

**The Diels-Alder Reaction of Anthracene with Maleic Anhydride
Microscale Diels-Alder Reaction**

Leah Monroe

March 6, 2003

Organic Chemistry Lab II

Experiment performed on February 25 and 27, 2003

Abstract:

This experiment involved a reaction between anthracene and maleic anhydride via a Diels Alder reaction to yield 9, 10-dihydroanthracene-9,10- α , β -succinic anhydride. Anthracene was the diene and maleic anhydride was the dienophile. The percent yield of the crude product was 69.03%. Following recrystallization of the product using xylene and vacuum filtration, a percent yield of 37.42% for the recrystallized product was collected. This was low due to the fact that some of the crude product was not recrystallized and was instead used to take a melting point of the crude product. It was also low due to several of the crystals being stuck inside the flask and not going into the funnel. The percent recovery from recrystallization was 54.21%. The melting point of the crude product was 261 - 264°C. The melting point of the recrystallized product was 261 - 263°C. Comparing these values with the literature melting point of 262 - 264°C shows that the product was indeed 9, 10-dihydroanthracene-9, 10- α , β -succinic anhydride and that recrystallization yielded a purer product. Upon examination of an infrared spectrum of the product and comparison with anthracene and maleic anhydride spectra, it was found that the product spectrum had similarities with both the anthracene spectrum and the maleic anhydride spectrum. This indicated that the product was an adduct of both anthracene and maleic anhydride, and thus that the experiment was successful.

Introduction: The purpose of this experiment is to form 9, 10-dihydroanthracene-9,10- α , β -succinic anhydride by way of a Diels Alder reaction between anthracene and maleic anhydride. Anthracene acts as the diene and maleic anhydride functions as the dienophile. Following the reaction, the crude product will be recrystallized. Melting points of both the crude product and recrystallized product will be taken and compared with the literature value. Also, an infrared spectrum of the recrystallized product will be taken. Both melting points and the infrared spectrum will be used to characterize the product.

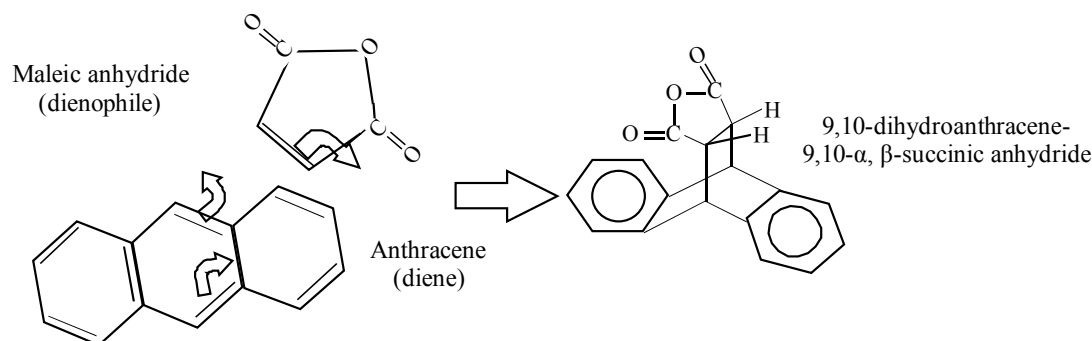
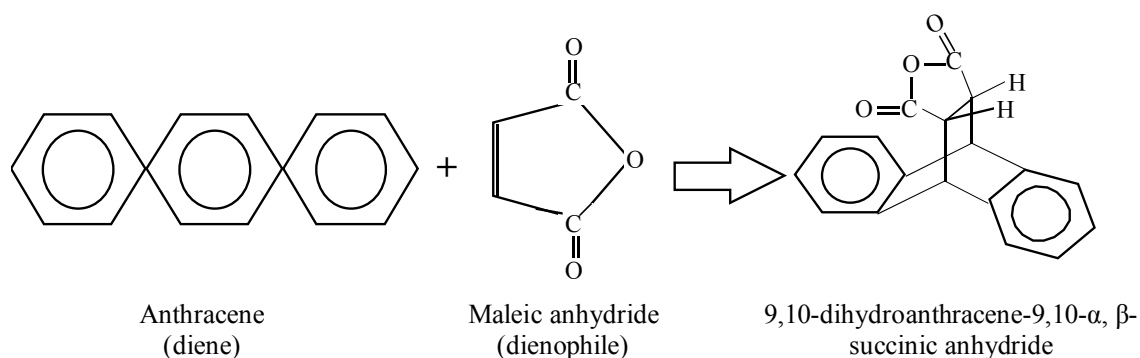
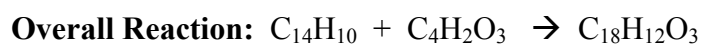
Materials Used:

