The Diels–Alder Reaction of Anthracene with Maleic Anhydride

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PURPOSE OF THE EXPERIMENT
Use the Diels–Alder reaction to form a bridged polycyclic anhydride. Recrystallize the product and characterize it by using melting point and infrared spectroscopy.

BACKGROUND REQUIRED
You should be familiar with reflux techniques, vacuum filtration, recrystallization, melting point measurement, and infrared spectroscopy.

EXPERIMENTAL OPTIONS
Semi-Microscale Diels–Alder Reaction
Microscale Diels–Alder Reaction

BACKGROUND INFORMATION
Otto Diels, Professor of Chemistry at the University of Kiel, Germany, and his student Kurt Alder published a paper in 1928 on additions of electron-poor alkenes and alkynes to electron-rich dienes to form cyclohexenes and cyclohexadienes. These [4 + 2] cycloadditions came to be known as Diels–Alder reactions. Diels and Alder received the 1950 Nobel Prize in chemistry for this work.

The Diels–Alder reaction is one of the most useful synthetic reactions in organic chemistry. In one step the reaction forms a six-membered ring with one or two double bonds from an open-chain compound, as shown in Equations 1 and 2 on the next page. A diene is the 4-π-electron component. It is electron-rich, like a nucleophile in a Lewis acid–base reaction. Simple dienes like 1,3-butadiene are sufficiently electron-rich to react, but electron-releasing groups such as alkyl groups (–R) or alkoxy groups (–OR) enhance a diene’s reactivity.

The 2-π-electron component is called a dienophile ("lover of dienes"). Good dienophiles contain relatively electron-poor double bonds or triple bonds; at least one strongly electron-withdrawing group (W) is needed. Therefore, ethylene and acetylene are not good dienophiles.

Because the reaction is concerted—that is, bond breaking and bond forming take place in the same step—the stereochemistry of the
When anthracene’s center ring reacts as a diene, the product has two fully aromatic rings, each with six pi electrons, as shown in Equation 3.

![Diagram of chemical reaction]

(Eq. 3)

anthracene (diene) + maleic anhydride (dienophile) → (adduct)

The reaction is carried out in xylene, which is actually a mixture of the three dimethylbenzenes, for three reasons. First, the 140 °C boiling point provides a good reaction temperature. Second, the xylene mixture does not freeze when it is cooled in ice water. Third, the reactants are more soluble in xylene than in the product, which crystallizes.

The product is a relatively stable anhydride. Although anhydrides react with water in air, this one reacts slowly and is easily isolated and characterized before much hydrolysis occurs. There are several possible ways to name the product, but 9,10-dihydroanthracene-9,10-α,β-succinic anhydride is probably the simplest.

### Semi-Microscale Diels–Alder Reaction

#### Equipment

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>250-mL beaker*</td>
<td>10-mL graduated cylinder</td>
</tr>
<tr>
<td>boiling chip</td>
<td>hot plate</td>
</tr>
<tr>
<td>Büchner funnel, with adapter</td>
<td>2 melting point capillary tubes</td>
</tr>
<tr>
<td>condenser, with tubing</td>
<td>microspatula</td>
</tr>
<tr>
<td>electric flask heater</td>
<td>25-mL round-bottom flask</td>
</tr>
<tr>
<td>50-mL Erlenmeyer flask</td>
<td>support stand</td>
</tr>
<tr>
<td>125-mL filter flask, with vacuum tubing</td>
<td>13 × 100-mm test tube</td>
</tr>
<tr>
<td>filter paper</td>
<td>2 utility clamps</td>
</tr>
<tr>
<td>glass stirring rod</td>
<td>3-mL product vial</td>
</tr>
<tr>
<td>*for ice bath</td>
<td>watch glass</td>
</tr>
</tbody>
</table>

