

Problem Set 4

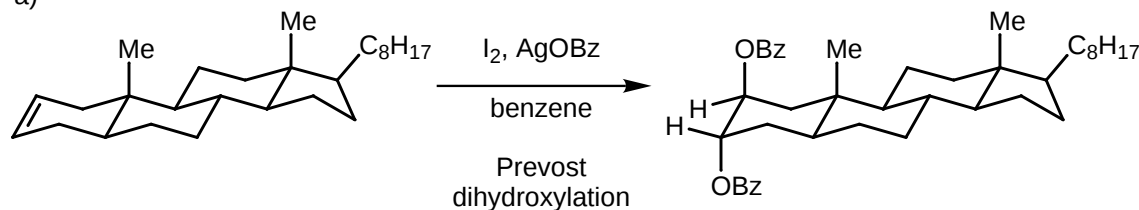
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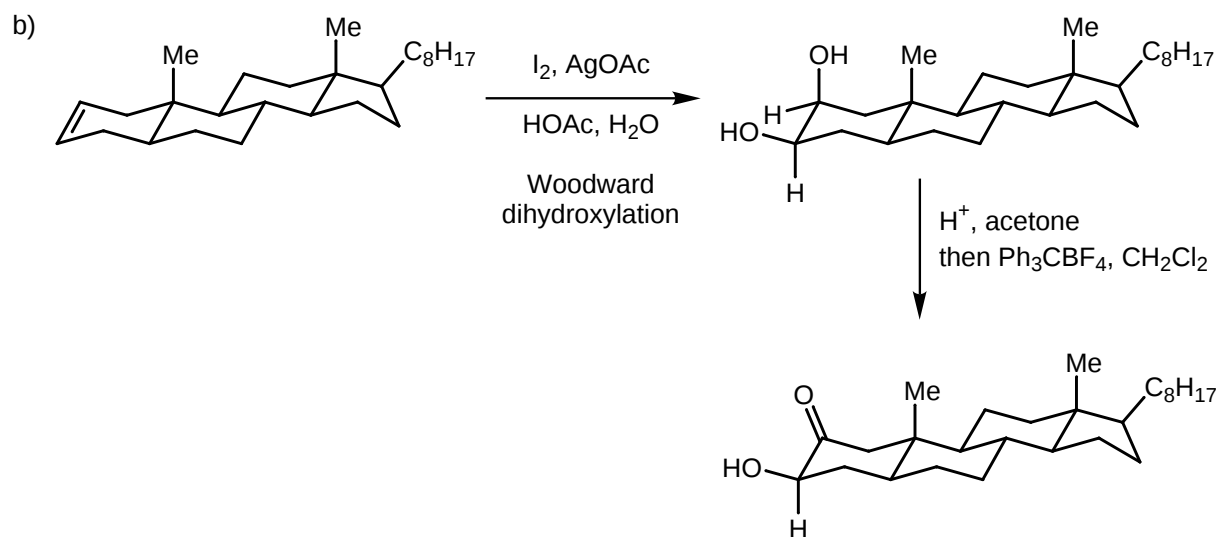
General Instructions: Neatly, in the space allocated, provide concise answers to the following questions using clear three-dimensional representations for all relevant structures. Address stereochemical and stereoelectronic issues where appropriate. Classify all pericyclic reactions.

Question 1.

Please explain (1) the different stereochemical outcomes of the following reactions, (2) the regioselectivity of the oxidation of the diol.

a)

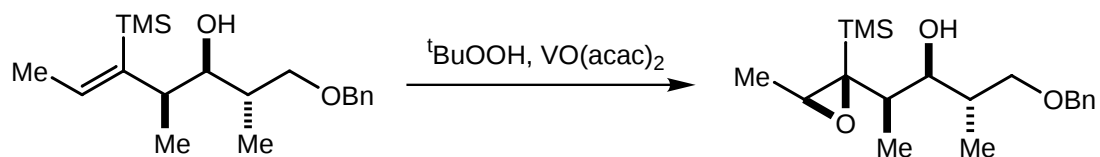




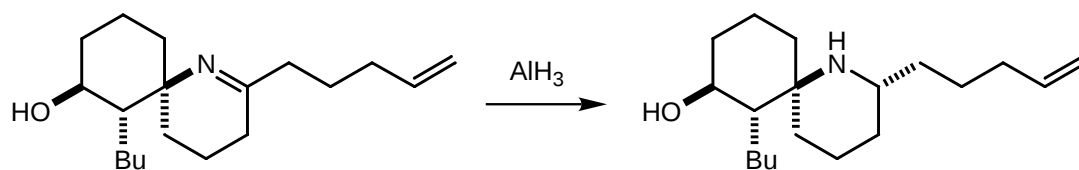
Question 2.

