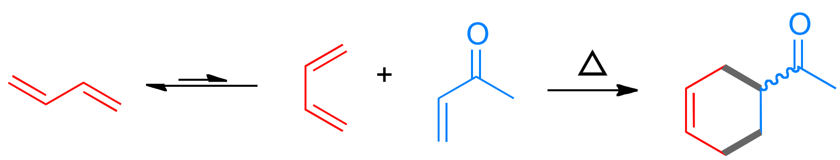
Experiment 5
The Diels-Alder Reaction[1]

Chemistry 251
Fall 2012

Background

The Diels-Alder reaction involves the reaction of a conjugated diene with an activated alkene (also known as the *dienophile*). The product of the reaction is a cyclohexene derivative as shown (Scheme 1). The remarkable feature of this reaction is that it does not require any acid, base or other mediating reagent—you get the product if you mix the two components and heat them! The Diels-Alder reaction is one of a class of reactions known as pericyclic reactions. Of note, it warranted the Nobel Prize in Chemistry in 1950!



Scheme 1. Example Diels-Alder cyclization. Notice two new C—C bonds have formed.

There is one practical problem with the reaction in Scheme 1; 1,3-butadiene is a gas and difficult to work with in a reaction. To get around this issue, we will generate the diene in situ by heating butadiene sulfone, which will release 1,3-butadiene in a retro-cycloaddition. Once generated, the diene reacts rapidly with the dienophile to form the cyclohexene adduct. You will then hydrolyze the initial product, opening up the anhydride to produce a dicarboxylic acid as your final product.

Perform the reaction according to the following procedure. Scheme 2 shows the Diels-Alder reaction for today.

SAFETY PRECAUTIONS: *Butadiene sulfone and maleic anhydride can irritate your skin. Wear gloves.* SO_2 *gas is corrosive and toxic if inhaled. Be sure that your gas trap is in place before you begin to heat and heat slowly!*

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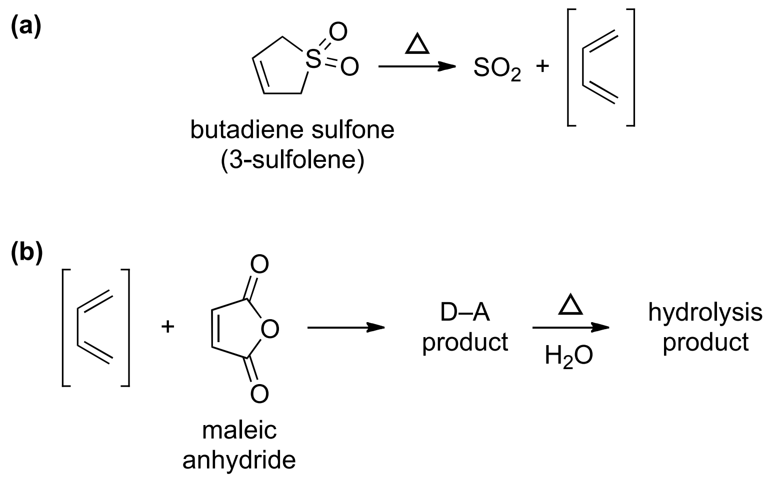
[1]adapted from Mohrig, J. R.; Morrill, T. C.; Hammond, C. N.: Neckers, D. C. *Experimental Organic Chemistry: Flexible Connector Version*; Freeman and Co.; New York: 1999; Experiment 16.



Scheme 2. (a) Generation of the diene *in situ*. (b) reaction of the diene and the dienophile (maleic anhydride) followed by hydrolysis of the diene product.

Experimental Procedure

Prepare a gas trap using a drying tube filled with sodium (or potassium) hydroxide pellets (use cotton or glass wool to plug both ends). Combine 8.5 mmol of butadiene sulfone with 6.0 mmol of maleic anhydride in 0.5 mL of xylenes in a 25-mL (or smaller) round bottom flask. Add a boiling chip. Clamp the flask and add the reflux condenser. In the top of the condenser, insert your thermometer adapter with the drying tube (see Figure 1 below).

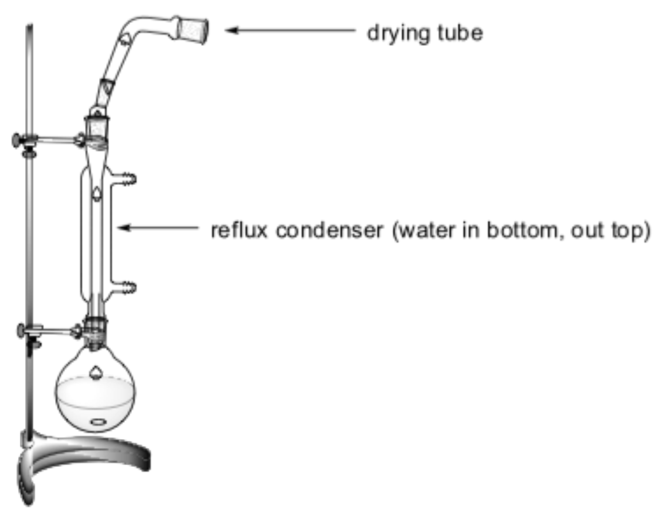


Figure 1. Approximate depiction of apparatus used for this experiment. The heating source is not shown. Our drying tubes will be different than that shown in this diagram.

Begin heating the mixture with a sand bath. After all of the solids have dissolved, heat the mixture at a gentle reflux (do not let the vapors climb more than 1/3 the height of the condenser) for 30 min. Remove the heat and allow the mixture to cool for 10 min.

Remove the thermometer adapter and drying tube (keep in the hood). Pour 4 mL of water down the condenser into the flask, and add another boiling stone. Continue to

heat the resulting mixture under reflux for an additional 30 minutes. Cool the solution to room temperature. Collect the product by vacuum filtration. Wash the crystals twice with 1 mL portions of ice water (while on the funnel). Allow the product to dry overnight.
Record the mass of product and calculate the percent yield. Record the melting point of the product. Make a sample for ^{1}H NMR analysis.

Clean Up/Waste Disposal

Place the waste organic liquids in the non-halogenated waste container.

Prelab Questions.

Answer these in your notebook along with the usual notebook prep. (See page 10 of course syllabus for notebook prep details.)

1. As part of the data table, convert the stated mmol amounts of your reagents into grams. How many grams of final product are expected for the theoretical (100%) yield?
2. Why are xylenes used as the solvent in this reaction?
3. Why is it essential that the gas trap be attached prior to heating the reaction?

Postlab Questions. **Due at next week's lab!**

1. Make a copy to hand in, and then paste, staple, or tape your NMR data in your notebook. Be sure to have all peaks labeled.
2. What is the product of your reaction? Draw its structure. Explain how you determined its identity.
3. Write a mechanism using electron pushing arrows that explains how your product formed.
4. What was the percent yield of your reaction? Show your calculations.
5. Include a summary where you discuss your technique, the purity of your product, and the overall results.