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Chemistry 502

Experiment #4, Diels-Alder Reaction

Experimental Organic Chemistry: A Miniscale and Microscale approach by Gilbert and Martin, Section 12.1-12.3

7-24-06

TA: Mike and Carolyn

INTRODUCTION:

The Diels-Alder reaction has been on of the most important reactions in chemistry. Thousands of scientific papers have referenced the Diels-Alder reaction and the chemistry is highly important to understanding the formation of rings. The purpose of this lab is to demonstrate the formation of six-membered ring s by a cyclo addition reaction. 3-sulfolene will be heated to produce 1,3-butadiene and SO_2 gas. The 1,3-butadiene will be reacted with maleic anhydride to produce 4-cyclohexene-cis-1,2-dicarboxylic anhydride. The anhydride will be hydrated to produce the diacid. A % yield will be determined on the diacid and a melting point will be used to determine the purity of both the anhydride and the diacid. Finally, Bromine and Baeyer test will be used to determine whether each product will be unsaturated.

PROCEDURE

- Set up the apparatus: 25-mL round bottom flask, gas trap, apparatus for heating under reflux, magnetic stiring, vacuum filtration, and flameless heating.
- Place 2.5 g of 3-sulfolene, 1.5 g. of finely pulverized maleic anhydride, and 1-mL of dry xylene in the flask. (use small stirbar) (confirm weights of reactants.)
- Maleic anhydride causes burns. Avoid contact
- Attach apparatus to a water trap like Experiment #3. The sulfolene decomposes to form butadiene and sulfur dioxide. Butadiene will react with maleic anhydride and the sulfur dioxide will bubble out of solution.
- Be sure the glass tube does not go below the water.
- Make sure the 3-sulfulene and maleic anhydride are completely dissolved in xylene (gentle warming) before you bring the mixture to a reflux.
- Avoid heating vigorously so that the butadiene doesn't distill out of the reaction but heat so all the sulfolene decomposes to butadiene and sulfur dioxide.
- Heat the reaction to moderate to strong reflux for 30 min after all the solid starting material has dissolved.
- After diluting the hot mixture with 10-mL xylene (let the reaction mixture cool very briefly before adding the extra xylene just to make sure that the temp is not above the boiling point of xylene), the reaction mixture should be heated and stirred using the thermowell heater and the magnetic stirrer to make sure all materials in solution, transfer the hot solution to a small Erlenmeyer flask.
- Crystals may begin to form before the addition of petroleum ether. Add ~5mL of petroleum ether to ensure good recovery of product. (Anhydride is soluble in xylene but quite insoluble in peteroleum ether) Cool flask in ice bath before collecting the crystals

on a buchner funnel. Flask and crystals may be washed with small amount of cold petroleum ether.

- Record the m.p. of crystals (anhydride) after it has been dried completely (m.p. of 4-cyclo-cis-1,2-dicarboxylic anhydride is 103-104ºC.

- In the hood…
- Test anhydride for unsaturation by carrying out Bromine Test
    - Dissolve small portion or your crystals (0.05 g) in dichloromethane (10 drops)
    - Warm if necessary and stir for a few minutes
    - If the solid persists, transfer solution to test tube with pipet.
    - Add 0.1 M bromine dropwise until a light orange color just persists
    - Rapid disappearance of the bromine color to give a colorless solution is a positive test for unsaturation.

- In the hood…
- Test Anhydride for unsaturation by carrying out Bayer Test
    - Dissolve 1-2 drops of anhydride in 95% ethanol
    - Add 0.1 M $KMnO_4$ (a few drops)-count the number of drops
    - If heavy brown precipitate (MnO2) form, there is a positive test for unsaturation.
    - For a blank determination, count the # of drops that can be added to 2-mL of 95% ethanol before the color persists.
    - A significant difference in the number of drops required in the 2 cases is a positive test for unsaturation

- Be sure you have enough anhydride to complete…
    - Unsaturation tests
    - Careful melting point
    - A sample to hand into your T.A. with the Lab Report.

