DIELS-ALDER REACTION OF 1,3-BUTADIENE AND MALEIC ANHYDRIDE TO PRODUCE 4-CYCLOHEXENE-CIS-1,2-DICARBOXYLIC ACID

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Introduction: The purpose of this experiment is to carry out a Diels-Alder reaction of 1,3-butadiene and maleic anhydride to produce 4-cyclohexene-cis-1,2-dicarboxylic anhydride. This type of reaction is named in honor of the German scientists, Otto Diels and Kurt Alder, who studied the reactions of 1,3-dienes with dienophiles to produce cycloadducts. Their research earned them the 1950 Nobel Prize in chemistry.

The saturation of anhydride will be tested with bromine and Bayer tests. It will also be observed that the product is in the cis position and not the trans position which indicates a concerted, single-step, reaction. Finally the product will be hydrolyzed to produce 4-cyclohexene-cis-1,2-dicarboxylic acid.

Main Reaction and Mechanism: 3-sulfolene was used to synthesize 1,3-butadiene in the reaction flask. It was easier to start with solid 3-sulfolene and then decompose it, rather than starting with gaseous 1,3-butadiene (Fig.1). The dienophile, maleic anhydride, attacks the diene forming 4-cyclohexene-cis-dicarboxylic anhydride (Fig.2). The final step of the mechanism is to add water to the anhydride to produce 4-cyclohexene-cis-dicarboxylic acid (Fig.3).

![FIGURE 1](image-url) The decomposition of 3-sulfolene to produce 1,3-butadiene.
FIGURE 2 The Diels-Alder reaction between 1,3-butadiene and maleic anhydride to produce 4-cyclohexene-cis-1,2-dicarboxylic anhydride.

FIGURE 3 The hydrolysis of 4-cyclohexene-cis-dicarboxylic anhydride to form 4-cyclohexene-cis-dicarboxylic acid.
Table of Reactants:

|---------------------|-----------|----------------|-----------|------------------------|-------------------------------------------------|
| xylene solvent      | ![Structure](attachment:image1.png) | 318.501        | 1mL       | --                     | Colorless liquid  
ρ = 0.862g/mL  
ρ\(_{\text{vap}}\) = 3.7  
f.p. = 25°C  
b.p. = 140°C  
P\(_{\text{vap}}\) = 5.1mmHg  
Sol. = 0.0175g/100mL H\(_2\)O |
| 3-sulfolene         | ![Structure](attachment:image2.png) | 118.1502       | 2.53g     | 1                      | ρ = 1.314g/cm\(^3\)  
f.p. = 112°C  
white/pale yellow crystal  
m.p. = 64-65°C (decomp)  
Sol. = 5-10g/100mL H\(_2\)O @ 16°C |
| Maleic anhydride    | ![Structure](attachment:image3.png) | 98.058         | 1.46g     | 1, L.R.                | Colorless or white solid. Penetrating odor  
ρ = 1.314g/cm\(^3\)  
ρ\(_{\text{vap}}\) = 3.4  
f.p. = 103°C  
m.p. = 52.8-60°C  
P\(_{\text{vap}}\) = 0.16mmHg  
Decomposes in hot solvent |
Table of Products:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-butadiene intermediate C₄H₆</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>54.0914</td>
<td>Intermediate</td>
<td>---</td>
<td>1</td>
</tr>
<tr>
<td>4-cyclohexene-cis-dicarboxylic anhydride C₈H₈O₃ CAS: 85-43-8</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>152.1494</td>
<td>14.9mmol</td>
<td>2.27g</td>
<td>1</td>
</tr>
<tr>
<td>4-cyclohexene-cis-1,2-dicarboxylic acid C₈H₁₀O₄ CAS: 2305-26-2</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>170.1646</td>
<td>14.9mmol</td>
<td>2.54g</td>
<td>1</td>
</tr>
</tbody>
</table>

**Yield Data:** Maleic anhydride served as the limiting reactant in this experiment. 14.9mmol of maleic anhydride should produce 2.27g of 4-cyclohexene-cis-dicarboxylic anhydride and 2.54g of 4-cyclohexene-cis-1,2-dicarboxylic acid (Eqs.1 and 2). The mass of the dicarboxylic anhydride before drying was 1.90g. The mass of the dried dicarboxylic acid was 1.06g, resulting in a 41.7 % yield.

\[
14.9 \text{mmol maleic anhydride} \times \frac{1}{1} \text{ mol ratio} \times \frac{152.1494 \text{g}}{1 \text{mol}} = 2.27 \text{g dicarboxylic anhydride} \quad (1)
\]

\[
14.9 \text{mmol maleic anhydride} \times \frac{1}{1} \text{ mol ratio} \times \frac{170.1646 \text{g}}{1 \text{mol}} = 2.54 \text{g dicarboxylic acid} \quad (2)
\]
Experimental Procedure: 3-sulfolene (2.53g), maleic anhydride (1.46g), and dry xylene (1.0mL) were placed in a 25mL round bottom flask with a magnetic stir bar. A reflux apparatus was assembled with a gas trap (Fig.4).

FIGURE 4 Reflux apparatus connected to an Erlenmeyer-flask gas trap.

The reaction flask was gently refluxed with the Thermowell heater set at 30V until all of the solids were dissolved. It took 13 minutes to completely dissolve. Afterwards, the reaction flask was moderately refluxed for 30 minutes with the Thermowell heater set at 70V. The reaction was refluxing at a rate of 1 drop every 3 seconds. The resulting mixture was tan. The reaction flask was cooled before adding an additional 10mL of xylene which cleared up the solution. The solution was transferred to an Erlenmeyer flask. It crystallized during the transfer, so the mixture had to be heated before finishing the transfer. Heating the solution prior to transferring would prevent the solution from crystallizing during the transfer. Petroleum ether (5mL) was added to the solution so that it became cloudy. The solution was cooled in an ice
bath and rinsed with 5mL of cold petroleum ether. The precipitate was vacuum filtered and air dried. The mass of the wet dicarboxylic anhydride was 1.90g. A small sample was used to perform bromine and Baeyer unsaturation tests. Another small sample was dried for a week before measure the melting point.

