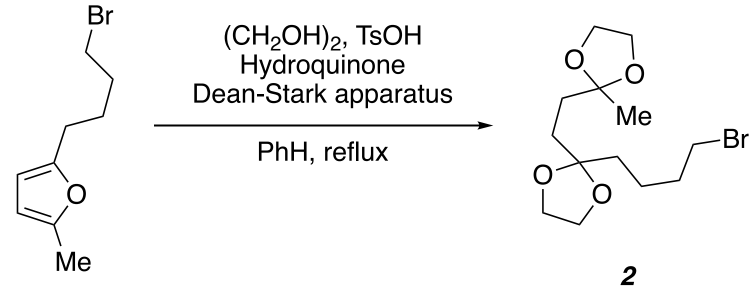
CHEM 8321/4321 **November 6, 2023**

Problem Set #9 **T. R. Hoye**

Due in class, Monday November 13, 2023

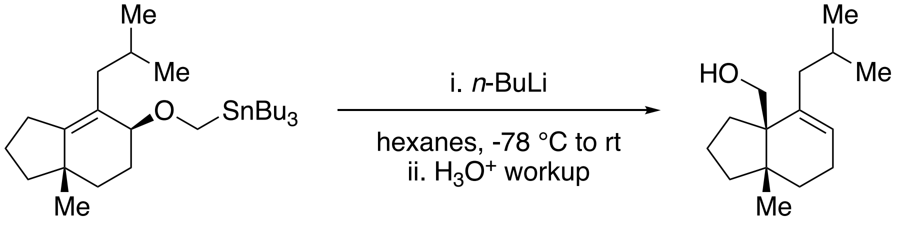
Detailed Mechanism Provide a <u>detailed mechanism</u> [i.e., *explicitly* show (using curly arrows) *EVERY* intermediate, formal charge (where relevant), equilibrium, and bond-making and -breaking step] to account for the following transformations:

a) The conversion of the furan derivative **1** to the bisketal **2**.



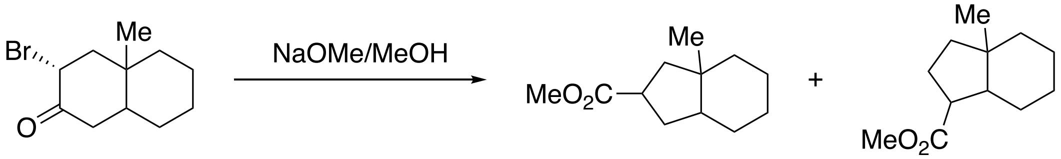
1 ***2***

b) The rearrangement of the allyl ether **3** to form the alcohol **4**.



3 ***4***

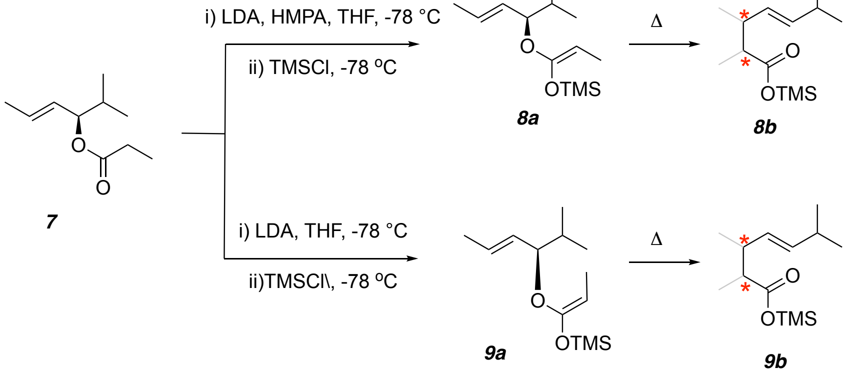
c) The Favorskii rearrangement of the bromoketone **5** to esters **6a** and **6b**, which have different constitutions. Several diastereomers of each constitution are formed; ignore that aspect of the problem.



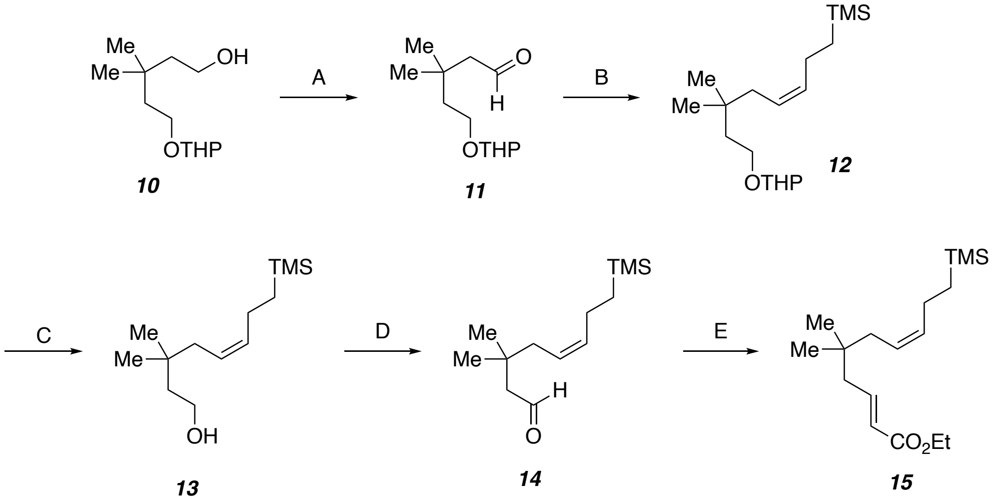
5 ***6a*** ***6b***

Other Problems

1. The Ireland-Claisen rearrangement involves the [3,3]-sigmatropic rearrangement of silylketene acetals. The *E* or *Z* silylketene acetal can be made selectively by changing the conditions to favor the initial formation of either an O-*E* or O-*Z* lithium enolate, which is then trapped by O-silylation of the enolate anion to give, preferentially, either **8a** or **9a**. This then translates into the relative configuration of the major diastereomer **8b** or **9b** formed from a substrate such as the propanoate ester shown below. Deduce and show the structure of the major stereoisomeric product formed from the indicated enantiomer of the propanoate ester **7** under each of these two complementary sets of reaction conditions.



2. Provide plausible reagents to achieve steps A-E in the multistep conversion of **10** to **15**. [*hint*: we haven't specifically seen this in lecture yet, but the tetrahydropyranyl (THP) acetal is frequently used as a protecting group for primary alcohols; look up its conditions for removal (and incorporation)]



3. The Diels–Alder reaction between the diene **16** and the enoate **17** proceeds with high regio- and diastereoselectivity to give **(±)-18**. Draw a transition state geometry to account for the formation of this as the major diastereomer. Rationalize the formation of the product **19** upon treatment of **18** under the indicated conditions. *Hint:* the conversion of **18** to **19** involves an intramolecular Diels–Alder reaction. (*hint*: aqueous HF is a sufficiently weak Bronsted acid that the Boc-protected amine survives)