This worksheet focuses on the stereoselectivity and regioselectivity of the Diels-Alder reaction.

**STEREOSELECTIVITY**

Shown here is the equation for the Diels-Alder reaction of 1-methoxy-1,3-butadiene with trans-3-penten-2-one. Note carefully the stereochemistry of the product. Identify the following in this equation: **diene**, **dienophile**, **cis relationship**, **trans relationship (2)**, **R**, and **S**. Point out the two new sigma bonds in the product.

1. Imagine folding this paper toward you on a vertical line going right through the + sign, between the two reactants, to “close the book” on the reaction. Using the template on the right, add all the groups and H atoms around the diene and dienophile. Draw dotted lines showing the two new bonds. Convince yourselves that the groups will end up with the stereochemistry shown in the equation.

2. Discuss why we say that the Diels-Alder reaction is **stereospecific**. What aspect of the reaction ensures that it is so?

3. Discuss why the CH$_3$ and the COCH$_3$ groups end up **trans** to each other. Why do the OCH$_3$ and the COCH$_3$ groups end up **cis** to each other? Which of these relationships arises from the stereospecific nature of the reaction? Which is simply a result of **endo** stereoselectivity?

Now imagine folding the paper the OTHER way, as if the diene and dienophile were on the cover of the book, and someone was closing it. Complete the template again based on the reaction above, including hydrogen atoms, and draw the dotted lines showing the new bonds. Draw the expected product, including all stereochemistry. Note particularly how useful it is to include the H atoms! Label **R** and **S**.

Discuss the relationship between this product and the one shown in the equation? Why is that? Will one or both be made in the actual reaction? If so, will their ratio be 50:50 or not?
4. Show on this template the orientation of diene and dienophile that would result in the *exo* addition product, shown on the right. What is the generally accepted reason given for why the *endo* product is favored over the *exo* product?

REGIOSELECTIVITY

5. The Diels-Alder reaction is an amazingly selective reaction. For example, the following is NOT observed:

Using ideas of electron delocalization in the diene and dienophile, show that this product does NOT optimally align the partial negative character in the “electron-rich” diene with the partial positive character in the “electron-deficient” dienophile at the indicated positions.

6. As time permits, determine the major *endo* product in each of the following Diels-Alder reactions. Draw only one enantiomer, but realize that both will be produced. When both the dieneophile and diene are different on the two ends, it’s a good idea to start with a quick assignment of partial negative and partial positive charges in the diene and dienophile, respectively. Watch out for reactants that aren’t aligned correctly on the paper! In these cases, redraw the reactants before closing the book on them.

see also: [http://www.chemtube3d.com/DARegioselectivity.html](http://www.chemtube3d.com/DARegioselectivity.html)