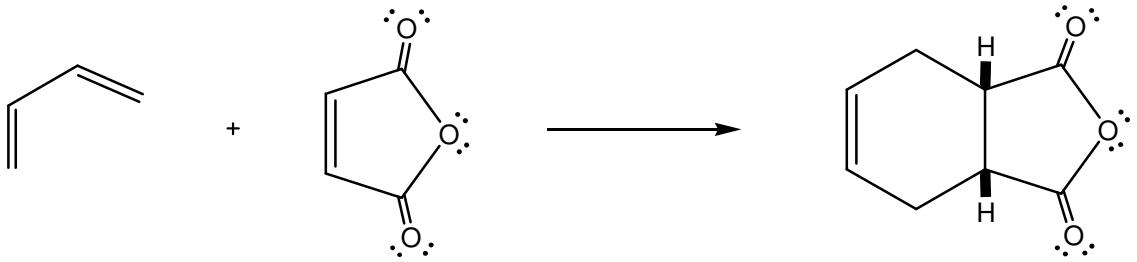
Hydrolysis

- Set up a hot plate as the heat source. Set up an ice-water bath, and apparatus for vacuum filtration and flameless heating.
- Place 1.0 g of anhydride from the previous experiment and 5 mL (or an appropriate amount) in a 25-mL Erlenmeyer flask and add a boiling stone.
- Heat the mixture until it boils and all the oil that forms initially dissolves. Allow the solution to cool to room temperature and then induce crystallization by scratching the flask at the air-liquid interface. After crystallization begins, cool the flask in an ice-water bath to complete the process, collect the solid by vacuum filtration, and air-dry it. Recyrstallize the diacid from water.
- When the sample is completely dry (until next lab period), determine the yield and melting point, test it for unsaturation, and set aside a small sample to hand in with your Lab Report #4. The reported melting point of the unsaturated diacid is 164-166ºC.

Clean up

- The unsaturation test wastes should be discarded in the specially marked waste container in the reagent hood.
- The organic filtrate should be discarded in the Organic Waste container.
- The aqueous filtrates can be washed down the drain.

REACTION AND MECHNAISM



The main reaction above is the 1,3-butadiene with the addition of maleic anhydride. The solvent is xylene. The result is 4-cyclo-cis-1,2-dicarboxylic anhydride. The other side reactions are listed below in the "Side Reactions section"

TABLE 1: REACTANTS

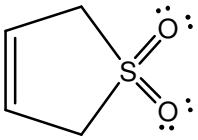
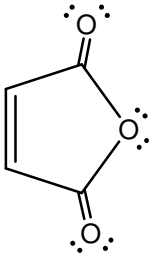
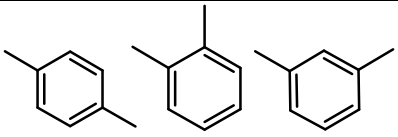
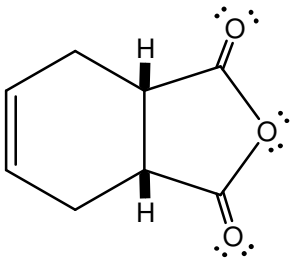
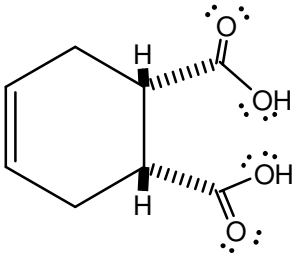
Compound Number	Compound	Amt used/required (g)	Molecular Weight (g/mol)	Physical Properties
1	 3-sulfolene	2.50	118.1502	Denstiy: 1.134 g/mL White or pale yellow crystal Solubility: 5-10 g/100 mL at 16 C
2	 Maleic anhydride	1.50	98.058	Denstiy: 1.314 g/mL Colorless or white solid with a penetrating odor. MOISTURE SENSITIVE. Solubility: SOLUBLE; DECOMPOSES IN HOT SOLVENT
3	 xylene (ortha, meta, and para forms shown)	1-mL	318.501	Density: 0.862 g/mL Colorless liquid with aromatic odors Solubility: Insoluble. 0.0175 g/100 mL

