The Diels-Alder Reaction: A reaction of a conjugated diene

Purpose
To perform a reaction of a diene with a dienophile, to perform a microscale recrystallization of the product, and to gain experience using the IR spectrometer.

Background
Conjugated dienes can react with alkenes via a 1,4-cycloaddition reaction, a Diels-Alder reaction. Interestingly, when the reaction creates a fused ring system, such as the molecule pictured in eq. 1., often only one of the two possible products is formed as the major product. The two possible products are an endo, large parts for the fused rings point away from each other, and an exo, large substituents of the fused ring system point toward each other, product.

![Image of diene and dienophile](image)

endO \hspace{1cm} \text{exo}

A theory that explains the selectivity of the reaction involves the orbital overlap of filled molecular orbitals on the dienophile that are not directly involved in bond formation with orbitals on the diene. These secondary orbitals of the dienophile donate electron density to the highest occupied molecular orbital (HOMO) of the diene to stabilize it as the HOMO of the diene transfers electron density to the lowest unoccupied molecular orbital (LUMO) of the dienophile. The aforementioned stabilizing interaction is referred to as secondary orbital overlap. The stabilization of the HOMO during the reaction lowers the activation energy for this path; thus, the endo product can form more quickly than the exo product as the transition state that leads to the exo product does not have any stabilizing secondary orbital overlap. In other words, the less thermodynamically stable product, the endo product, is formed under kinetic conditions, where as the more thermodynamically stable product predominates when the reaction is done in such a way that the reactants and products can equilibrate.

![Image of cyclic products](image)

endo \hspace{1cm} \text{exo}

A second equally interesting aspect of this reaction is that the stereochemistry of the diene and the dienophile are maintained in a Diels-Alder reaction. To align the orbitals so that they may make new
bonds, in this reaction, the ends of the diene must rotate in opposite directions (one end rotates clockwise and the other counter clockwise). The result of this disrotatory motion is that if the diene is a trans-trans or cis-cis diene, the substituents will be in a cis arrangement in the product (see eq. 2). On the other hand, if the alkene is a cis-trans alkene, the result is that the substituents will have a trans relationship in the product. For the dienophile, if a cis alkene is used as the dienophile, then those substituents will have a cis orientation in the ring (see eq. 3). Similarly, if the dienophile’s substituents start in a trans arrangement on the dienophile the relative positions of those substituents will be maintained in the product. Other techniques allow chemists to control the stereochemistry of this reaction to an even greater degree.

The fact that this reaction creates six-membered rings in one step and that it does so while allowing for a high degree of control over the stereochemical outcome of the reaction makes this reaction an important tool for the synthetic organic chemist.

**Procedure**

**Reaction of cyclopentadiene with maleic anhydride**

1. Add 0.100 g of maleic anhydride and 0.40 mL of ethyl acetate to a Craig tube.
2. Add 0.40 mL of ligroin and shake.
3. Gently shake (or use a vortex stirrer) and warm the tube (approximately 40 °C) to dissolve the maleic anhydride, a small amount of ethyl acetate can be added.
4. Add 0.10 mL of cyclopentadiene and shake the tube to dissolve the cyclopentadiene.
5. If a solid forms immediately, add a drop of ethyl acetate and gently warm the suspension. When the exothermic reaction begins, you should be able to feel the heat escaping from the reaction.
6. Allow the reaction to cool slowly to room temperature. Once crystal formation at room temperature has stopped, cool the Craig tube in an ice water bath.
7. Collect the crystals by centrifuging the Craig tube.
8. Dry the product on a watch glass.

**Analytical Data**

8. Collect IR data for maleic anhydride and for your product, cis-5-norbornene-endo-2,3-dicarboxylic anhydride.
9. Determine the melting point of your product.

**Modeling**

1. Use short bonds to connect H atoms to the C atoms and bendable bonds to connect all other atoms, build 1,3-butadiene and E-2-butene.
2. Using the electron movement arrows shown to the right as a guide, move the appropriate bonds on your models to create the product.
3. In your notebook, draw the product(s) of the reaction performed in step 2.
4. Rebuild the original molecules.

The Diels-Alder reaction is a concerted reaction (a reaction were multiple bonds are broken and formed in one step), and the stereochemical outcome of this reaction supports that conclusion. Test this idea by doing the following.

5. Repeat step 2, but only move the bonds associated with arrows a and b.
6. Draw the intermediate that would result.
7. If the intermediate in step 6 actually formed, what implications would that have for the stereochemical outcome of the reaction?

Diels-Alder reactions only occur with conjugated dienes (dienes where the electrons are delocalized over both \( \pi \) bonds). Test this idea by doing the following.

8. Build models for 1,4-pentadiene and E-2-butene.
9. Using the arrows in step 2 as a guide form a six remembered ring (the key here being that only electrons from \( \pi \) bonds participate in the reaction).
10. In your notebook, draw a the result of the reaction performed in step 9.
11. Describe the problems with the making of the product (moving the electrons to form the bonds), and the product itself.

**Report**

Do not write a formal “experimental”; instead, do the following:

Draw the reaction of cyclopentadiene with maleic anhydride. Draw the six-membered ring as a regular hexagon and indicate the relationship between the bridging “CH\(_2\)” and the anhydride substituent using wedge (\(\text{—}\)) and dashed (\(\cdots\)) bonds where appropriate. Determine the limiting reagent for the reaction (show all data and calculations).

List the mass of the product, determine the percent yield (show all data and calculations), and list the melting point of your product.

Include copies of your IR data to support the identification of the molecule as cis-5-norbornene-endo-2,3-dicarboxylic anhydride.

Also complete the following.

Draw the reactions referenced in parts 2 and 3 of the “Modeling” section—remember to use wedge (\(\text{—}\)) and dashed (\(\cdots\)) bonds where appropriate. Draw the six-membered rings as a regular hexagon.

Draw the intermediate referenced in part 6 of the “Modeling” section, and answer the question posed in part 7. Remember to explain your conclusion regarding the stereochemical outcome of this modified reaction.

Draw the reaction referenced in parts 9 and 10 of the “Modeling” section. Do not worry about drawing the stereochemical outcome using wedge (\(\text{—}\)) and dashed (\(\cdots\)) bonds.

Include your response to part 11 as part of your report.

\(^1\text{cis-cis} \) dienes are not particularly good reactants for Diels-Alder reactions due to steric constraints.


\(^3\) The obvious implication from the arrows drawn in step 2 is that the electrons are flowing in a counter-clockwise direction. That is not the case as the HOMO-LUMO overlap that allows for the electron transfer occurs at both ends of the diene simultaneously.