150-mL beaker	Hirsch funnel, with adapter
boiling chip	2 melting point capillary tubes
Condenser, with tubing	Pasteur pipet, with latex bulb
5-mL conical vial	microspatula
2 Erlenmeyer flasks, 10-mL	1-mL pipet
25-mL filter flask, with vacuum tubing	sand bath
filter paper	support stand
glass stirring rod	13 x 100-mm test tube
thermometer, -10 to 260°C	

Reagents and Properties:

Substances	Formula Weight g/mol	Quantity	Moles Used	Mole Ratio	Melting Point °C	Boiling Point °C
anthracene	178.23	100 mg	5.611×10^{-4}	1 to 1	216 – 218	N/A
9,10-dihydroanthracene-9, 10- α , β -succinic anhydride	276.29	product	N/A	1 to 1	262 – 264	N/A
maleic anhydride	98.06	55 mg	5.609×10^{-4}	1 to 1	54 – 56	N/A
potassium bromide	119.01	100 mg	8.4×10^{-4}	N/A	N/A	N/A
xylene	106.17	6 mL	N/A	N/A	N/A	137 – 144

Reaction and its Mechanism:



Procedure:**Part 1 – Reacting Anthracene with Maleic Anhydride**

Tare a 5-mL conical vial (or 10x 100-mm reaction tube) and record the mass. Weigh 100 mg of anthracene and 55 mg maleic anhydride and place them in the vial or reaction tube. Add 1.0 mL of xylene and a boiling chip. Fit the vial or tube with a condenser, as shown in Figure 3 on page 79 of Chemistry Lab Experiments. Turn on the water to the condenser or add a wet pipe cleaner around the reaction tube. Use a 200°C sand bath to heat the mixture at reflux for 30 minutes, boiling vigorously to ensure good mixing. Cool the mixture to room temperature and prepare an ice bath using a 150-mL beaker. Then cool the mixture in the ice bath for approximately 5 minutes. At the same time, pour 2 mL xylene into a test tube and chill the xylene in the ice bath. Collect the recrystallized solid by vacuum filtration using a Hirsch funnel and rinse the crystals with 1 mL of ice-cold xylene. Weigh the crude product and set aside a small sample to dry. This sample will later be used to measure the melting point of the crude product.

Part 2 – Purifying the Product

To perform recrystallization, place the product in a 10-mL Erlenmeyer flask. Add 1 – 2 mL of xylene and heat the mixture gently in a sand bath until the xylene boils. Gradually add more xylene until all the product dissolves or until no more appears to be dissolving. Be sure not to exceed 3 mL of total volume xylene. If solid impurities are still present, use a Pasteur pipet to transfer the solution to another 10-mL Erlenmeyer flask. Allow the solution to cool to room temperature and then cool the solution in an ice bath for 5 minutes. If it's necessary, scratch the bottom of the flask with a glass rod to induce crystallization. Collect the crystallized solid by vacuum filtration, using a Hirsch funnel. Rinse the crystals with 1 mL of ice-cold xylene. Spread the product crystals thinly over a clean watch glass and allow them to dry for approximately fifteen minutes. Then weigh the product and record the mass. Place the product in a labeled vial.

Part 3 – Characterizing the Product

Measure the melting points for both the crude product and the recrystallized product. Perform an infrared spectrum on both products. Add 100 mg KBR to approximately 1 mg of the product. Mix the two using a mortar and pestle, being sure to grind the two compounds into a fine powder. Place some of this mixture in a microcup, making sure the surface is smooth. Then place the pellet in the infrared spectrometer and obtain an infrared spectrum of the product. Compare the product spectrum with the spectra of maleic anhydride and anthracene in order to characterize the product.

Part 4 – Clean-Up

Place all materials in their appropriate waste containers.

Data:

Mass of anthracene used: 0.100 g

Mass of maleic anhydride used: 0.054 g

Mass filter paper: 0.014 g

Mass filter paper and crude product: 0.121 g

Mass of crude product: 0.107 g

Mass filter paper: 0.019 g

Mass filter paper and recrystallized product: 0.077 g

Mass of recrystallized product: 0.058 g

Melting point of crude product: 261 - 264°C

Melting point of recrystallized product: 261 - 263°C

Literature value of melting point of DA adduct: 262 - 264°C

Theoretical Yield: 0.155 g DA product

Percent Yield for Crude Compound: 69.03%

Percent Yield of Recrystallized Compound: 37.42%

Percent Recovery from Recrystallization: 54.21%

Calculations:**Finding Limiting Reagent**

$$\begin{array}{l}
 \text{Anthracene} \quad \frac{(100 \text{ mg anthracene})}{(178.23 \text{ mg anthracene})} \times \frac{(1 \text{ mmol anthracene})}{(1 \text{ mmol anthracene})} = 0.5610 \text{ mmol} \\
 \\
 \text{Maleic Anhydride} \quad \frac{(55 \text{ mg MA})}{(98.06 \text{ mg MA})} \times \frac{(1 \text{ mmol MA})}{(1 \text{ mmol MA})} = 0.5608 \text{ mmol}
 \end{array}$$

The limiting reagent for this Diels Alder reaction is maleic anhydride. Although both reagents yield approximately the same amount of product, the maleic anhydride yields just a fraction less product than the anthracene, and therefore maleic anhydride is the limiting reagent.

Theoretical Yield

$$\frac{(55 \text{ mg maleic anhydride})}{(1000 \text{ mg MA})} \times \frac{(1 \text{ g MA})}{(98.06 \text{ g MA})} \times \frac{(1 \text{ mol MA})}{(1 \text{ mol MA})} \times \frac{(1 \text{ mol DA product})}{(1 \text{ mol DA product})} \times (276.29 \text{ g DA product}) = 0.155 \text{ g DA product}$$

Percent Yield

$$\text{For crude product} \quad \frac{(\text{mass of crude product})}{(\text{theoretical yield})} \rightarrow \frac{(0.107 \text{ g crude product})}{(0.155 \text{ g crude product})} \times (100) = 69.03\%$$

$$\text{For recrystallized product} \quad \frac{(\text{mass of recrystallized product})}{(\text{theoretical yield})} \rightarrow \frac{(0.058 \text{ g})}{(0.155 \text{ g})} \times (100) = 37.42\%$$

Percent Recovery from Recrystallization

$$\frac{(\text{mass recrystallized compound})}{(\text{mass crude compound})} \rightarrow \frac{(0.058 \text{ g})}{(0.107 \text{ g})} \times (100) = 54.21\%$$

Observed Properties and IR Data and Interpretation:

Infrared spectra of anthracene and maleic anhydride were obtained from computerized spectrum libraries. They were then compared with the infrared spectrum of the product obtained in the experiment. Upon comparison, it was found that the spectrum of the product had similarities with both the spectrum of anthracene and maleic anhydride, as should be expected since the Diels Alder product is a combination of both anthracene and maleic anhydride.

On the product spectrum, there is small peak around 3600 cm^{-1} . This peak represents an $-\text{OH}$ group and is due to atmospheric H_2O moisture. The peak located at 3073.89 cm^{-1} represents aromatic carbon-hydrogen bonds. The peak at 2969.78 cm^{-1} indicates the presence of alkane carbon-hydrogen bonds. These can be compared with the peaks located at 3047.46 cm^{-1} , 2924.76 cm^{-1} , and 2856.11 cm^{-1} on the anthracene spectrum. The peaks on the anthracene spectrum indicate the presence of aromatic C-H bonds and alkane C-H bonds, and likewise, the two peaks on the product spectrum indicate the same carbon-hydrogen bonds.

The product spectrum also yields two distinctive peaks at 1862.45 cm^{-1} and 1782.73 cm^{-1} . These peaks represent the carbonyl groups of the maleic anhydride, and together indicate anhydride functionality. They can be compared with the peaks located at 1850.43 cm^{-1} and 1778.98 cm^{-1} on the maleic anhydride spectrum.

