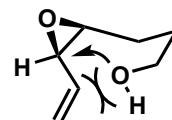


Thursday, December 7th, 2017

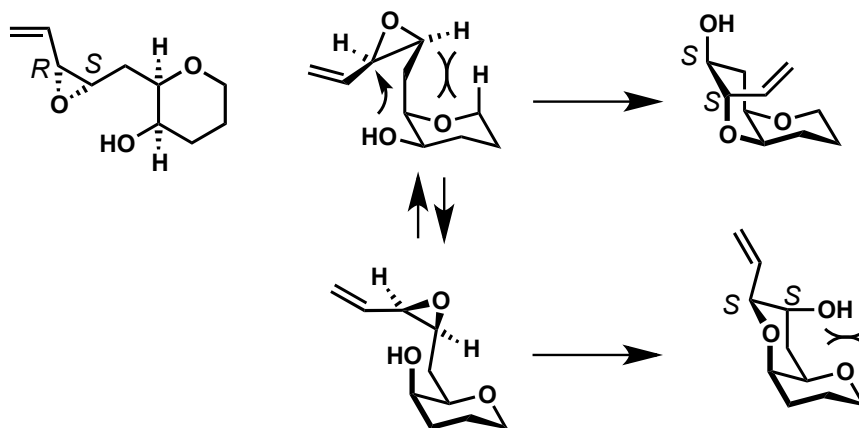
Problem 1 (JACS 1989, 111, 5330)

A) Under acidic conditions, opening of epoxide **1** occurs preferentially at the allylic position (stabilization of partial positive charge). However, in the *cis*-epoxide **4** the incoming nucleophile is hindered by the vinyl substituent, making this mode of attack less favorable, leading to relatively more 5-membered ring product formation.



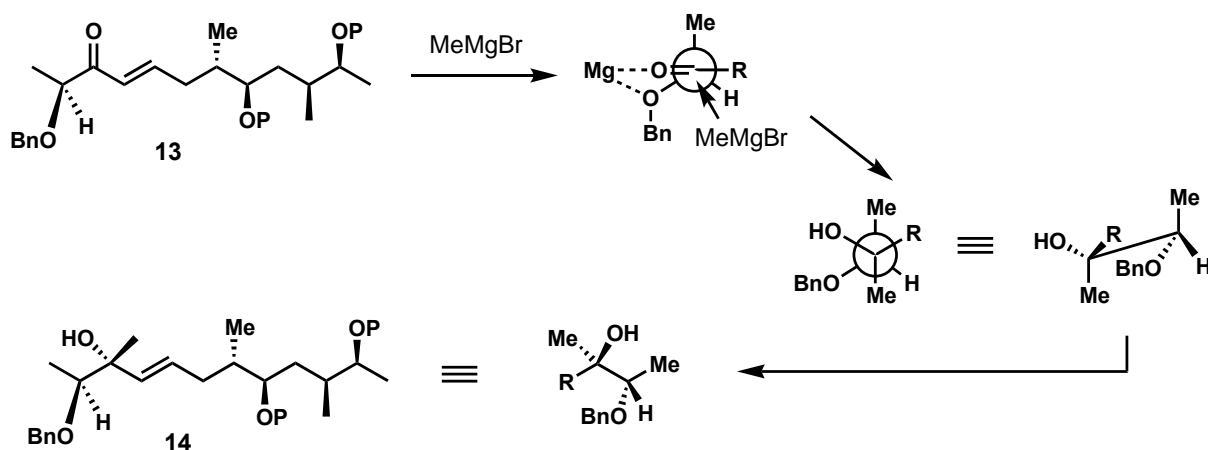
B) Here we are dealing with a *cis*-epoxide again. Now the relative amount of the 5-membered ring product (**8**) is diminished with respect to the situation starting from epoxide **4**. This can be explained by the fact that the formation of a *cis*-fused 5,6-ring system is relatively unfavorable, leading to relatively more of the 6,6-fused system.

When we start with epoxide **10**, formation of the *cis*-fused 5,6-bicycle is possible and is in fact way favored over the formation of the *cis*-6,6-bicyclic (a *cis*-decalin). See for a relevant t.s.:

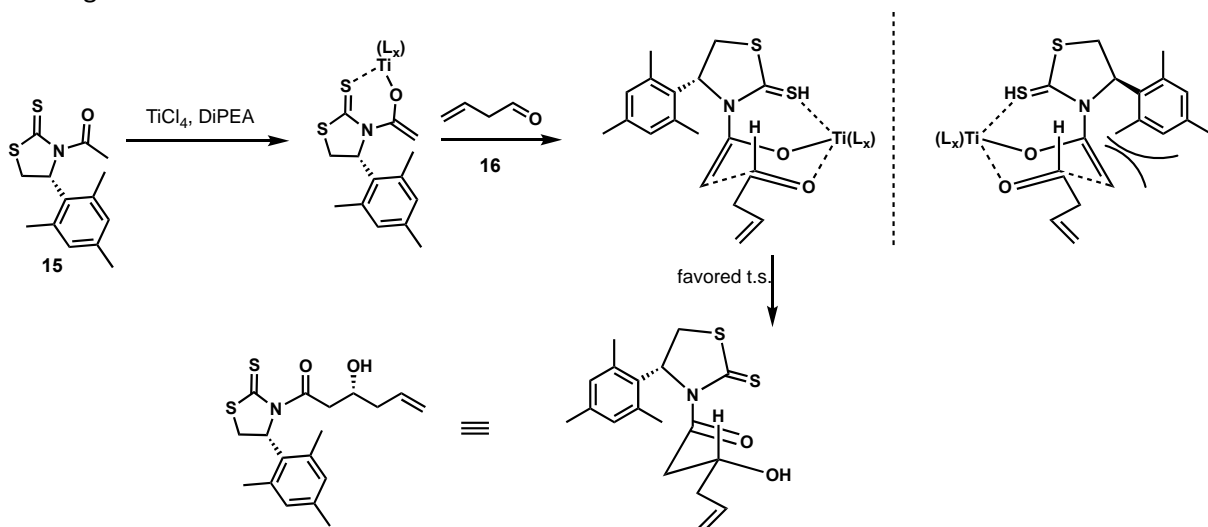


Problem 2 (Org. Lett. 2012, 14, 23656)

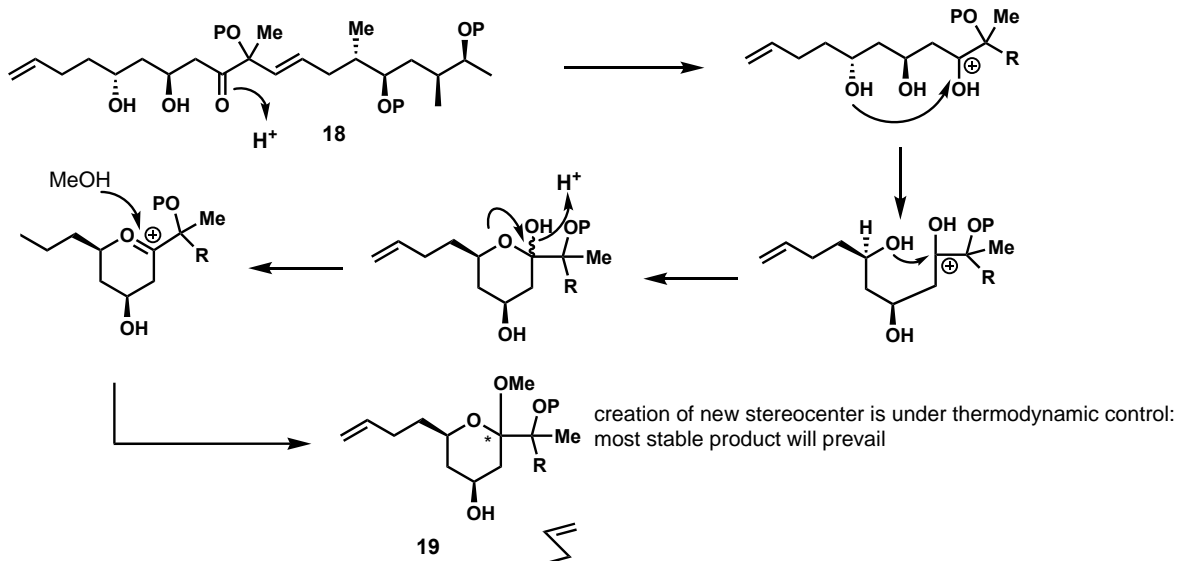
- A)** The major product in this addition reaction is formed through a Chelation controlled Felkin-Ahn transition state:



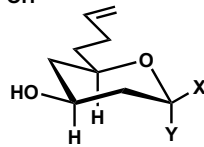
- B)** Through chelation of the titanium the following Zimmerman-Traxler transition states can be drawn up. The most favorable t.s. will place the bulky trimethylphenyl substituent away from the ring:



c)

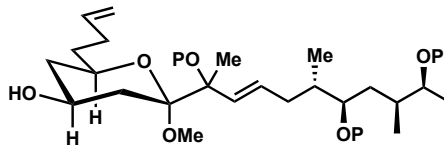


The "core" 6-membered ring will look like this:



The position of X and Y will be determined by the size and electronic properties of the substituents. The OMe is small and electronegative (available s^*C -OMe), therefore an axial orientation is most attractive for this group (anomeric effect)

So this will be the most favorable product:



Opgave 3

The major product of this iodolactonization reaction can be accounted for by a Houk-transition state:

