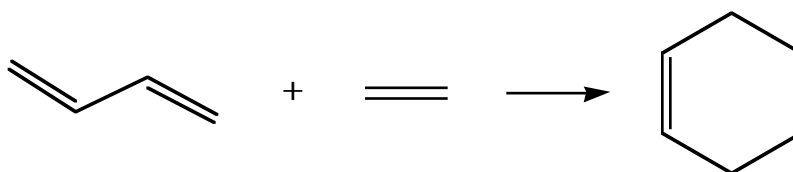
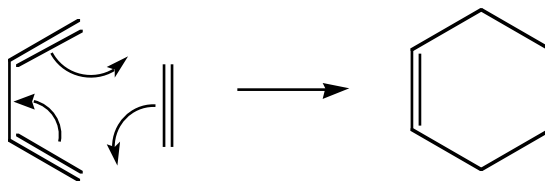


Experiment 13: The Diels-Alder Reaction of a Conjugated Diene in Eucalyptus Oil

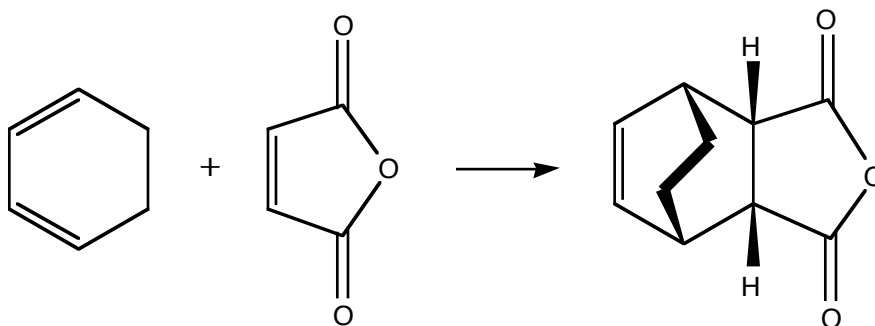
The Diels-Alder reaction is one of the most powerful tools used in the preparation of important organic molecules. When two carbon-carbon double bonds are positioned next to one another, a *conjugated diene* is formed. A non-conjugated diene is a molecule that has two olefins which are not next to each other. Conjugated dienes undergo a cycloaddition reaction with certain double bonds to afford cyclohexenes and related compounds. This reaction is named for Otto Diels and Kurt Alder, who received the 1950 Nobel prize for discovering this useful transformation. The simplest Diels-Alder reaction is between 1,3-butadiene and ethylene:



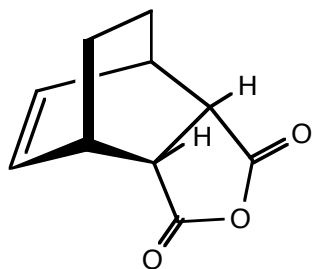
The mechanism of the reaction begins with the diene assuming the higher energy, but more reactive, *cis* conformation. As the diene and the *dienophile* (the mono-ene component) approach each other, the two terminal carbons of the diene meet the two carbons of the dienophile:



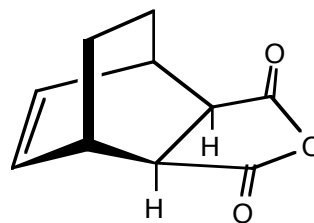
The Diels-Alder reaction is facilitated by the presence of electron donating groups on the diene and by the presence of electron withdrawing groups on the dienophile. For instance, maleic anhydride is a very good dienophile because it contains two highly electron withdrawing carbonyl groups. In fact, maleic anhydride was one of the original dienophiles that Diels and Alder used in their studies. It will react with a variety of dienes to afford the corresponding cyclohexene system. The reaction of maleic anhydride and cyclohexadiene is shown as an example:



This example illustrates what is known as the *Endo Rule*. The addition of maleic anhydride to a diene yields entirely the *endo* product in which the bulkier parts of the dienophile are closer to the carbon-carbon double bond.

