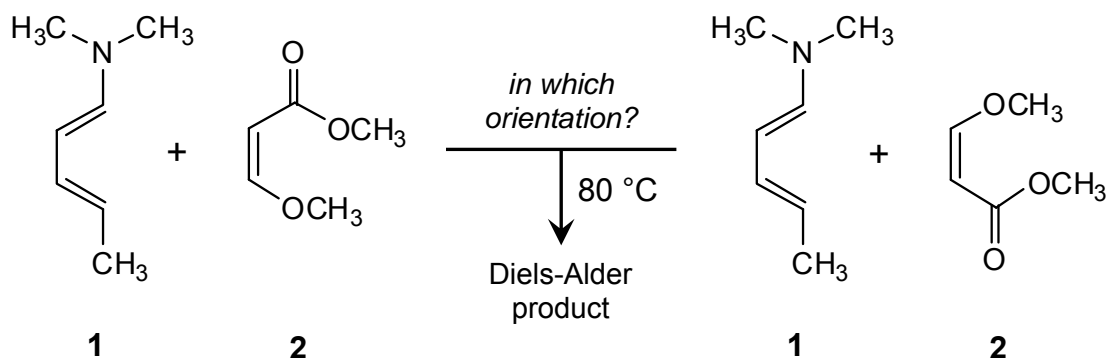
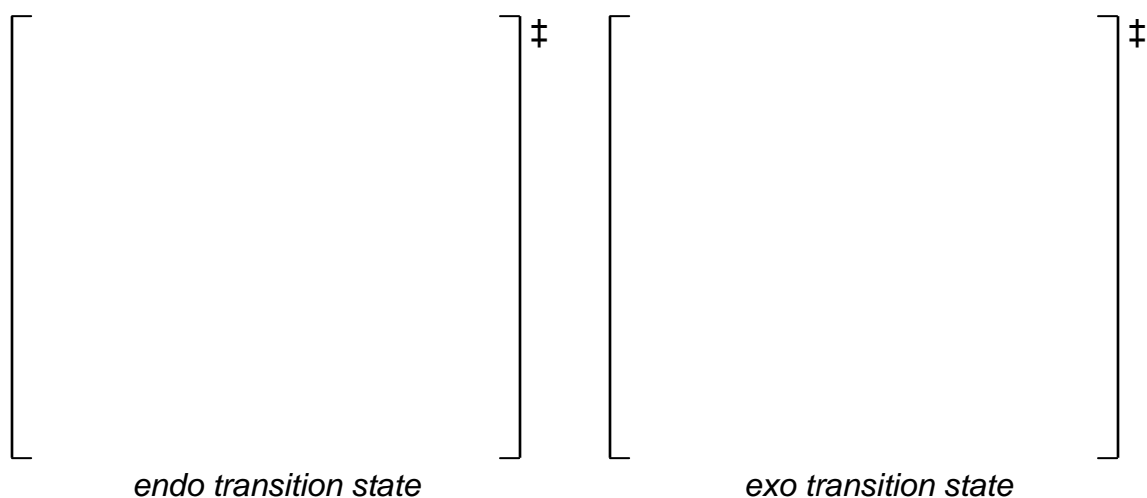


**Workshop 3**  
**Reversible Diels-Alder Reactions**

1. Diene **1** and dienophile **2** undergo the Diels-Alder reaction. The diagram below illustrates the two molecules approaching each other in two different orientations; which *regiochemistry* is correct?



