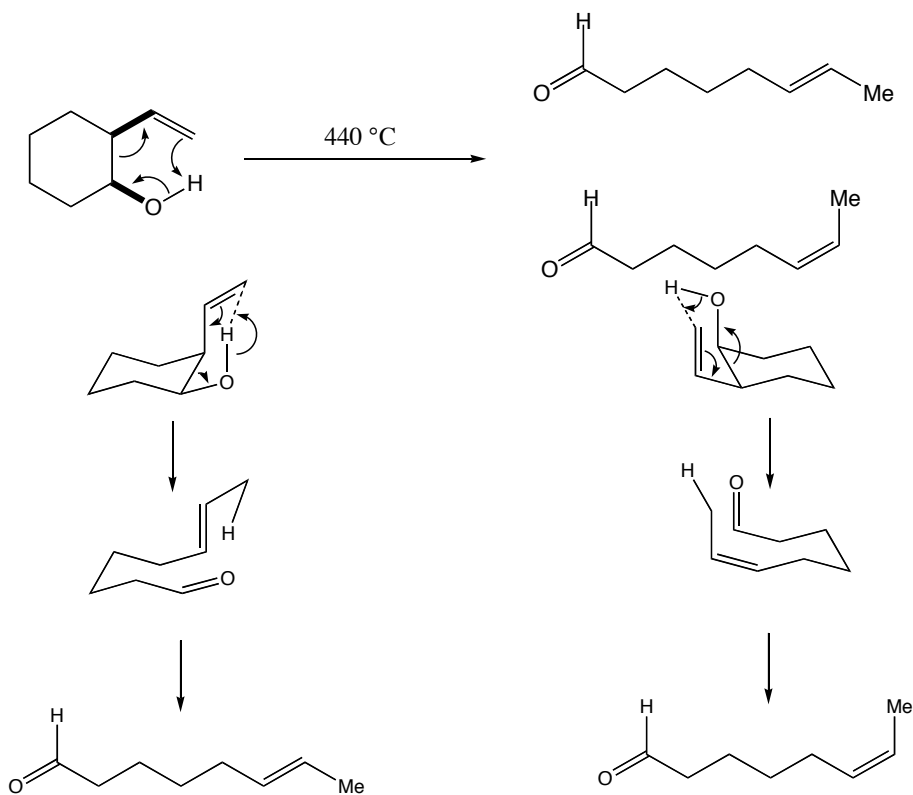
b) The related compound below is stable and isolable. Why doesn't this compound thermally decompose? How might we induce the decomposition?



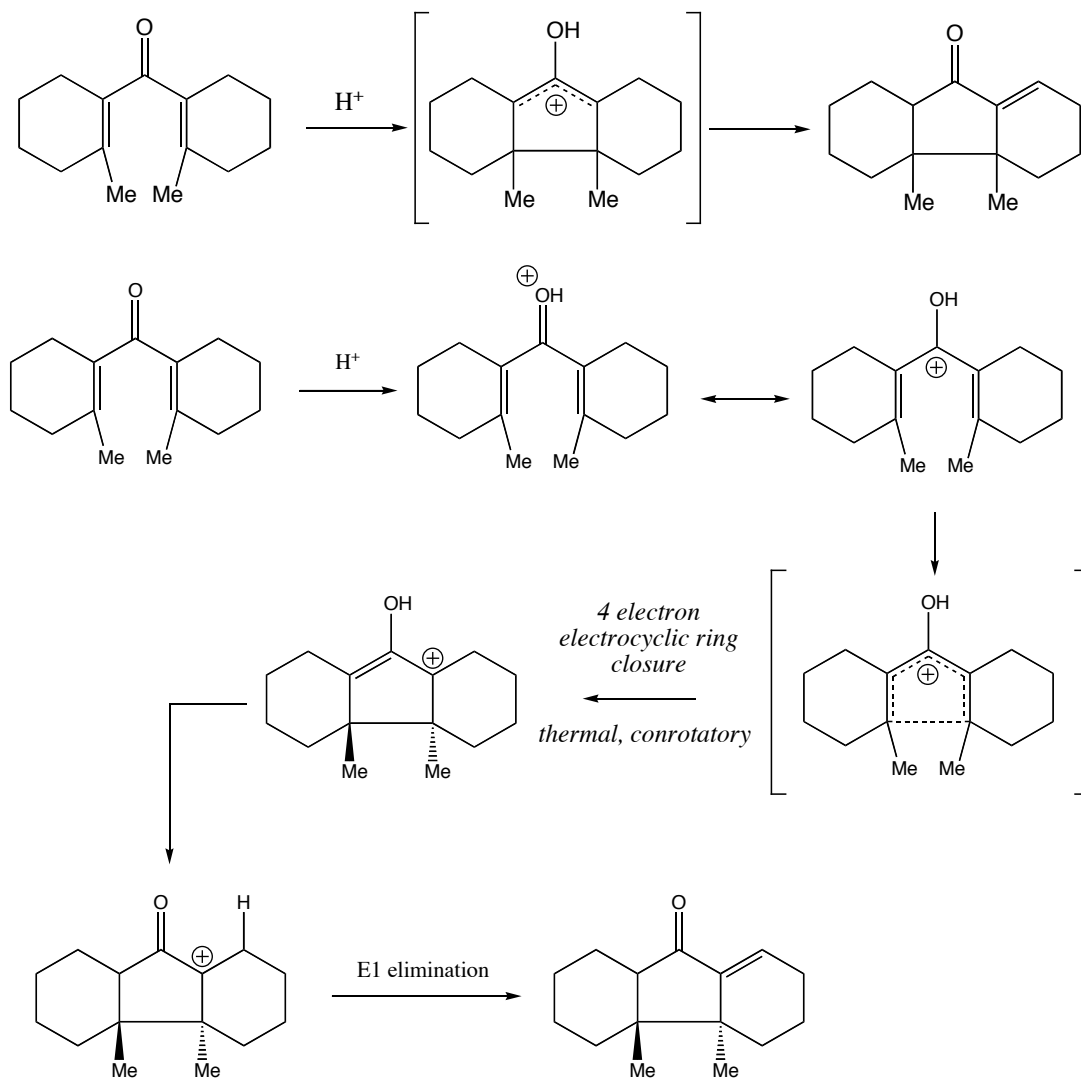
Question 2. a) Draw the two chair conformers of the vinylcyclohexanol shown below. Based on A values, predict which of the two is the most stable.



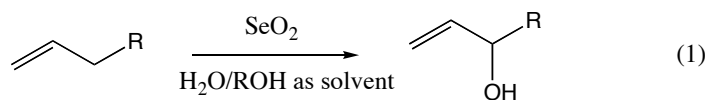
b) Vinylcyclohexanols undergo retro-ene reactions at high temperatures as shown below. Draw 3-D transition states leading to the two products.



Question 3. The reaction shown below is known as the Nazarov cyclization, and has been determined to proceed through a pericyclic mechanism. Provide a mechanism for the Nazarov cyclization and use FMO theory to predict the stereochemical relationship of the methyl groups in the product.

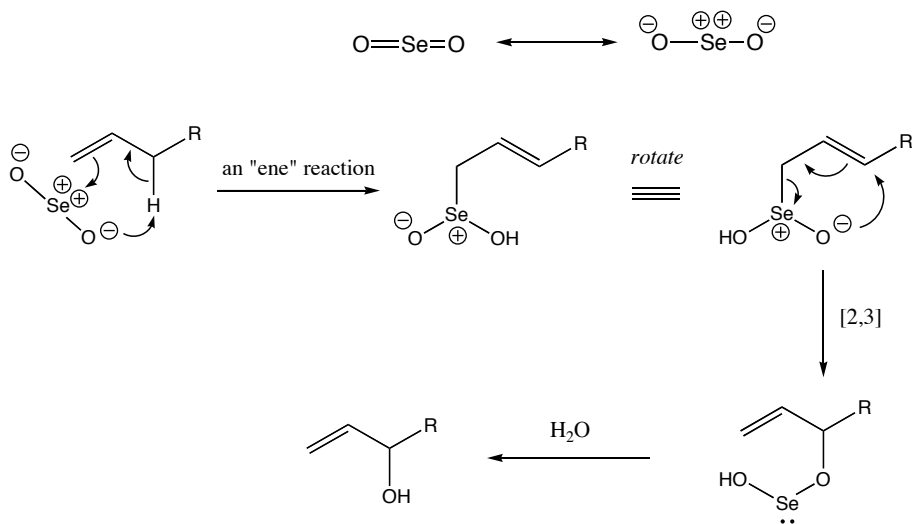


Question 4. Olefins can be oxidized at the allylic position with selenium dioxide (equation 1). This looks like a "magic" reaction since we are selectively oxidizing an unfunctionalized carbon, but it is actually a logical sequence of pericyclic reactions.