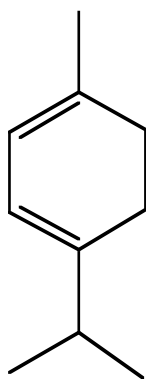


ENDO (favored)

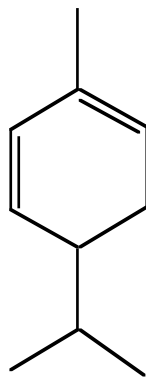


EXO (disfavored)

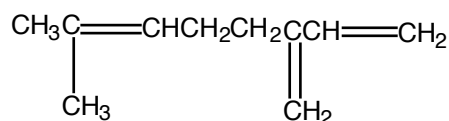
Dienes and trienes occur in the essential oils of a number of plants and contribute to their flavors and aromas. You will separate the conjugated diene that is present in eucalyptus oil by reacting it with maleic anhydride. The unknown diene will be one of the four conjugated dienes shown below:



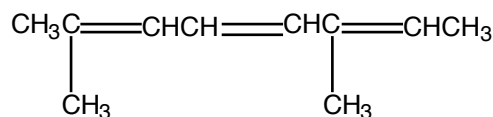
α -terpinene
M.P. Diels-Alder
product: 60-61°



α -phellandrene
M.P. Diels-Alder
product: 126-127°



β -myrcene
M.P. Diels-Alder
product: 33-34°



allo-ocimene
M.P. Diels-Alder
product: 83-84°

In order to determine the amount of maleic anhydride that will be necessary to react with all of the conjugated diene present, you will estimate the percentage of diene found in eucalyptus oil using the gas chromatogram on [Fig. 1, Expt. 13](#). Since both maleic anhydride and the product of the Diels-Alder reaction can be hydrolyzed by water, it is important to use dry glassware and to exclude moisture during the reaction and the work-up.

The melting point of the product will reveal the identity of the conjugated diene present in the oil. In addition, you will characterize the product by obtaining an infrared spectrum. Read pp 311-344 in *LTOC*, and study Figure 21.14 on p. 326 and Table 21.2 on p. 328. You will obtain a spectrum of your solid product as a cast-film, so read page 321 carefully. You will compare your spectrum to that of maleic anhydride itself, shown on [Fig. 2, Expt. 13](#).

Pre-lab Assignment (you must complete the following calculation and hand it to your TA before beginning the experiment)

Estimate the mass of the unknown diene present in 2.5 g of eucalyptus oil using the GC trace that is found on [Fig. 1, Expt. 13](#). Assume that the unknown conjugated diene corresponds to the largest peak on the chromatogram and that the peak areas are

proportional to the component masses. Calculate the mass of maleic anhydride needed to react with that much diene.

Outline the steps of the following procedure:

Measure 3 mL (approximately 2.5 g) of eucalyptus oil in a graduated cylinder, and pour it into a *tared* 25 mL round bottom flask. Record the exact mass of the oil in your notebook. Dissolve the eucalyptus oil in 5 mL of anhydrous diethyl ether, and then add the amount of maleic anhydride that you calculated above.

Caution: Diethyl ether is highly flammable! Maleic anhydride is corrosive and toxic.

Attach a condenser to the round bottom flask. Be sure the connection is tight. Gently reflux the mixture over *low* steam for 45 minutes (review section 7.1, pp 87-89, in *LTOC*). While it is warm, transfer the reaction mixture to a small beaker, cover with a watchglass, and let cool to room temperature. Cool it further on ice before collecting the crystals by vacuum filtration. Wash the crystals with 5 mL of **cold petroleum** ether.

Recrystallize the Diels-Alder product from methanol. Heat the methanol on a steam bath. **Important!** Methanol can cause the product to undergo solvolysis, so it is important that you avoid prolonged boiling during recrystallization. Measure the melting point of the product so that you can identify which of the four possible dienes is present in eucalyptus oil. Leave the solid in your drawer until next week and re-measure the melting point when it is dry. Weigh the dry product next week.

Place a spatula-tip amount of your product in a small test tube. Add a minimum number of drops of dichloromethane, CH_2Cl_2 , and stir to dissolve the solid.

Caution: Dichloromethane is toxic and a suspected carcinogen. Wear gloves when handling this chemical.