A small sample (0.05g) of dicarboxylic anhydride was dissolved in 10 drops of methylene chloride in a test tube. A bromine solution (0.1M in methylene chloride) was added dropwise until a light orange persisted. The orange color rapidly dissipated, indicating a positive test for unsaturation. Another small sample (0.05g) of dicarboxylic anhydride was dissolved in 2mL of 95% ethanol. Potassium permanganate (0.1M) was added dropwise. The solution turned brownish-purple and cloudy. This indicated that MnO₂ was precipitated, a positive test for unsaturation.

The remaining dicarboxylic anhydride (~1.4g) was placed in an Erlenmeyer flask with 7mL of water. The flask was heated on a hot plate until it boiled. The solution was cooled to room temperature. The flask was scratched at the interface between the liquid and air and then cooled in an ice-bath. The dicarboxylic acid was vacuum filtered and dried for a week. The mass of the dry dicarboxylic acid was 1.06g. The sample tested positive for unsaturation in both the bromine and Baeyer tests.

**Properties of Products:**

<table>
<thead>
<tr>
<th>Product</th>
<th>Mass (g)</th>
<th>Bromine Test</th>
<th>Baeyer Test</th>
<th>Melting Point #13 (°C)</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-cyclohexene-cis-dicarboxylic anhydride</td>
<td>1.90 wet</td>
<td>positive</td>
<td>positive</td>
<td>Uncorrected: 96.0-99.0</td>
<td>Off-white powder</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Corrected: 92.0-95.0</td>
<td></td>
</tr>
<tr>
<td>4-cyclohexene-cis-1,2-dicarboxylic acid</td>
<td>1.06</td>
<td>positive</td>
<td>positive</td>
<td>Uncorrected: 173.4-174.5</td>
<td>White, fluffy solid</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Corrected: 169.9-171.0</td>
<td>Turned blue litmus paper pink</td>
</tr>
</tbody>
</table>
**Significant Side Reactions:** The 4-cyclohexene-cis-1,2-dicarboxylic acid can rotate between two boat conformations and a twisted boat conformation (Fig. 5). The first boat conformer, which is favored, has both carboxyl groups equatorial. This twisted boat conformer has one carboxyl group equatorial and the other axial. The second boat conformer, which is least the least stable, has both carboxyl groups axial.

![Conformations of 4-cyclohexene-cis-1,2-dicarboxylic acid. The stability increases from right to left.](image)

A positive bromine test for unsaturation is indicated by the rapid clearing of the orange bromine solution. Bromine attacks the double bond in a stepwise, ionic addition (Fig. 6). The result of this stepwise addition is a trans-dibromo product.
FIGURE 6 Stepwise, ionic addition of bromine to 4-cyclohexene-cis-1,2-dicarboxylic acid. The bromine atoms are trans to the ring.

A positive Baeyer test for unsaturated is indicated by the purple potassium permanganate solution turning a cloudy brown color. The permanganate ion attacks the double bond in a concerted step forming a cis-diol (Fig.7)
FIGURE 7 Concerted addition of permanganate to 4-cyclohexene-cis-1,2-dicarboxylic acid. The hydroxyl groups are cis to the ring.

Method of Purification: The products were purified according to Figure 8. The dicarboxylic anhydride was soluble in hot xylene. Petroleum ether was added to precipitate the anhydride. The dicarboxylic acid was dried for a week to remove any water.

FIGURE 8 Purification of dicarboxylic anhydride and dicarboxylic acid.
Conclusions: The results support both the synthesis of 4-cyclohexene-cis-1,2-dicarboxylic anhydride and 4-cyclohexene-cis-1,2-dicarboxylic acid. The melting point range of the anhydride was 92.0°-95.0°C, while the literature value was 97.0°-103.0°C. The range is a few degrees too low, but the small 3°C range indicates a relatively pure sample. Both the bromine and the Baeyer unsaturation tests were positive for unsaturation. The melting point range of the dicarboxylic acid was 169.9°-171.0°C, while the literature value was 167°-168°C. The blue litmus paper test turned pink in the acid, indicating the anhydride was hydrolyzed. Further tests would need to be done to test whether the products were cis or trans to support a concerted mechanism or a stepwise mechanism.
2) Write structures for the products expected in the following possible Diels-Alder reactions. If no reaction is anticipated, write N.R.

a) \[
\begin{align*}
\text{diene} & \quad + \quad \text{dienophile} \\
\end{align*}
\]

b) \[
\begin{align*}
\text{diene} & \quad + \quad \text{dienophile} \\
\end{align*}
\]

c) \[
\begin{align*}
\text{diene} & \quad + \quad \text{dienophile} \\
\end{align*}
\]

N.R.

The diene is not in the s-cis conformation.
The dienophile does not have an electron withdrawing group.

d) \[
\begin{align*}
\text{diene} & \quad + \quad \text{dienophile} \\
\end{align*}
\]
5) Why should 3-sulfolene and maleic anhydride be completely dissolved in xylene before heating the mixture to effect reaction?

Both reactants should be completely dissolved before heating because the 3-sulfolene must decompose to form butadiene. If the butadiene forms and evaporates before the maleic anhydride dissolves, a reaction will not take place. Likewise, if the maleic anhydride is dissolved, but the 3-sulfolene is decomposing while not in solution, the 1,4 addition will not take place.

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

The two bromines will be trans to the ring.