TABLE 2: PRODUCTS

Compound Number	Compound	Theoretical Yield (g)	Molecular Weight (g/mol)	Physical Properties
4	 4-cyclo-cis-1,2-dicarboxylic anhydride	2.31	152.08	m.p. 103-104 ° C
5	 4-cyclo-cis-1,2-dicarboxylic acid	1.12	170.1	m.p. 164-168 ºC White granular

YIELD DATA: Theoretical and Observed

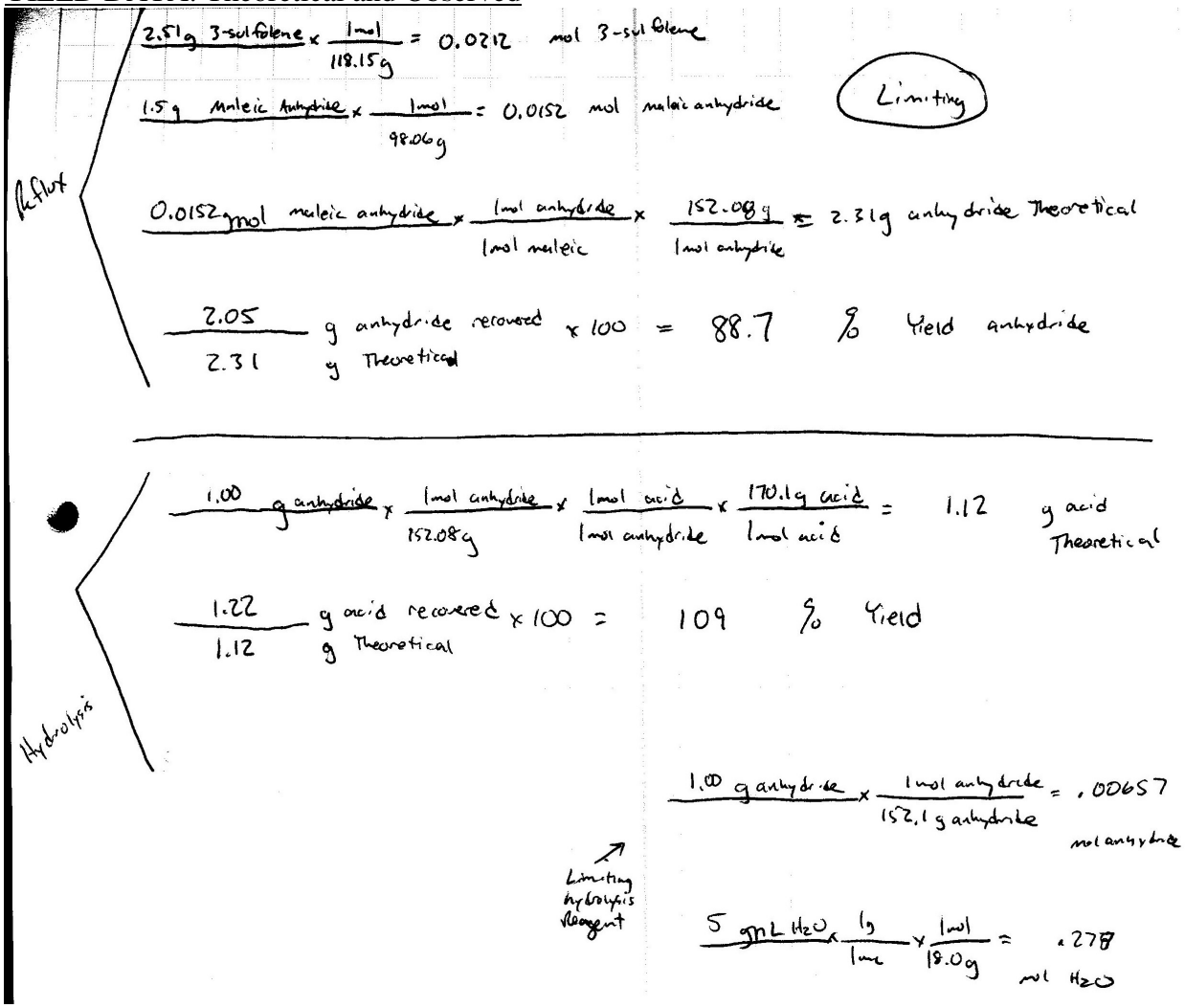


TABLE 3: % Yield from Anhydride

Compound	Theoretical	Observed	% Yield
Anhydride	2.05 g	2.31g	88.7 %

The % Yield from the initial reaction of 3-sulfolene and maleic anhydride was 88.7%. This was a fairly good yield of products. The reaction was put through reflux for approximately 1 hour, but only 25 minutes of the hour was a constant dripping from the reflux. One would assume that longer reflux would have yielded a greater product.

TABLE 4: % Yield from Diacid

Compound	Theoretical	Observed	% Yield
Diacid	1.22 g	1.12g	108.9 %

Due to time constraints the semi-wet product was weighed with the filter paper to determine the % yield. Residual water appeared to have contributed to the % yield being over 100%.

TABLE 5: Weight Results from Reaction

Anhydride Weight (g)		Diacid Weight (g)	
Product, Watch-glass, and filter paper	56.90	Product, Watch-glass, and filter paper	56.05
Watch-glass and filter paper	54.85	Watch-glass and filter paper	54.83
Product	2.05	Product	1.22

Table 5 shows the weight recovered for both parts of the experiment. The anhydride was a pale-yellow-white crystalline splinters. The diacid recovered was a white granular powder.

TABLE 6: Melting Points Results from Reaction