All of the peaks below 1500 cm^{-1} can not be used to help characterize the product because these peaks are in the fingerprint region and are not helpful in characterizing the product. The other peaks, however, indicate that the product is a Diels Alder product that is a combination of both anthracene and maleic anhydride. Therefore, the experiment was successful and the experiment yielded the expected Diels Alder product.

Results and Conclusions:

The Diels Alder reaction between anthracene and maleic anhydride to form 9, 10-dihydroanthracene-9,10- α , β -succinic anhydride was successful and occurred via the Diels Alder mechanism (see Reaction and its Mechanism section for details). Anthracene served as the diene and maleic anhydride was the dienophile. Maleic anhydride was also the limiting reagent (see calculations section). The percent yield of the crude product was 69.03%. This was low due to some of the crystals remaining inside the original reaction tube. In Part 1 when the crystallized solid was collected by vacuum filtration, some of the crystals remained inside the original reaction tube instead of transferring to the filter. This would have caused some loss of crystals and a subsequent lowering of the percent yield for the crude product.

Following recrystallization of the product, the percent yield of the recrystallized product was 37.42% and the percent recovery was 54.21%. Both of these percentages were low due to a couple factors. First of all, a small unmeasured amount of the crude product was set aside in order to take a melting point of the crude sample. This would have lowered both the percent yield of the recrystallized product and the percent recovery. In addition, many crystals were lost due to them being stuck in the flask. During transfer of the crude product into the 10-mL Erlenmeyer flask for recrystallization, some crystals were probably lost and some more were lost during the filtration because some crystals remained stuck to the inside of the flask, just as they had in Part 1. This would also cause the lowering of both the percent yield for the recrystallized product and the percent recovery.

The melting point of the crude product was 261 - 264°C. The melting point of the recrystallized product was 261 - 263°C compared to the literature value of 262 - 264°C for dihydroanthracene-9,10- α , β -succinic anhydride. The melting point of the crude compound had a broader range of 3°C and was a little bit lower due to impurities in the product. Upon recrystallization of the product, the melting point range narrowed (range of only 2°C instead of 3°C) and was higher, indicating that the recrystallized product was more pure than the crude product. Therefore, recrystallization was successful in purifying the product. In addition, both the melting point of the crude product and that of the recrystallized product were very close to the literature value, indicating that the product obtained was indeed 9, 10-dihydroanthracene-9,10- α , β -succinic anhydride and that the reaction was successful.

Upon examination of the infrared spectrum of the product and comparison with infrared spectra of maleic anhydride and anthracene, it was determined that the product was 9, 10-dihydroanthracene-9,10- α , β -succinic anhydride, as was expected. On the product spectrum, peaks at 3073.89 cm^{-1} represented aromatic carbon-hydrogen bonds and 2969.78 cm^{-1} indicated the presence of alkane carbon-hydrogen bonds. These were comparable to peaks at 3047.46 cm^{-1} , 2924.76 cm^{-1} , and 2856.11 cm^{-1} on the anthracene spectrum. The product spectrum also yielded peaks at 1862.45 cm^{-1} and 1782.73 cm^{-1} . These indicated the presence of carbonyl groups from the maleic anhydride, and together represent anhydride functionality. They are comparable to peaks at 1850.43 cm^{-1} and 1778.98 cm^{-1} on the maleic anhydride spectrum. Therefore, the Diels Alder product spectrum had similarities to both the anthracene spectrum and the maleic anhydride spectrum. This indicates that the product was an adduct of both anthracene and maleic anhydride, and thus that the experiment was successful.