Please draw the most stable conformations of the reactants and explain the facial selectivity of the following reactions.

a)

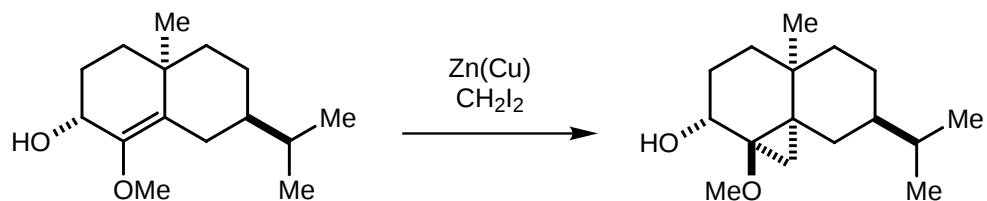


b)

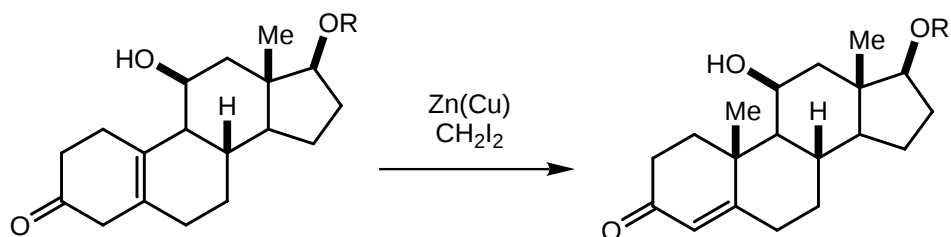


Question 3.

a) Please draw the most stable conformation of the reactant and explain the facial selectivity of the following reaction.

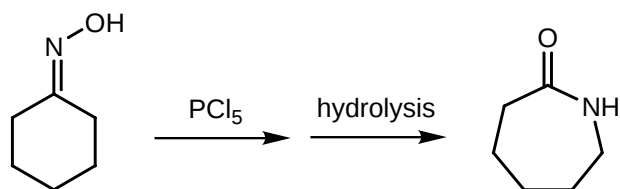


b) The Simmons-Smith reaction below served to introduce an angular methyl group indirectly but stereoselectively. Please give a mechanism and explain the stereochemical outcomes of the following reaction.

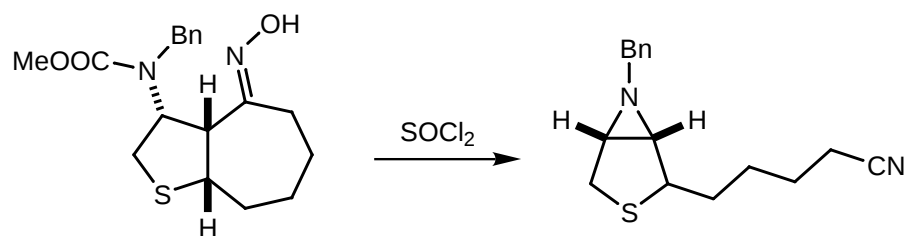


Question 4.

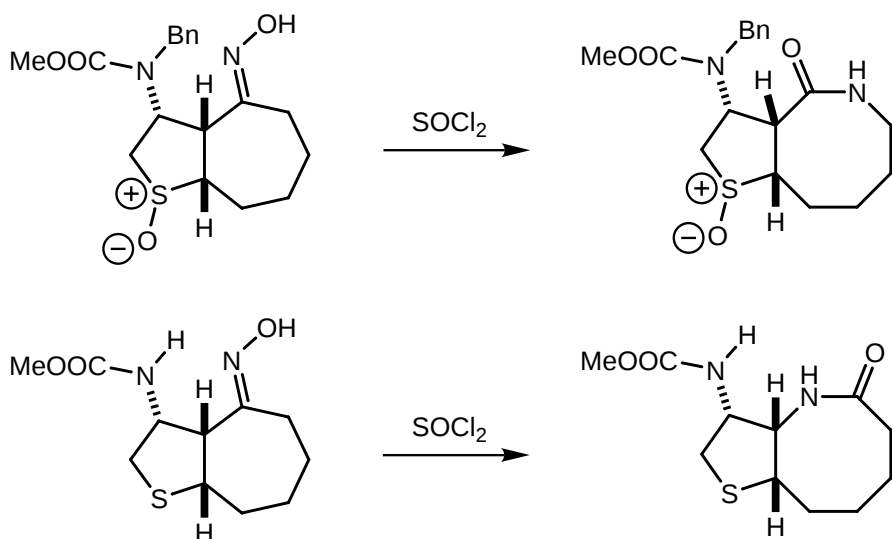
a) The Beckmann rearrangement is used analogously to the Baeyer-Villiger reaction to insert a nitrogen atom. Please provide a mechanism of this reaction, and identify the stereochemical requirement of the migrating group relative to the oxime.



b) (**OPTIONAL**) An unexpected result was obtained in the following case. Please provide a mechanism for this transformation.