If some solid does not dissolve after 10-15 drops have been added, allow it to settle to the bottom of the test tube.

Avoid touching the flat surface of the salt plate with your bare fingers, as moisture will etch the plate. Draw out a small portion of your product solution with a Pasteur pipet, and place three drops on a salt plate. As the solvent evaporates, move the plate so that a thin, even film of the solid compound is deposited on the surface. Rest the plate in the plastic holder found inside the instrument. Your TA will assist you in using the FT-IR spectrometer.

After you have obtained the spectrum, clean the plate by rinsing it with CH_2Cl_2 and drying with a Kimwipe. Place all waste solvent in the appropriate **Byproducts** jar. ***Never rinse a salt plate with water or even with acetone, which may contain enough water to damage it.***

Use the Spartan program along with the instructions on the next page to watch the bending and stretching of bonds and their corresponding frequencies in the infrared.

The frequency of the absorption bands in infrared spectra can be correlated with the energies required to stretch and bend the covalent bonds in a molecule. When a bond stretches, the distance between the two atoms increases and decreases. When a bond bends, the positions of atoms change relative to the bond axis. Today, you will use the Spartan program to observe the bending and stretching of the bonds in **maleic anhydride** and correlate these movements with their frequencies. (Review Chapter 8 in *LTOC*.)

Instructions for finding the vibrational frequencies for **maleic anhydride**

Before building a molecule, close any previously built molecules by pulling down the **File** menu and choosing **Close** followed by **Do Not Save**.

1. Pull down the File menu and select **New Build**. The Organic Model Kit will appear.
2. Click on the sp^2 hybridized carbon.
3. Click in the middle of the Spartan screen. The atom should appear. Place the cursor near the atom and move to rotate so you can see the double bond.
4. To continue to build the molecule, click at the end of the double bond, and a new carbon should appear.
5. Now click on one of the single bonds and yet another sp^2 hybridized carbon will appear.
6. Click on the single bond of the other carbon to make another sp^2 hybridized carbon.
7. In the atom grid, click on the sp^2 hybridized oxygen.
8. Click at the end of one of the carbon double bonds.
9. Repeat steps 7 and 8 so the other terminal carbon has a double bonded oxygen attached to it.
10. In the atom grid, click on the sp^3 hybridized oxygen.
11. Click on the single bond of one of the terminal carbons.
12. Under the menu **Build**, choose **Make bond**,
13. Click on the yellow bond of the sp^3 oxygen and then click on the yellow bond of the terminal carbon. A bond should appear.
14. Under the Build menu, choose **Minimize**.
15. Under the Build menu, choose **View**.
16. Under the Setup menu, choose **Calculations...** In the dialog box that appears, select **Equilibrium Geometry** with **Hartree-Fock/3-21G**. The Total Charge should be **Neutral**. *Click to put a check in the box next to the words **Infrared Spectra***. Click on **Submit**.
17. A Save dialog box appears. If necessary, give the molecule a name, then click on **Save**.
18. A dialog box will tell you that the calculation has begun. Click on **OK**.
19. It may take a few minutes for the calculation to be completed, depending on the complexity of the molecule. A dialog box will appear telling you when the calculation is finished. *Do not continue on to the next step until this box has appeared!*
20. When the calculation is complete, click on **OK**.
21. Under the Display menu, select **Spectra**. Click on the green plus sign (+). In the window that appears, click on IR Calculated. Click on the (i) in a brown circle (at the left of the screen). A box appears that lists several vibrational frequencies for maleic anhydride. Place a check mark in a box next to a frequency. You can do this with all the frequencies individually and watch the bonds vibrate. You may want to rotate or enlarge the molecule (enlarge using the scroll wheel).
22. You should record any frequencies associated with the carbon-oxygen double bonds.

Name _____ Date _____

T. A. _____ Lab period _____

Results and Calculations (to be handed in two days after the next lab period along with the discussion)

Calculate the percent yield of the Diels-Alder product based on the mass of maleic anhydride used.

Melting range for the Diels-Alder product _____

Attach your IR spectrum.

Identity of the diene found in eucalyptus oil _____