

CHEM 8321/4321

October 30, 2023

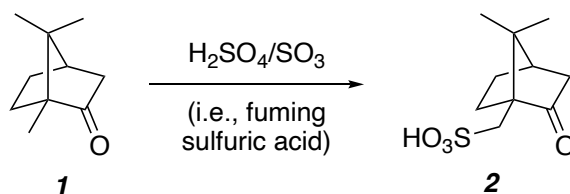
Problem Set #8

T. R. Hoye

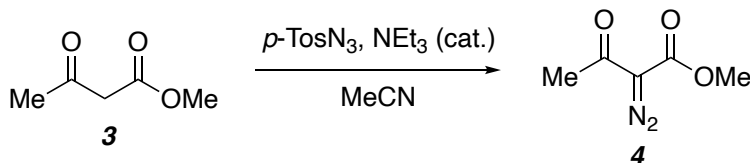
Due in class, Monday November 6, 2023

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:

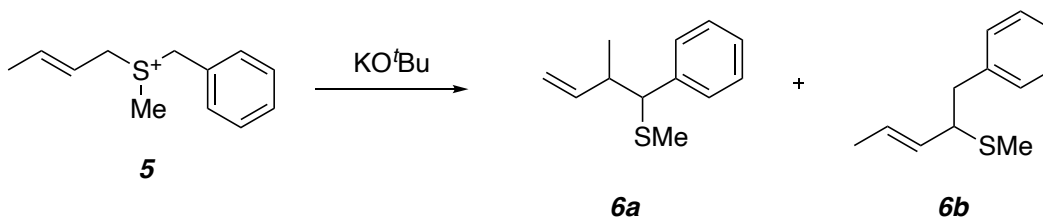
a) The sulfonation of camphor (**1**) to form camphorsulfonic acid (**2**) using fuming sulfuric acid, which is a solution of sulfur trioxide in sulfuric acid.



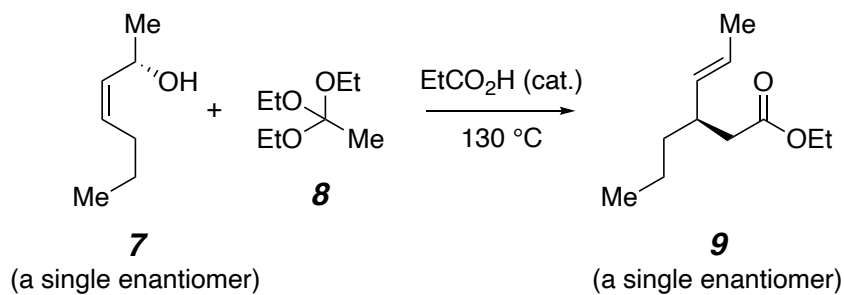
b) The installation of a diazo group on the β -ketoester **3** to form compound **4**. (*hint*: balance the reaction equation)



c) The conversion of the sulfonium ion **5** to a mixture of the thioethers **6a** and **6b**.



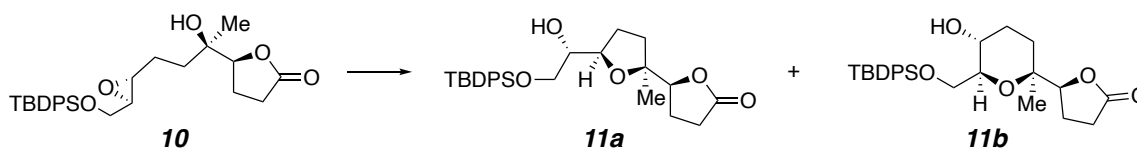
d) The Johnson-Claisen rearrangement of the allylic alcohol **7** and triethyl orthoacetate (**8**) to form the alkene ester **9**.



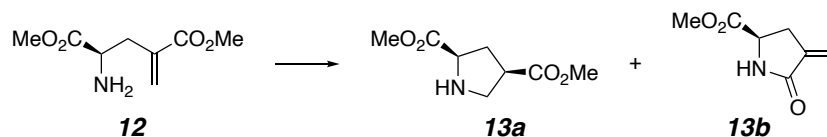
Other problems

1. Classify the following ring-closing events by Baldwin's rules to form both possible products and indicate whether each is "favored" or "disfavored".

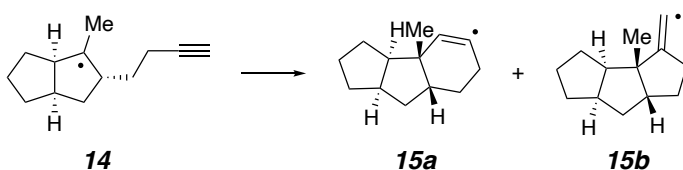
a)



b)

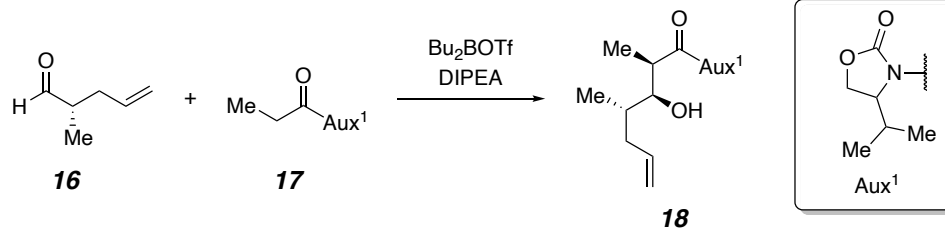


c)

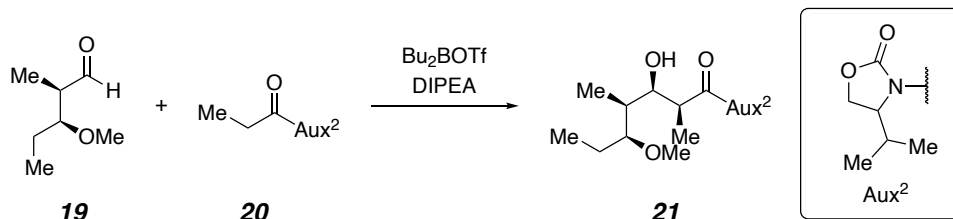


2. Below are two examples of asymmetric aldol reactions used from a total synthesis executed in the labs of Prof. Christina White (UICU). Based on the stereochemical outcome of the reaction, deduce the structure (i.e., R or S) of the chiral auxiliary used.

a)



b)



Reaxys: How many reactions invert the stereocenter of a secondary benzylic alcohol [i.e., PhCH(OH)R, where R is any kind of substituent – alkyl, aryl, etc.] using di-isopropyl azodicarboxylate (DIAD)? DIAD is a less toxic alternative to DEAD commonly used in Mitsunobu reactions.