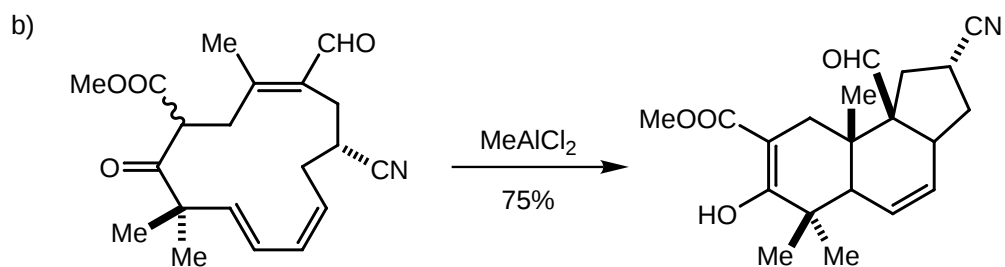
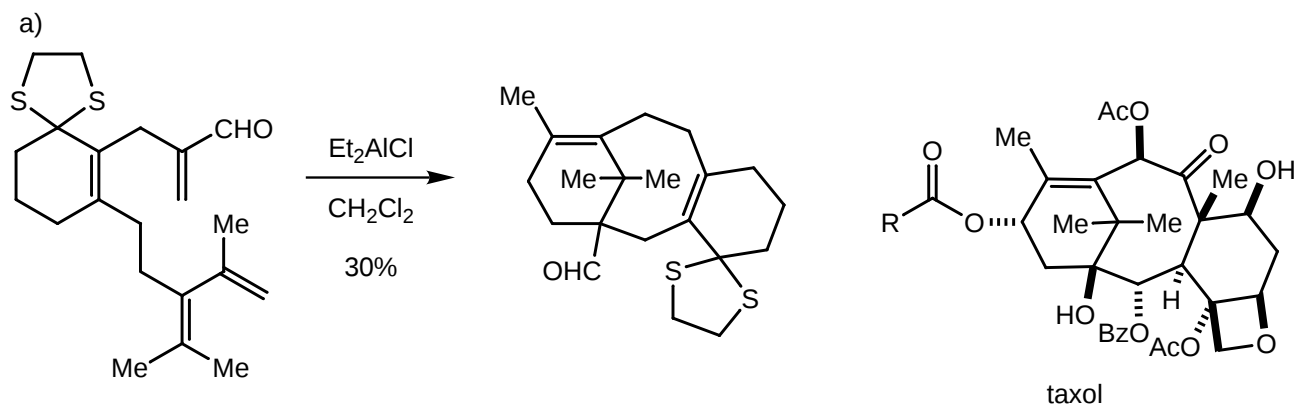


c) To solve this problem, the sulfide group was first oxidized to sulfoxide. The Beckmann rearrangement did proceed but with the nitrogen atom inserted into the unexpected position. However, after the benzyl protecting group on nitrogen was removed, the expected Beckmann rearrangement proceeded. Please explain these rather counterintuitive results based on the Curtin-Hammett principle.

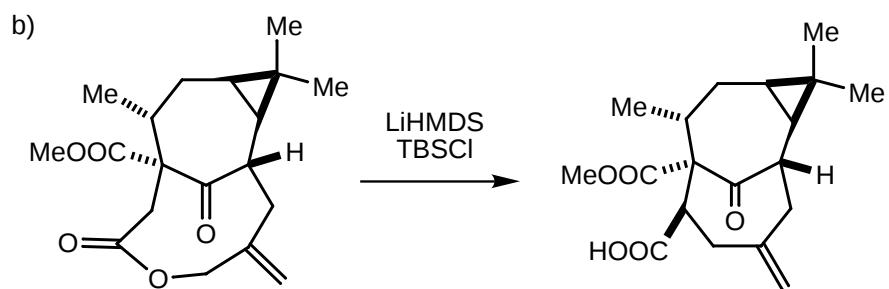
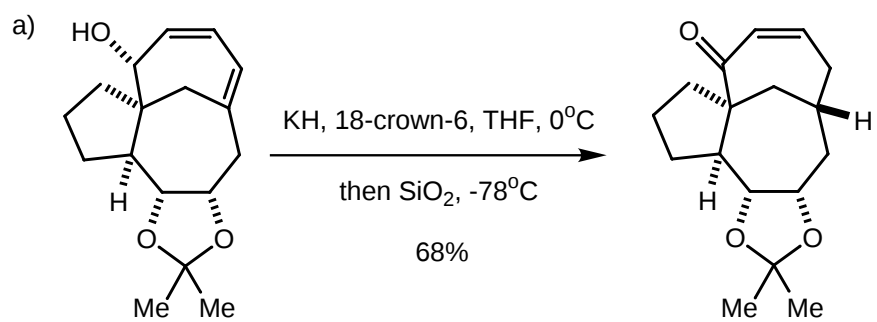


Question 5.

Please provide mechanisms for the following transformations.



Question 6. Please provide mechanisms for the following transformations.



Question 7. Please provide a mechanism for this reaction and a rationale for the stereochemical outcomes.

