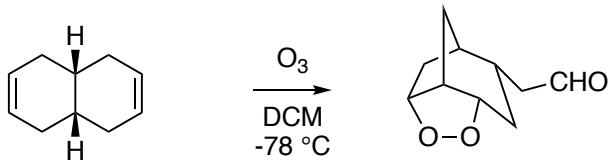
CHEM 8321/4321 **October 16, 2023**

Problem Set #6 **T. R. Hoye**

Due in class, Monday October 23, 2023

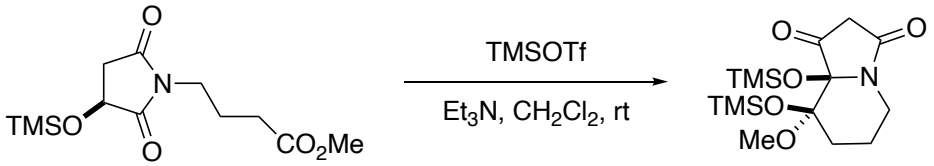
Detailed Mechanism Provide a detailed mechanism [i.e., *explicitly* show (using curly arrows) *EVERY* intermediate, formal charge (where relevant), equilibrium, and bond-making and -breaking step] to account for the following transformations:

a) The ozonolysis of diene **1** *in the absence of methanol* to give the cyclic peroxide **2**.



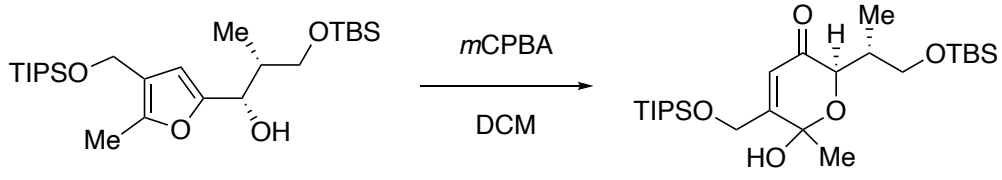
1 ***(±)-2***

b) The conversion of imide **3** into the β-ketolactam **4** upon exposure to more than one equivalent of TMSOTf and triethylamine. This is a variant of an acid-catalyzed Dieckmann cyclization.



3 ***4***

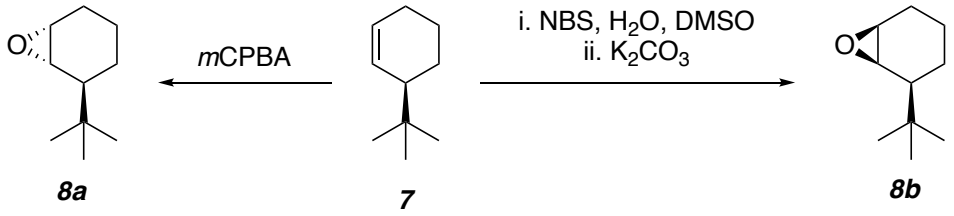
c. The conversion of furan **5** to enone **6** using *m*CPBA.



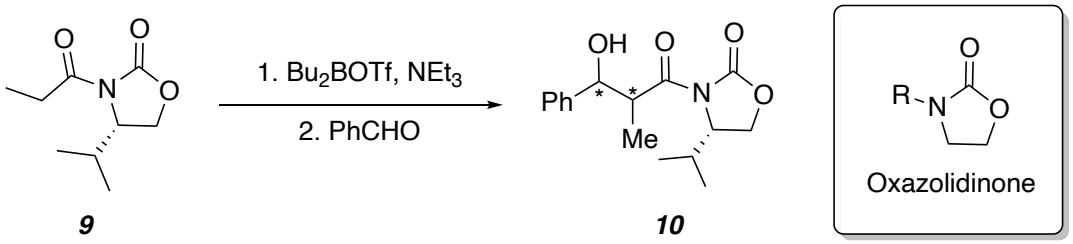
5 ***6***

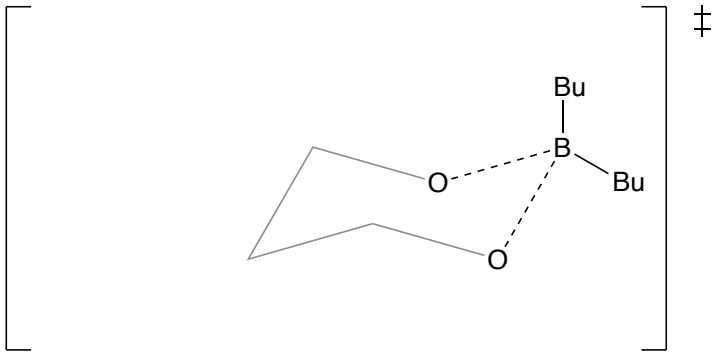
Other questions:

1. The reaction of *m*CPBA with the cyclohexene **7** forms epoxide **8a**. The same cyclohexene **7** forms epoxide **8b** upon subjection to NBS followed by potassium carbonate. Explain this observation.



2. The Evans asymmetric aldol reaction utilizes an oxazolidinone as a chiral auxiliary that contains a stereocenter to obtain high diastereoselectivity in an aldol addition reaction. Deduce the configuration of the starred stereogenic carbon atoms in compound **10** following the reaction of the oxazolidinone **9**. Draw the fully elaborated, six-membered transition state structure on the template below.





3. Reaxys search questions

a) How many substances in the Reaxys Database have an oxetane ring fused to a 6-membered carbocycle?

b) How many bicyclic compounds (i.e. exactly 2 rings) are there on the Reaxys Database? *Hint:* Specify "no additional ring closures" to limit the search appropriately.

c) The conversion of acetone to a 3-methyl-butenoate in a single step? How many of these examples use a phosphonate ester?