	Anhydride (ºC)	Diacid (ºC)
Melting Point (experimental)	99.5-100.1	162.4-163.8
Melting Point in Literature	103-104	164-166

Table 6 shows the melting point for each of the separate experiments. Each melting point determined experimentally was fairly close to the literature values. The purity of the anhydride was slightly in question because of the 3 degree difference and its pale-yellow, white color. The purity of the diacid was fairly good.

TABLE 7: Unsaturated Test Results from Reaction

	Anhydride	Diacid
Bromine Test	Positive	Positive
Baeyer Test	Positive	Positive

Table 7 shows that all tests for unsaturation were positive. Some of the solutions had to be warmed to promote dissolving. The bromine test yielded an orange color and then a clear solution again. The Baeyer test yielded a brown precipitate in each instance.

SYNOPSIS OF AND NOTES ON EXPERIMENTAL PROCEDURE-RESULTS

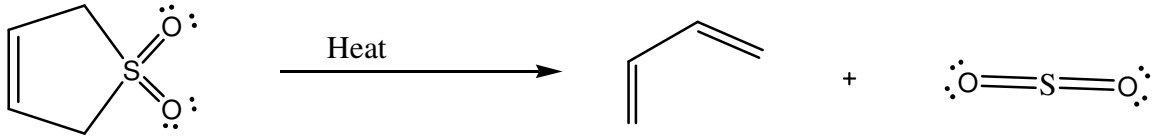
According to the data the anhydride and diacid from the reaction of 3-sulfolene and maleic anhydride produced the correct anhydride product, 4-cyclo-cis-1,2-dicarboxylic anhydride. Refluxing for a full 30 minutes with constant dripping from the condenser produced a 88.7% yield. This proved very effective. In addition, complete drying of the product was difficult because of the need to weight the first product and use the anhydride for the second reaction to produce the diacid. Both products were proven to be the correct compound by using melting point determination and the two tests for unsaturation.

