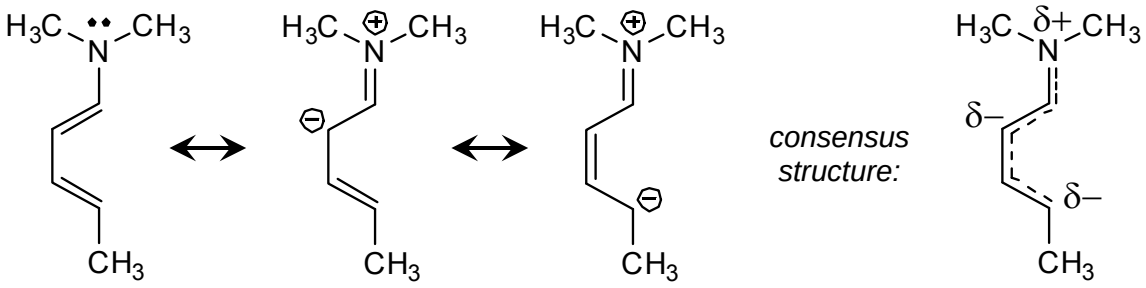
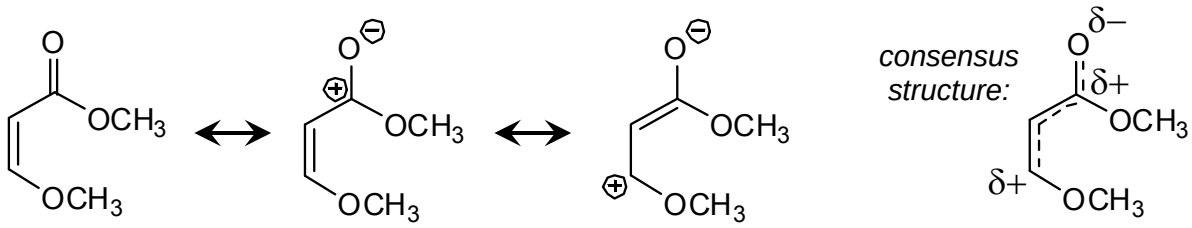
Chemistry 2302

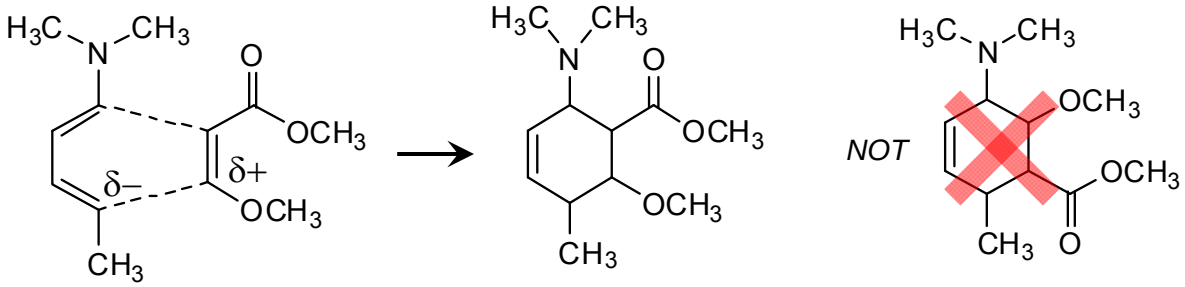
Workshop 3 Solutions
Reversible Diels-Alder Reactions

1. To answer this question, we need to draw resonance structures of the two starting materials:



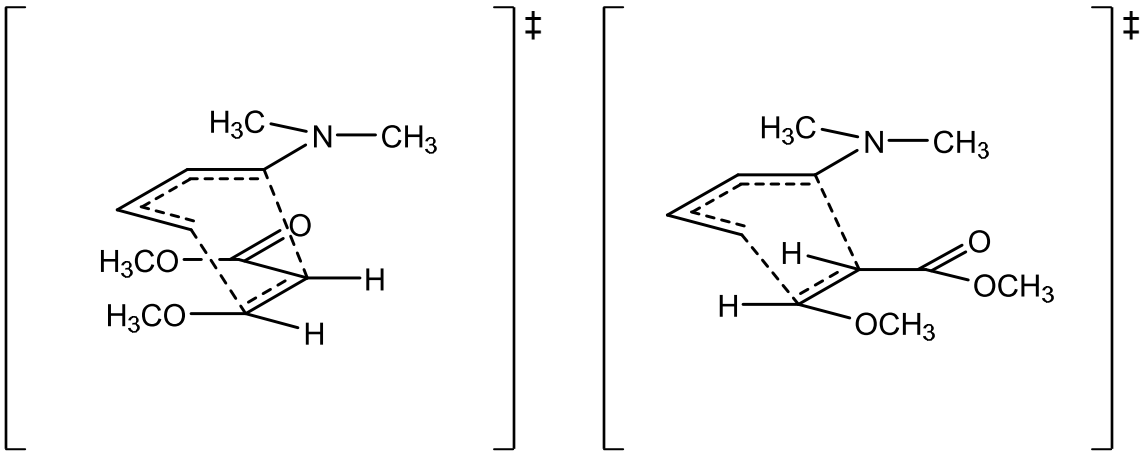


Opposite charges attract, and so our diene and dienophile are going to arrange themselves such that the partial negative charge on the diene terminus ends up next to the partial positive on the dienophile:



Important note: I haven't drawn stereochemistry on my product yet; we'll deal with that in the next part.