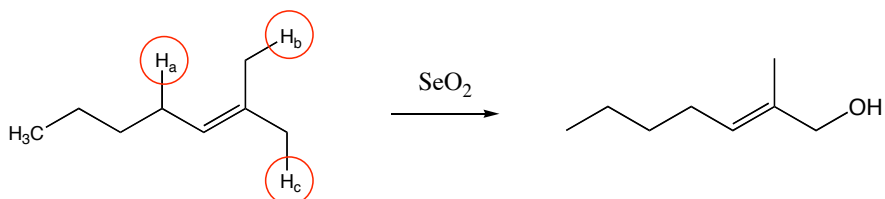


a) Provide a mechanism for the reaction shown in equation 1. *Here are a series of hints: The first step is a "group transfer reaction" that forms a Se-C bond. The second step is a sigmatropic rearrangement that breaks the Se-C bond.*

Note: It may help to think of selenium dioxide as:

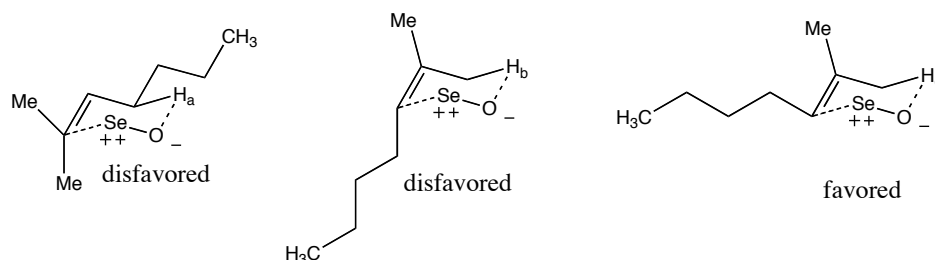


b) Using your newly discovered mechanism for allylic oxidation, explain the product outcome of the reaction shown below. How is one product formed when there are multiple allylic sites? Explaining this is daunting until you are able to accurately draw the three-dimensional transition state(s) for the important mechanistic step(s).

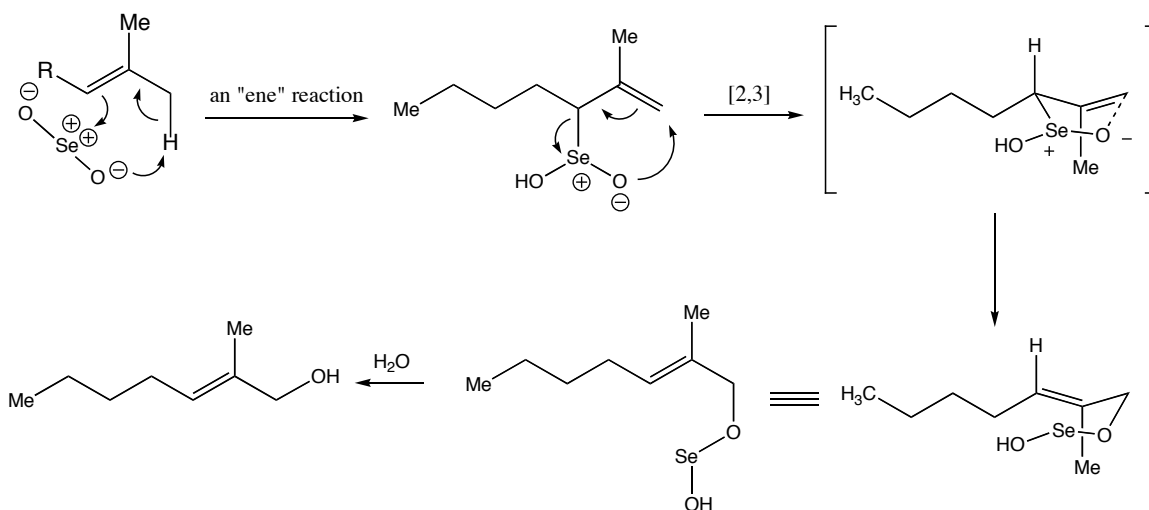


There are 3 allylic hydrogens for the initial ene reaction.