OBSERVED PHYSICAL PROPERITES OF THE PRODUCTS OBTAINED

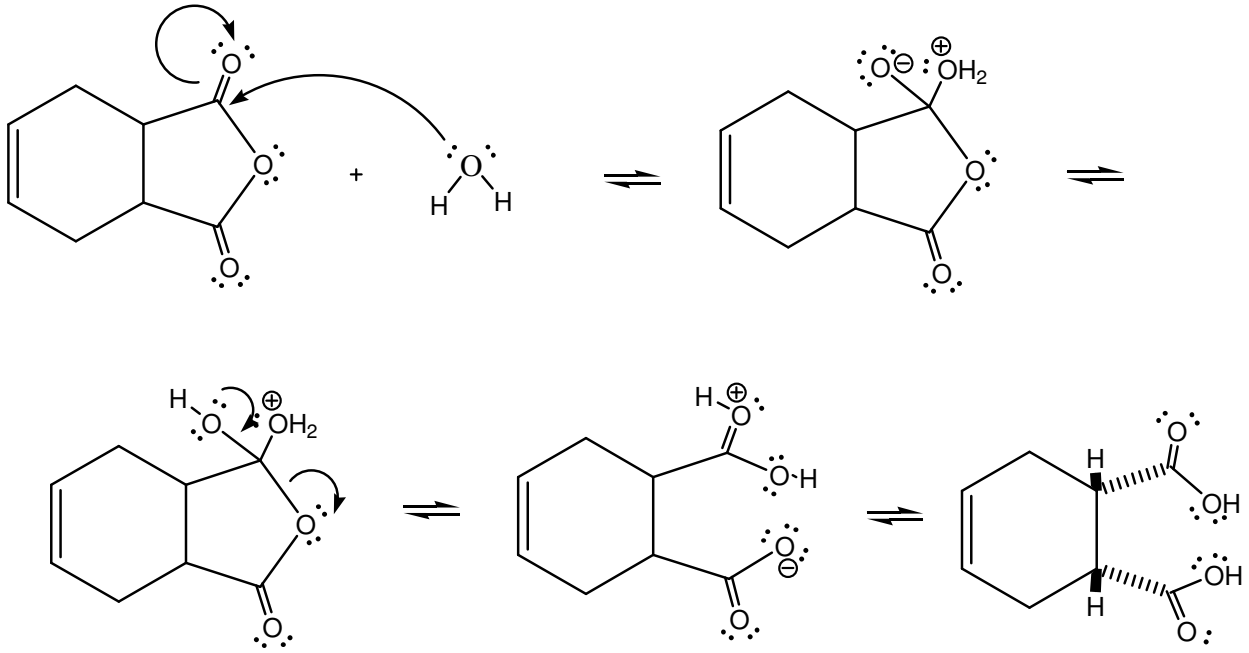
After the 3-sulfolene (which turned into 1,3-butadiene) and maleic anhydride was refluxed for 30 minutes, the anhydride product was a pale-yellow-white crystalline splinters.

0.05 g of the anhydride was reacted with 5 mL of water and the diacid recovered was a white granular powder.