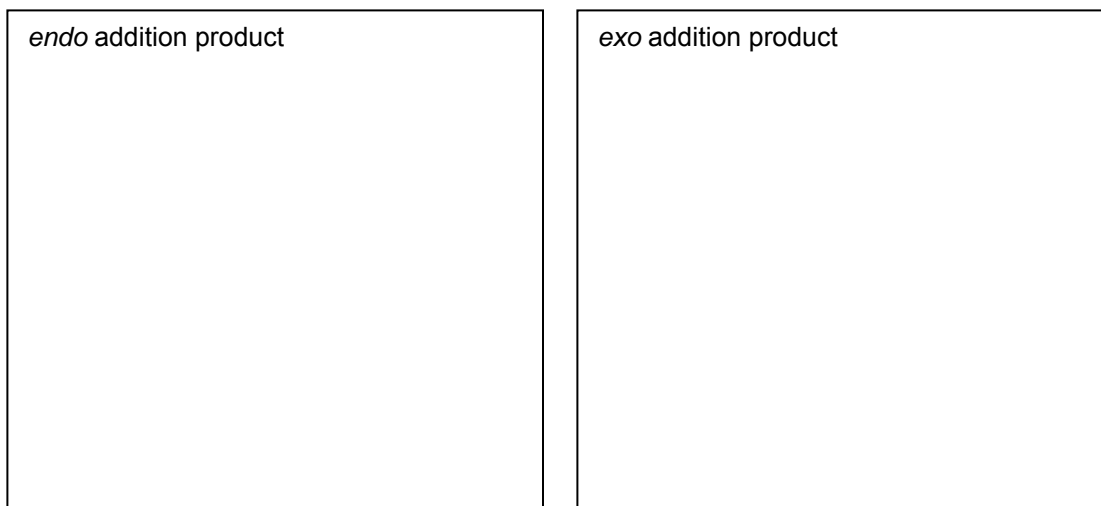
2. In order to determine the *stereochemistry* in the preferred product of this Diels-Alder reaction, we also need to consider which face of the dienophile approaches the diene. In the spaces below, draw transition states—as 3D as you can make them—that correspond to *endo*- and *exo*-approach of the dienophile  $\pi$  components.



(This is Smith's way of solving Diels-Alder problems. You'll remember that I introduced a simpler mnemonic in class for figuring out stereochemistry in this reaction. For this Workshop, we'll go ahead and draw out Smith's 3-D drawings.)

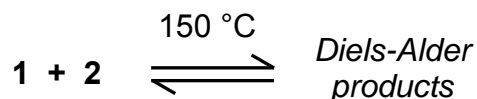
3. Which of these transition states is lower in energy, and why?

4. Each of the transition states on the previous page would lead to a different product. Draw those two products below.

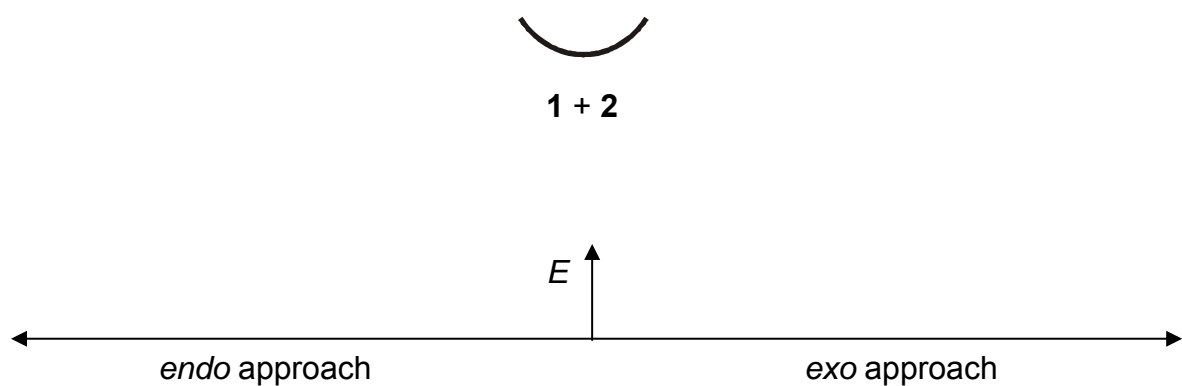


5. Which of these products would be lower in energy, and why?

At higher temperatures (> 150 °C), the Diels-Alder reaction can revert, regenerating **1** and **2** from the cyclohexene product via the “retro-Diels-Alder” reaction. This “retro” reaction is endothermic, and the diene and dienophile can immediately recombine via a Diels-Alder reaction.



6. Below, complete the potential energy diagram for the Diels-Alder reaction of **1** and **2** via both *endo* and *exo* approach. Make sure your diagram indicates which transition state is lower in energy, and which product is lower in energy.



7. Which Diels-Alder product would you expect to be favored at 150 °C (a pretty high temperature), and why?