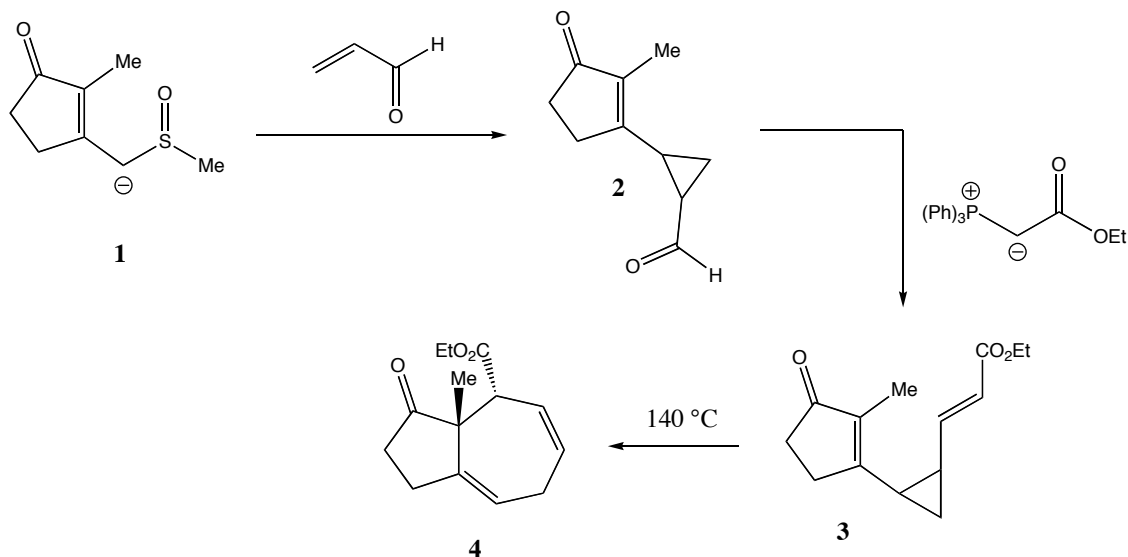
There are 3 transition states possible for the initial ene reaction (one for each allylic hydrogen H_a , H_b , and H_c above (the second oxygen on selenium has been omitted from the drawings for clarity):



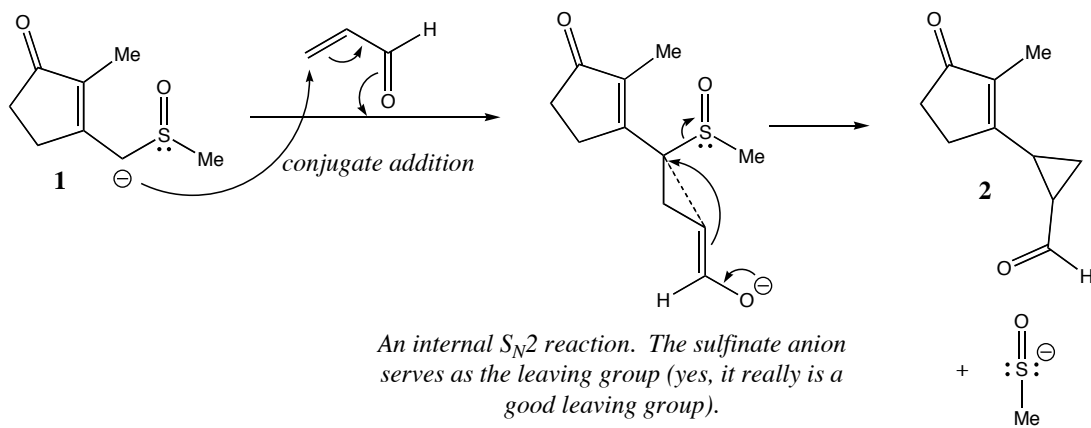
Note that the regioselectivity is determined by both sterics (as shown in the above transition state drawings), and by electronics (as the olefin attacks the selenium, a partial positive charge forms on the more substituted carbon).



Question 5. We have encountered some, but not all, of the chemical reactions used by Marino for the synthesis of hydroazulene derivatives (such as **4**) as shown below.



a) The conversion of sulfoxide **1** to cyclopropane **2** is a reaction that you have not seen before. Can you puzzle out the mechanism? *Note: This is a general method for the synthesis of cyclopropanes with α -carbonyl groups.*



b) Provide a mechanism for the conversion of **2** to hydroazulene **4**. In your mechanism, include a three-dimensional drawing that explains the stereochemistry obtained in the thermal rearrangement of **3** to **4**.