2.



endo transition state *exo transition state*

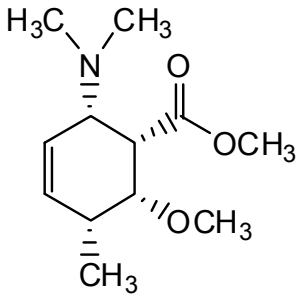
The *endo* transition state has the π-substituent (ester) tucked under the diene, whereas the *exo* transition state has it sticking out away from the diene. I've drawn partial bonds to indicate how bonds are changing in the transition state, and not yet reached their final states.

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

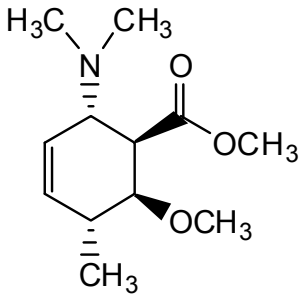
   The *endo* transition state is lower in energy (favored) because of interactions between the ester π orbitals and the diene π orbitals.

4. Each of the transition states above leads to a different product. Draw those two products below.

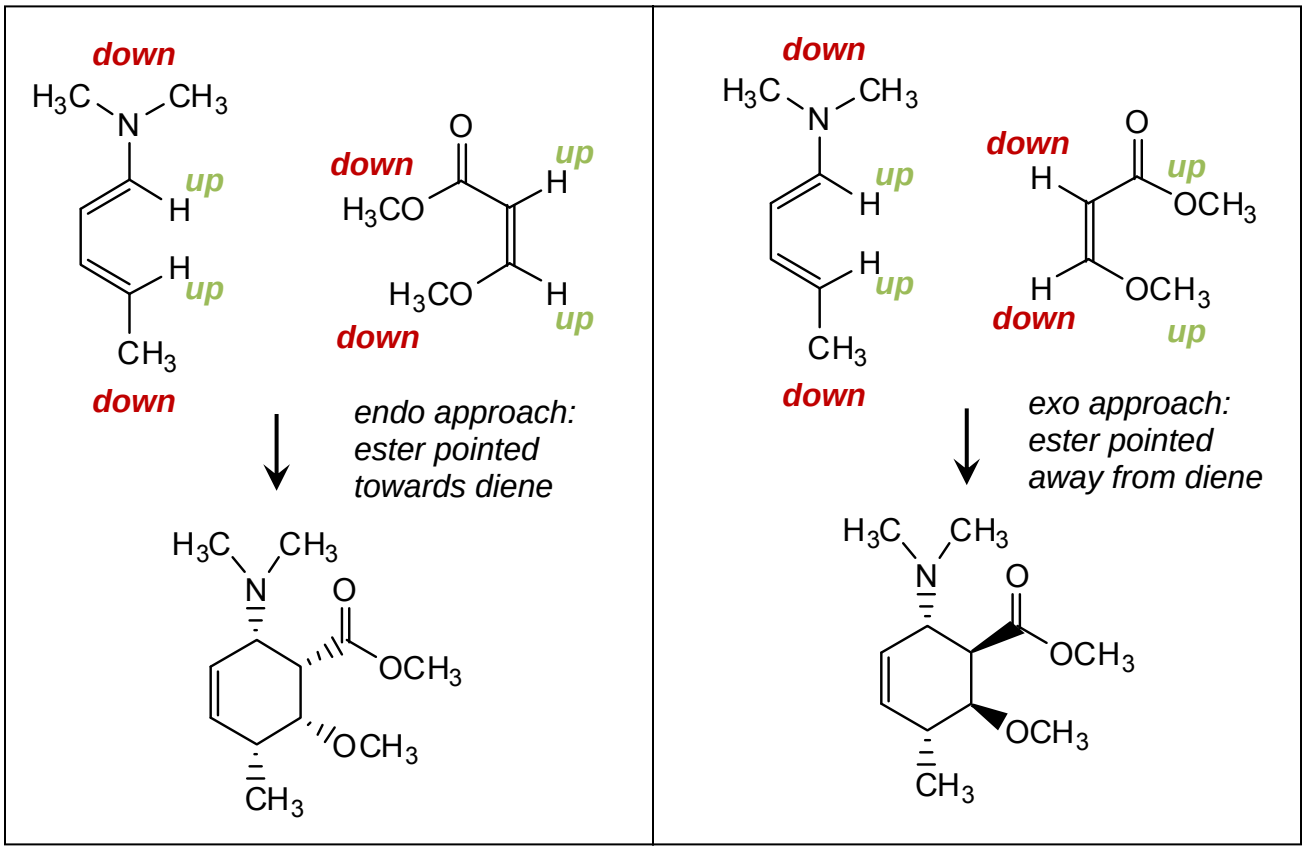
endo addition product



exo addition product



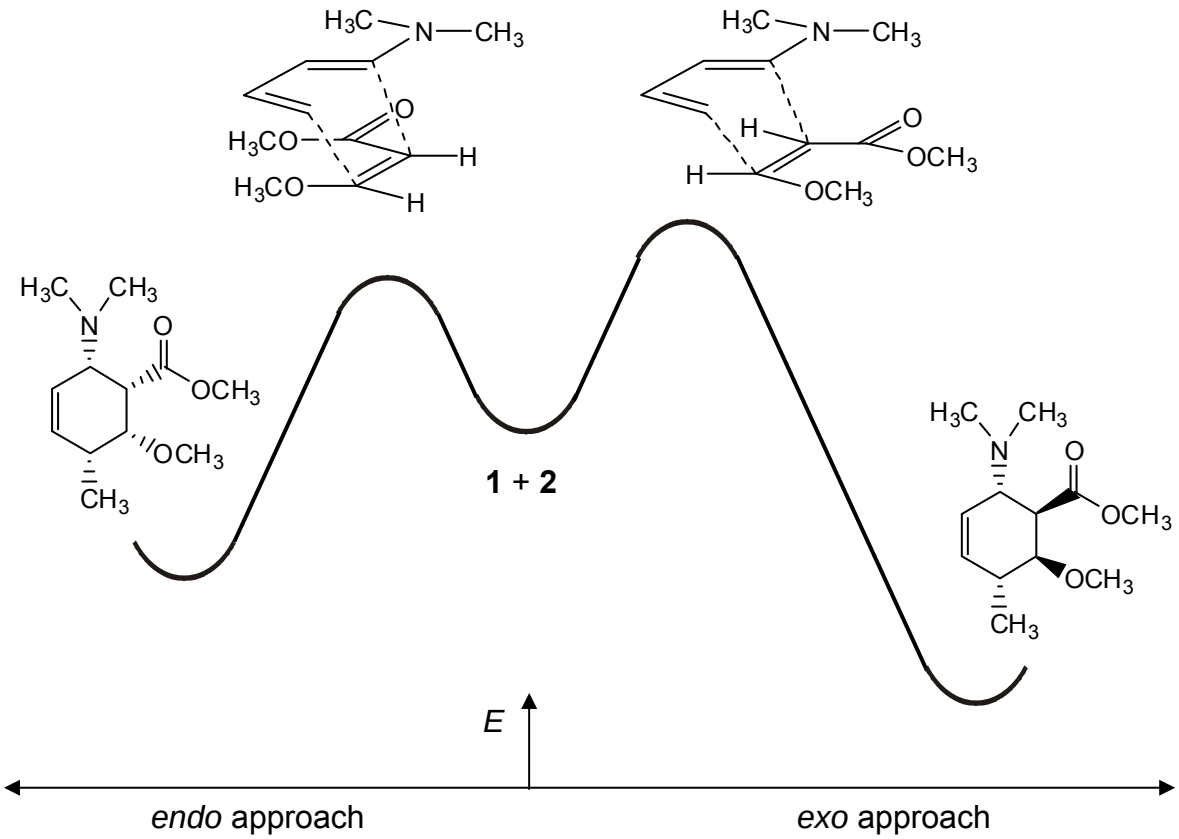
One way to get at these answers would be to look at the transition-state drawings and to try and decipher which group ends up and which ends down. Personally, I like to use the mnemonic that we discussed in class better; in which we draw the approach of the two molecules flat on the page, and then mark groups on the right as oriented *up* and groups on the left *down*:



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

   The *endo* product has all four groups on the same side of the ring, and these will all interact sterically. The *exo* product, on the other hand, distributes the groups on both sides of the ring. So the *exo* product should be more stable.

6. In a potential energy diagram for this reaction, we have to integrate the two things we've learned so far. First, the *endo* reaction pathway has the most stable *transition state*; second, the *exo* reaction pathway has the most stable *product*.



7. Which Diels-Alder product would you expect to be favored at 150 °C, and why?

   At higher temperature, the *endo* and *exo* products and the starting materials will all be in equilibrium, and so the system will find its lowest energy state. That's the *exo* product—even though the transition state to get to that product is less favored than the *endo* transition state. We'd argue, then, that the *endo* product is the kinetic product, and the *exo* product is the thermodynamic product.

   Accessing the retro-Diels-Alder mechanism and equilibrating all Diels-Alder products requires high temperatures—usually, temperatures that are so high that they pyrolyze (burn) the starting materials. So generally speaking, it is safe for us to say that Diels-Alder reactions prefer *endo* approach.