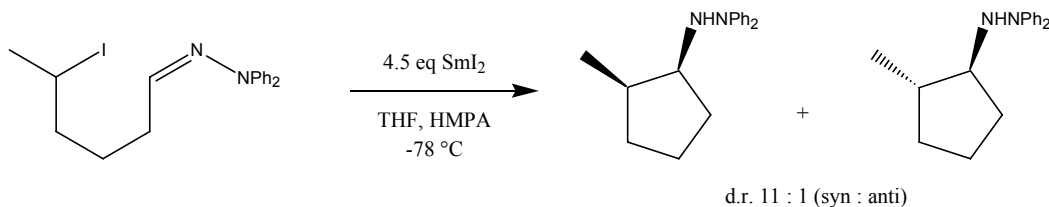
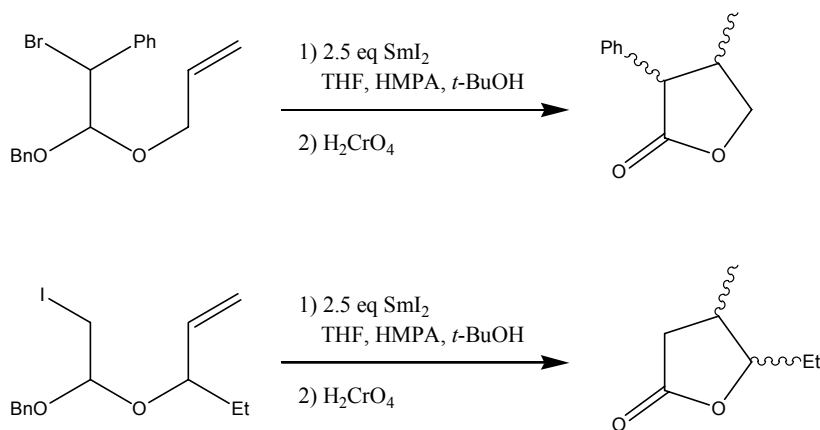


A Sampler of Samarium (II) Iodide Chemistry

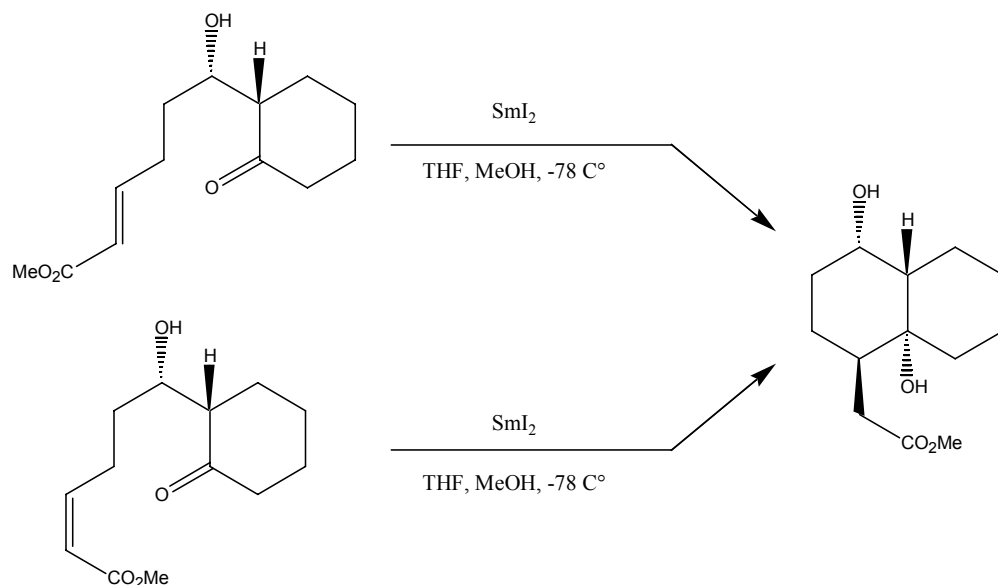
- 1) Both SmI_2 and SnBu_3H have been shown to affect the cyclization of halohydrazones to cyclopentylhydrazines. Reactions which utilize SmI_2 , however, can be performed at much lower temperatures, yielding higher diastereoselectivities as a result.



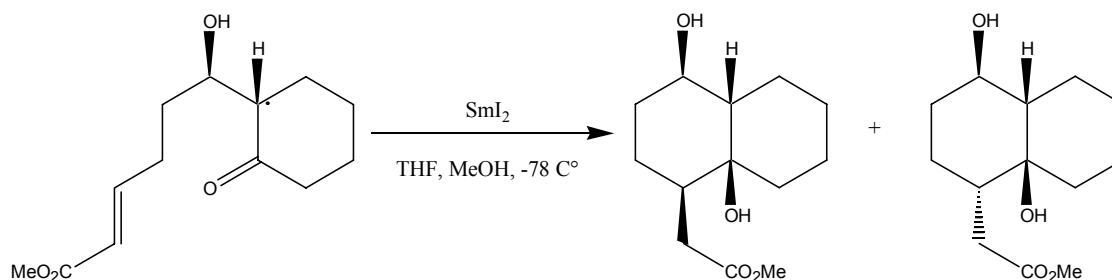
- a) Please propose a transition state that is consistent with the observed product distribution shown above.
- b) SmI_2 can also promote the lactonization of allylic haloethers. Propose a mechanism for the reaction, and predict the stereochemistry of the products illustrated below. Explain.



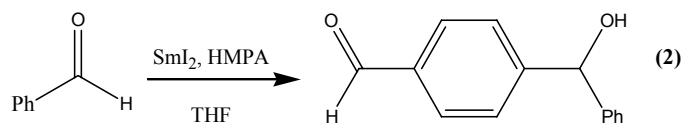
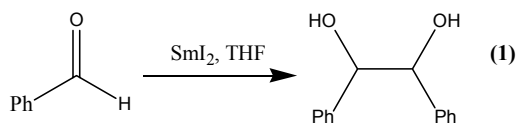
- 2) Hydroxyl groups have been shown as having a significant influence on intramolecular coupling reactions of ketyl olefins. In the reaction shown below, both the *E* and *Z* diastereomers yield the same major product.



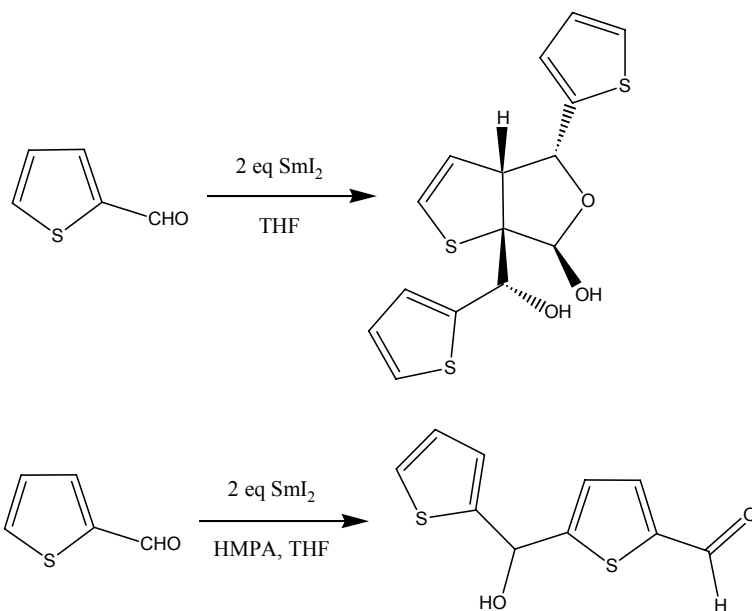
- a) Propose a transition state that explains the diastereoselectivity observed in the product. (Hint: It is argued to be dominated by an electronic effect.)
- b) In the following reaction, the products are formed in a 5.4:1 ratio, favoring the all-syn product. Please rationalize the stereochemistry seen.



- c) HMPA is a common additive in SmI_2 promoted reactions. Generally, HMPA complexes with samarium to give complexes which have increased redox potentials over SmI_2 . Why then in the reactions shown above does HMPA decrease the diastereoselection of the reactions?
- 3) As seen above, HMPA is commonly added to reactions with SmI_2 . This additive has interesting effects on the reactivity of aromatic aldehydes. In 1993, Fang (*Tet. Let.*, **1993**, 34, 335) reported that upon addition of HMPA to reductive SmI_2 conditions, rather than seeing the pinacolic coupling of benzaldehyde (1), they observed aryl-carbonyl coupling (2).

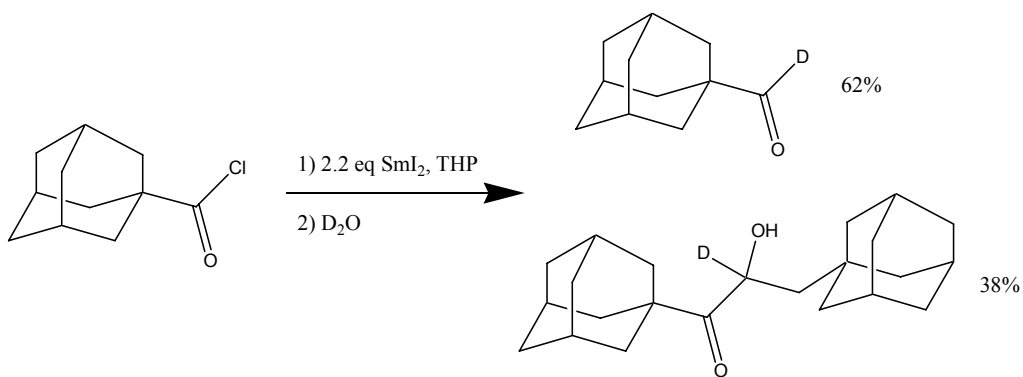


More recently, Fang has reported on the interesting SmI_2 induced coupling of thiophene carbaldehydes.



Provide mechanisms that account for the product formation in the absence and presence of HMPA.

- 4) In 1994, Kagan reported on SmI_2 and acyl chloride chemistry being performed in THP, rather than THF. The following reaction was performed in order to probe the mechanism.



Kagan reports that there was quantitative C-deuteration of the products. What do these results suggest about the mechanism of the reaction of acyl chlorides and SmI_2 (read: what are the functional intermediates)? Also, what is the advantage of using THP in place of THF as the solvent?

- 5) In 2001, Nicolaou and company made the complete aromatic core of Diazonamide A (shown below at the end of the roadmap) using a hetero pinacol macrocyclization cascade as the key step. Fill in the missing intermediates.

