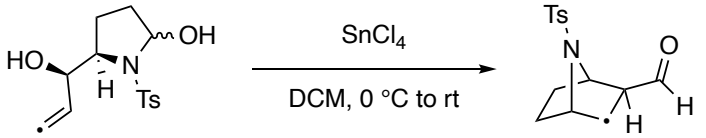
CHEM 8321/4321 **November 13, 2023**

Problem Set #10 **T. R. Hoye**

Due in class, Monday November 20, 2023

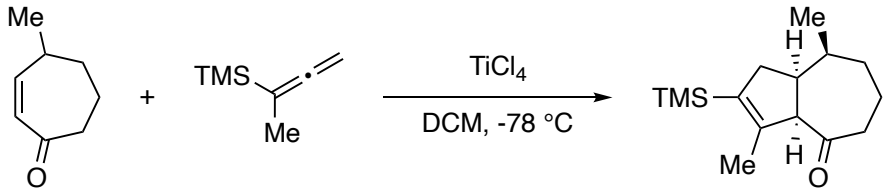
Detailed Mechanism Provide a detailed mechanism [i.e., *explicitly* show (using curly arrows) *EVERY* intermediate, formal charge (where relevant), equilibrium, and bond-making and -breaking step] to account for the following transformations:

a) The dehydration of the allylic alcohol **1** to the aldehyde **2**. (*hints*: the dotted carbon in the starting material appears in the product as indicated; a [3.3]-sigmatropic rearrangement is involved.)



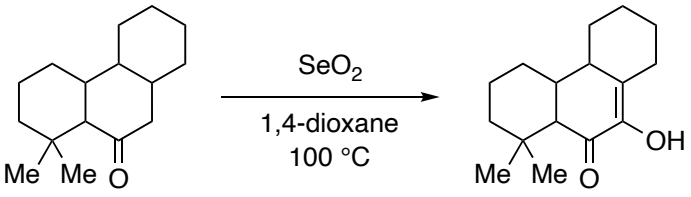
1 one enantiomer ***2*** one enantiomer

b) The formation of the [5.3.0]-bicycle **4** from the enone **3a** and the allene **3b**. (*hints*: recall that a silyl substituent can stabilize β-carbenium ions and that the TMS group is not vicinal to the allylic methyl group in the product.)



3a ***3b*** ***4***

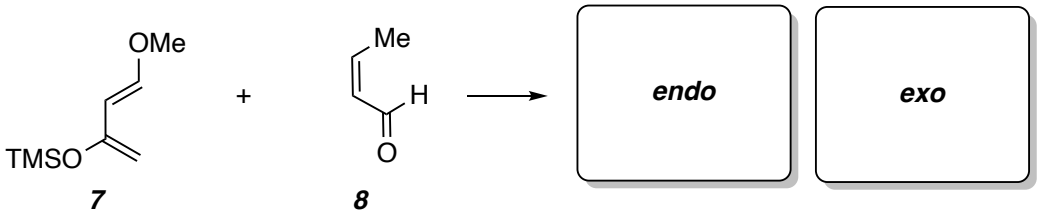
c) The oxidation of the ketone **5** with selenium dioxide to form the 1,2-diketone **6**.



5 ***6***

Other Problems

1. a) Draw the structure of the (major) *endo* and (minor) *exo* products for the reaction between the diene **7** and the dienophile **8** in a Diels–Alder reaction.

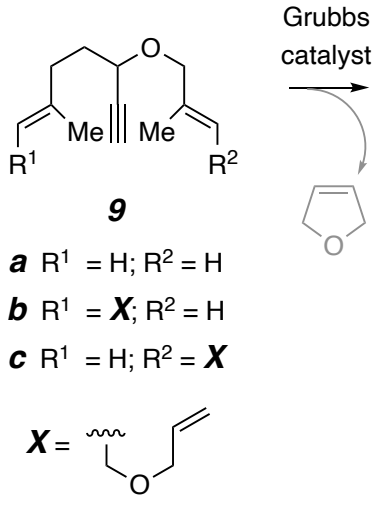


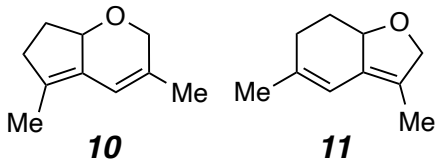
b) Show the relative energies of the molecular orbitals for the π-systems of the diene and the dienophile and indicate which are primarily involved in interaction in the transition state for the cycloaddition (orbital overlap).

c) How would the HOMO/LUMO gap for this reaction change if the methoxy substituent on the diene was changed to a methyl group?

d) How would the HOMO/LUMO gap for this reaction change if the methyl substituent on the dienophile was changed to an aldehyde?

2. Account for the following three, substrate-dependent, product ratios. The differences here highlight a powerful strategy known as relay ring-closing metathesis (RRCM).





from	product ratios		
9a	~1.0	to	1.0
9b	26	to	1.0
9c	1.0	to	45

3. Reaxys

a) The Ullmann coupling can be used to cross coupling a phenol with an aryl halide. How many such reactions in Reaxys use as the cuprous ion source CuI? CuBr? CuCl?

b) How many acyclic 1,4-disubstituted butadiene derivatives having one E- and one Z-alkene geometry are in the Reaxys database?