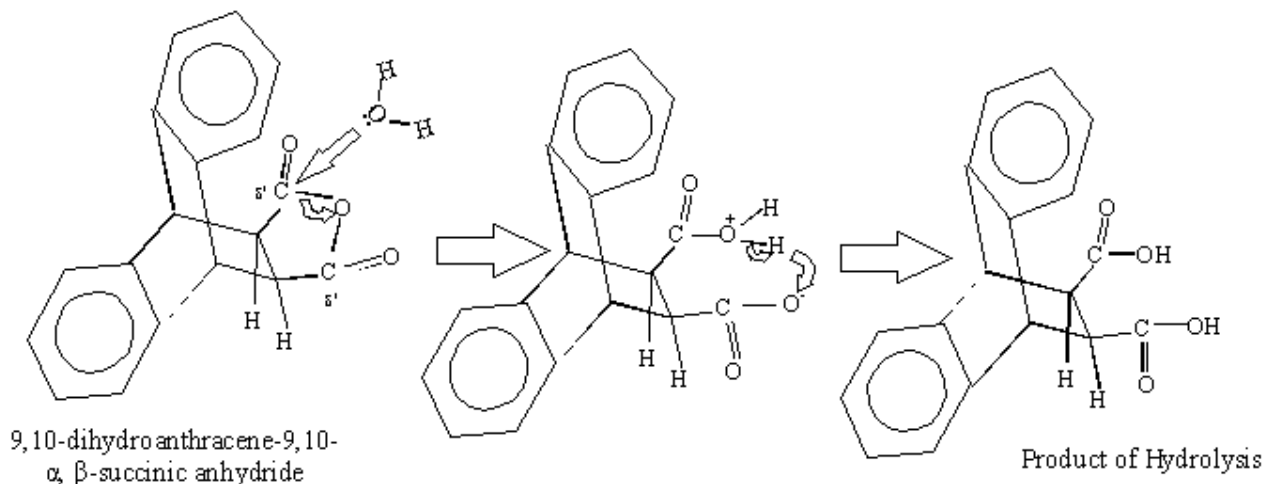
Reference:

Chemistry Lab Experiments CHEM 224 Synt 717 pgs. 73 – 84
By Wigal/Manion/LeFevre/Wade, Jr./Rapp/Lee/Wikholm

Post-Lab Questions

1. The percent yield for the crude product was 69.03%. The percent yield for the recrystallized product was 37.42%. Please see calculations section for the calculations and the Results/Conclusions section for an explanation of the yields, if desired.
2. The percent recovery from recrystallization was 54.21%. Please see calculations section for the calculation and the Results/Conclusions section for an explanation of the low yield, if desired.

3. Hydrolysis of the Product:



The carbons which are attached to the oxygen molecules by a double bond carry a slightly positive charge. Since oxygen is more electronegative than carbon, it pulls the electrons towards it and carbon is left with a slight positive charge. A water molecule with a lone pair of electrons on the oxygen attacks the slightly positive carbon atoms. The water attaches, then loses a proton in order to stabilize the positive charge. Thus, two hydroxide groups are added to the molecule. The mechanism of the reaction and the product of this hydrolysis reaction are both shown above.

4. Recrystallizing an anhydride such as the product from this experiment from water or from an alcohol is rarely a good idea. This is because anhydrides react with water in the air and form a new product. When water or alcohol is around, the lone pair of electrons on the oxygen react with the product and the product undergoes a hydrolysis reaction to form a different product, as shown above in question 3. Thus, the recrystallized product would not be the same product obtained in the Diels Alder reaction between anthracene and maleic anhydride. The product (9, 10-dihydroanthracene-9,10- α , β -succinic anhydride) in the reaction that was performed in this experiment reacts slowly and is easily isolated and characterized before hydrolysis can occur.
5. (a) The carbonyl region of the product IR spectrum yielded peaks at 1862.45 cm^{-1} and 1782.73 cm^{-1} . On the maleic anhydride spectrum, the carbonyl peaks were located at 1850.43 cm^{-1} and 1778.98 cm^{-1} . These are relatively close, and indicate that both the product and the maleic anhydride have carbonyl groups that together have an aldehyde functionality.
- (b) Yes, the product IR spectrum allows me to confirm that the structure of the product is a combination of the reactants anthracene and maleic anhydride. The product spectrum yields peaks at 3073.89 cm^{-1} and 2969.78 cm^{-1} . These indicated the presence of two benzene rings, and were comparable to peaks at 3047.46 cm^{-1} , 2924.76 cm^{-1} , and 2856.11 cm^{-1} on the anthracene spectrum. The product IR spectrum also contained peaks at 1862.45 cm^{-1} and 1782.73 cm^{-1} . These peaks indicated the presence of carbonyl groups, and were comparable to peaks located at 1850.43 cm^{-1} and 1778.98 cm^{-1} on the maleic anhydride spectrum. Because the product spectrum shares similarities with both the maleic anhydride spectrum and the anthracene spectrum, it can be concluded that the product is a combination of the two reactants.