SIGNIFICANT SIDE REACTIONS



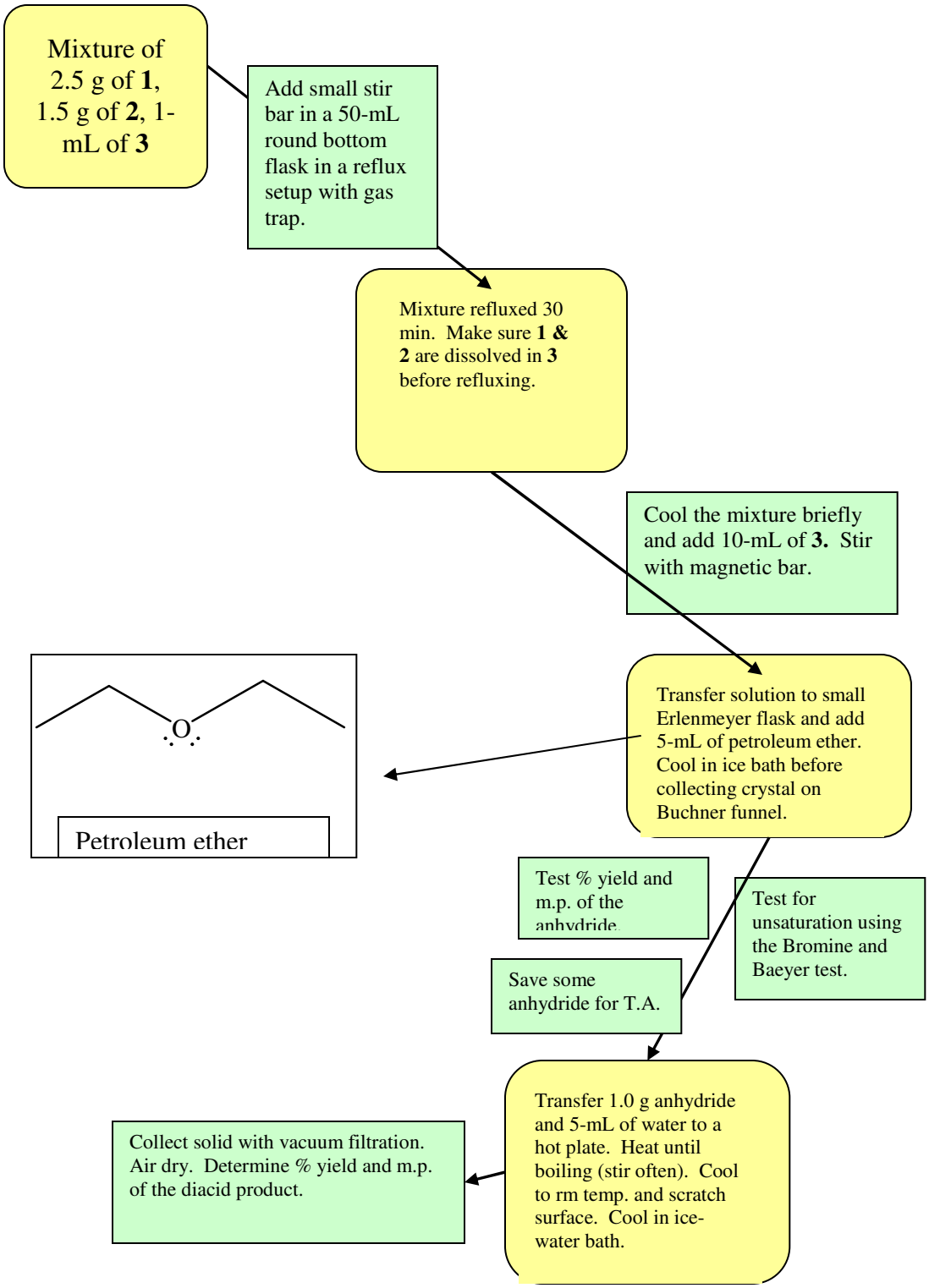
Because 1,3-butadiene does not exist naturally due to its low reactivity, it was created by taking 3-sulfulene and heating it to "crack" the cyclic ring and produce our desirable reactant needed in this experiment.



The anhydride was hydrolyzed as shown above. After the addition of water and the subsequent movement of electrons, 4-cyclo-cis-1,2-dicarboxylic anhydride was our final product in which we measured the resulting % yield.

METHOD OF PURIFICATION

Flow Chart of Lab (The numbers in the following flow chart are derived from Table 1: Reagents and Table 2: Products)



CONCLUSIONS

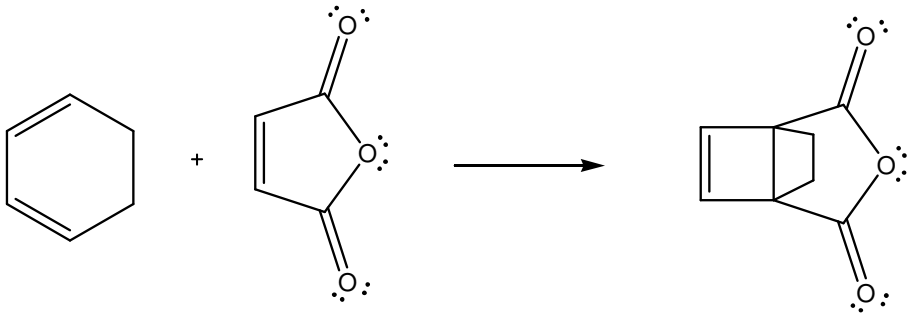
In this experiment, the famous Diels-Alder reaction was performed. Because the reaction mechanism was concerted, there was an excellent yield of products and no intermediates. An