#### Reagents and Properties

<table>
<thead>
<tr>
<th>Substance</th>
<th>Quantity</th>
<th>Molar Mass (g/mol)</th>
<th>Mp (°C)</th>
<th>Bp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>anthracene</td>
<td>0.5 g</td>
<td>178.23</td>
<td>216–218</td>
<td></td>
</tr>
<tr>
<td>9,10-dihydroanthracene-9,10-α,β-succinic anhydride*</td>
<td>0.25 g</td>
<td>276.29</td>
<td>262–264</td>
<td></td>
</tr>
<tr>
<td>maleic anhydride</td>
<td>0.25 g</td>
<td>98.06</td>
<td>54–56</td>
<td>200</td>
</tr>
<tr>
<td>potassium bromide</td>
<td>100 mg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>xylene</td>
<td>27 mL</td>
<td>106.17</td>
<td>137–144</td>
<td></td>
</tr>
</tbody>
</table>

*product
1. Reacting Anthracene with Maleic Anhydride

**Caution:** Anthracene is irritating. Maleic anhydride is toxic and corrosive. Xylene is flammable and irritating. Keep away from flames or other heat sources. Use a *fume hood*. Prevent eye, skin, and clothing contact. Avoid inhaling and ingesting these compounds.

Tare a 5-mL conical vial (or 10 × 100-mm reaction tube) and record the mass. Weigh 100 mg of anthracene and 55 mg of maleic anhydride and place them in the vial (reaction tube). Add 1.0 mL of xylene. Add a boiling chip. Fit the vial (tube) with a condenser, as shown in Figure 3.

![Figure 3](image)

**Figure 3** Reflux apparatus for (a) vial, or (b) reaction tube

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 min, boiling vigorously for good mixing. **[NOTE 1]**

Cool the mixture to room temperature. Prepare an ice bath, using a 150-mL beaker. Then cool the mixture in the ice bath for 5 min. At the same time, pour 2 mL of xylene into a test tube and chill the xylene in the ice bath.

Collect the crystallized solid by vacuum filtration, using a Hirsch funnel. Rinse the crystals with 1 mL of ice-cold xylene.

Weigh the crude product. Set aside a small sample to dry for a melting point measurement.

2. Purifying the Product

For recrystallization, place the product in a 10-mL Erlenmeyer flask. Add 1–2 mL of xylene. 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. Do not exceed 3 mL total volume of xylene. If solid impurities remain, use a Pasteur pipet to transfer the solution to another 10-mL Erlenmeyer flask.

Allow the solution to cool to room temperature. Then cool the solution in an ice bath for 5 min. If 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. Allow the crystals to dry for about 15 min. Weigh the product and record the mass. Place the product in a labeled product vial.

3. Characterizing the Product  

**Caution:** Potassium bromide (KBr) is irritating. Prevent eye, skin, and clothing contact. Avoid inhaling dust and ingesting KBr.

Measure the melting points for both the crude product and the recrystallized product.

Make a KBr pellet or a mineral-oil mull. Take an IR spectrum of the product and compare it with the spectra of maleic anhydride and anthracene, provided by your laboratory instructor.

4. Cleaning Up  

Place your recovered materials in the appropriate labeled collection containers, as directed by your laboratory instructor. Clean your glassware with soap or detergent.

**Caution:** Wash your hands thoroughly with soap or detergent before leaving the laboratory.
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Pre-Laboratory Assignment

1. Briefly describe the hazards associated with xylene, anthracene, and maleic anhydride.

2. Calculate the theoretical yield for your product. Show the calculation here and in your laboratory notebook.

3. List three reasons why xylene is often used in Diels–Alder reactions.

4. Write the equation for each of the following Diels–Alder reactions.

\[ \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{O}^\|\text{C} \rightarrow \text{CH}_3\text{O}^\|\text{C}\text{CH}_2\text{CH}=\text{CH}_2 \]

\[ \text{C} + \text{CH}_3\text{C}^\|\text{O} + \text{O}^\|\text{C} \rightarrow \text{C} + \text{CH}_3\text{O}^\|\text{C} \]
5. Draw the structures for the diene and dienophile you would use to synthesize each of the following: