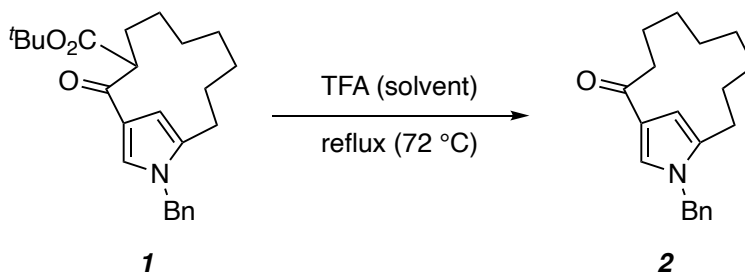


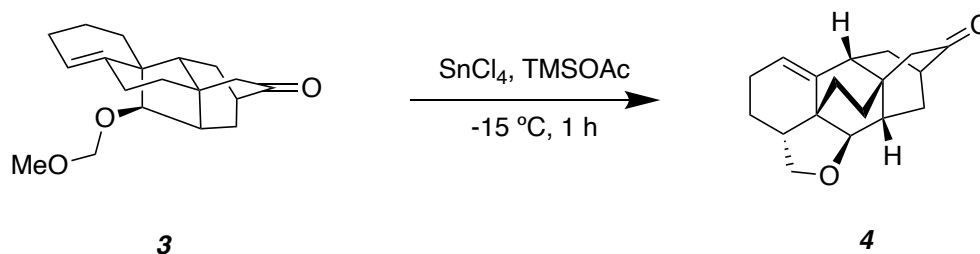
CHEM 8321/4321**Problem Set #4****September 25, 2023****T. R. Hoye****Due in class, Monday October 2, 2023**

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. For each reaction, balance the equation (i.e., clearly show any byproducts that are produced while determining your mechanism).

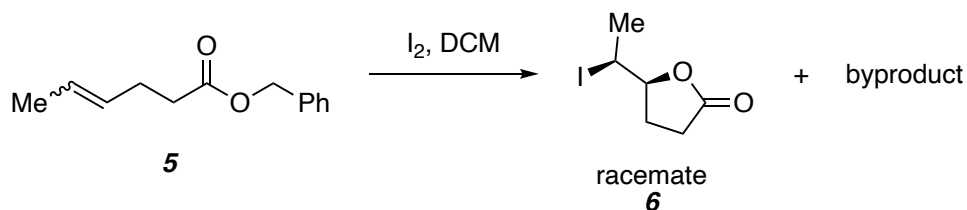
a) The β -ketoester **1** to form the macrocyclic ketone **2** upon treatment with trifluoroacetic acid.



b) Formation of the ketone **4** from the methoxymethyl (MOM) ether **3** involves a Wagner-Meerwein rearrangement of an intermediate carbenium ion. (*hint*: the Lewis acidic stannic chloride promotes formation of an initial oxocarbenium ion.)

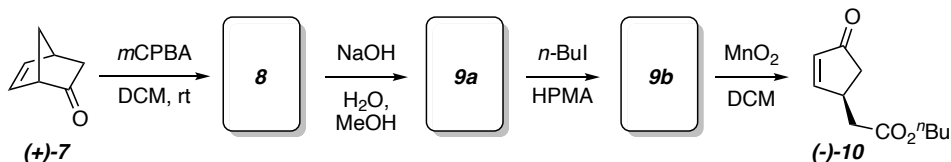


c) The cyclization of alkene **5** to iodide **6**. This reaction occurs in the absence of a protic solvent or base, and there is no work up. Identify the structure of the byproduct (i.e., balance the equation) even before you start working on the mechanism. Deduce whether the alkene in **5** is the *E*- or the *Z*-isomer. (*hint*: iodolactonization, like other halocyclizations, occurs by net trans addition of the I and O to the alkene.)

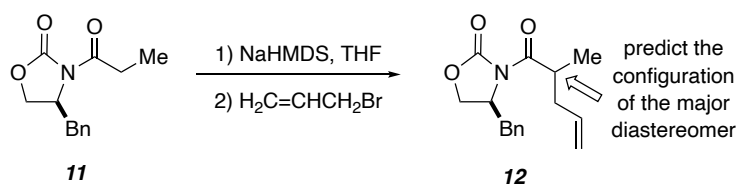


Other Problems

1. Provide the structures of the compounds **8**, **9a**, and **9b** in the following reaction sequence to form the enone **10** from ketone **7**. The first reaction is a Baeyer-Villiger oxidation (there is no acidic workup used following the NaOH treatment; only removal of the aq MeOH solvent).



2. Provide the structure of the major diastereomer you expect for the following transformation of the acyloxazolidinone **11** to the allylated derivative **12**. This is an Evans alkylation. The diastereocontrol is exerted via chelation of the sodium ion in the intermediate enolate and approach of the allyl bromide to the less hindered face of that chelated enolate. Draw a structure of the intermediate enolate.



3. Indicate whether each of the following equilibria lies predominantly to the left or to the right by circling the side corresponding to the more stable species and provide a <5-word explanation for your answer.