electron poor Lewis acid, maleic anhydride, was reacted with an electron rich Lewis base, 1,3-butadiene. After refluxing the mixture the anhydride, 4-cyclo-cis-1,2-dicarboxylic anhydride, was recovered using vacuum filtration. The only improvement that could be made to the first part of the experiment is to dry the product for 10-15 minutes in a low temperature drying oven. Then the % yield would have been more accurate. The second part of the lab involved hydrating the anhydride. The solid crystals were again collected using vacuum filtration. The diacid product, 4-cyclo-cis-1,2-dicarboxylic acid, was also wet from the filtration. I wish that I would have dried the product more effectively to prevent the percent yield being over 100%. Overall the addition of reactants to make a ring proved effective using the Diels-Alder reaction.

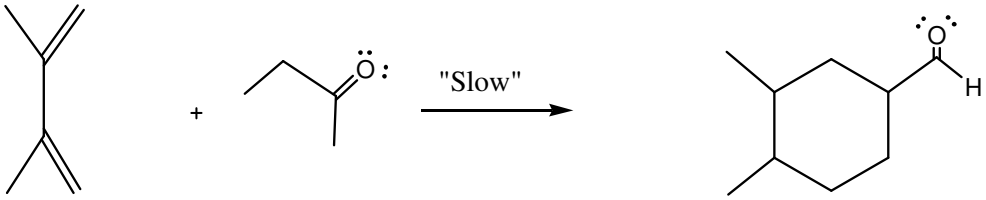
ANSWERS TO ASSIGNED QUESTIONS

2. *What structures for the products are expected in the following possible Diels-Alder reactions. If no reaction is anticipated, write "N.R."*

a.



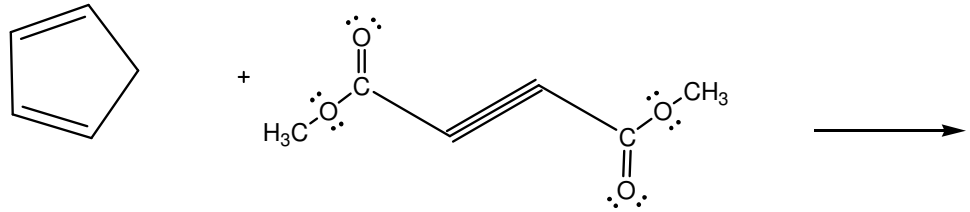
b.

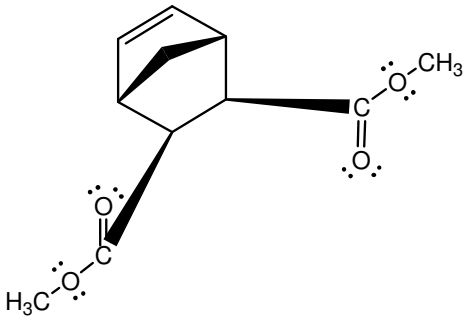


c.

No Reaction. No reactive carbonyl group present.

d.





5. *Why should 3-sulfolene and maleic anhydride be completely dissolved in xylene before heating the mixture to effect reaction?*
    - 3-sulfolene and maleic anhydride should be completely dissolved in xylene because if it is not we will loose product. If 3-sulfolene is not dissolved, it will boil out of our reaction flask and we will not get our desired product. By

dissolving the 3-sulfolene and then successively heating it, it is able to be "cracked" to 1,3-butadiene. Then we have 1,3-butadiene to react with maleic anhydride. If the 3-sulfolene is lost initially, we have nothing to react with maleic anhydride.

6. *Write the structure, including stereochemistry, of the expected addition product of bromine to the Diels-Alder adduct obtained by this procedure.*