

Diels-Alder Reaction of Cyclopentadiene with Maleic Anhydride

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Introduction

In 1950, the chemists Otto Paul Hermann Diels, from Germany, and Kurt Alder, originally born in Prussia and then moved to Germany after World War I, received the Nobel Prize in chemistry for the discovery of a new way to synthesize cyclic molecules. Aptly titled the Diels-Alder Cycloaddition Reaction, this new mechanism allowed conjugated dienes to undergo addition reactions with alkenes, yielding substituted cyclohexene products (McMurry 492).

While there were numerous immediate uses for this new reaction mechanism, commercial exploits led to the development of powerful insecticides. These particular compounds usually consisted of a carbon ring (or rings) and many chlorine atoms. Chemicals such as Aldrin, Dieldrin, Chlordane, and DDT were all used to protect fruits, vegetables and cotton from soil insects, termites and moths. Some had other applications and were used to treat parasites like fleas, ticks and lice (Pavia 412). Although

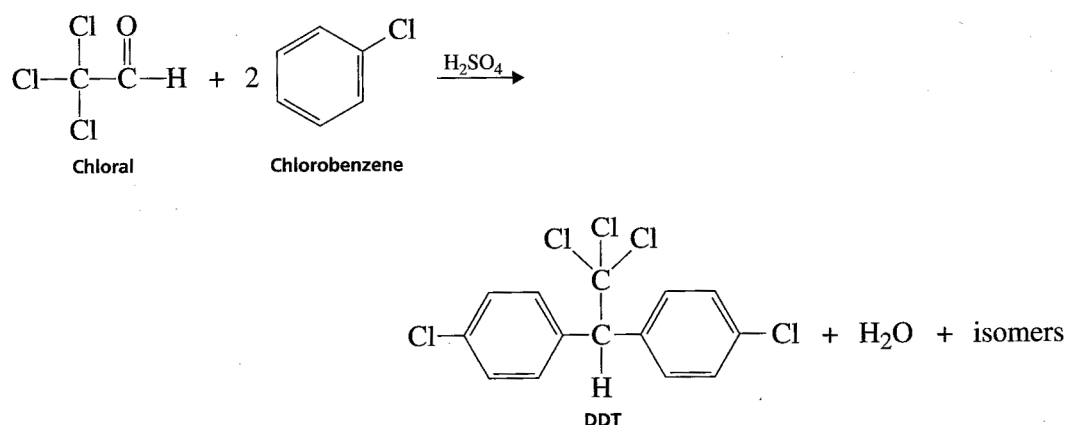


Figure 1. Synthesis of the insecticide DDT from Chloral and Chlorobenzene (Pavia 413).

widely used for a time, many of these insecticides have damaging long term effects and have been replaced by newer, less harmful compounds. Problems included the evolution of immunities for insects, accumulation of compounds in the environment and the food chain, and mass destruction of bird populations, such as the bald eagle and brown pelican.

In this experiment I used the Diels-Alder Cycloaddition Reaction mechanism to form *cis*-Norbornene-5,6-*endo*-dicarboxylic anhydride from the reaction of the conjugated diene Cyclopentadiene with the dienophile Maleic anhydride (see Figure 2). While the product is not an insecticide and does not

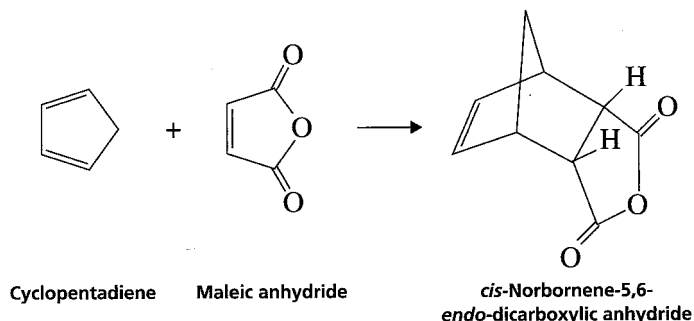


Figure 2. Reaction to form *cis*-Norbornene-5,6-*endo*-dicarboxylic anhydride (Pavia 417).

seem to have any practical application, it is a simple reaction that serves as an effective example of this important mechanism.

Experimental Procedure

Cracking of Dicyclopentadiene

Before the beginning of lab the cyclopentadiene was prepared by a lab technician by “cracking” it. When pure cyclopentadiene is stored it also undergoes a Diels-Alder Cycloaddition reaction and forms Dicyclopentadiene. This new compound must be separated before the desired compound can be used. The separation process is done with a fractional distillation apparatus. Afterward the product is stored in a cold environment to prolong its state and ward off the eventual dimerization that will once again occur.

Reaction of Cyclopentadiene with Maleic anhydride

To begin the reaction I added 1.003g of Maleic anhydride to a 25ml Erlenmeyer flask. Next, 4.0mL of Ethyl acetate and 4.0mL of Ligroin (Petroleum ether) were separately poured into the same flask. Finally, 1.0mL of Cyclopentadiene was carefully added to the other substances. The addition of this final compound produced an immediate but brief boiling, along with the release of heat for a short time afterward. A white solid began to form, indicating that recrystallization had begun, and the flask was then left to cool to room temperature to allow this process to continue. After about 15 minutes the mixture

changed into a cloudy white liquid with sediment. To complete recrystallization, I placed the flask within an ice bath, which produced more cloudiness and sediment.

Retrieval of cis-Norbornene-5,6-endo-dicarboxylic anhydride

I prepared a filtration system by configuring a Büchner funnel lined with filter paper, a filter adapter and a filter flask attached directly to an aspirator, as detailed by the *Filtration* techniques section within our lab manual (Pavia 652). The filter paper was sprayed with cold Ethyl acetate to ensure that it was wet. I carefully added the contents of the 25mL Erlenmeyer flask to the funnel, washing out residual crystals with more cold Ethyl acetate. After transferring all of the solid, the contents were left alone for about 10 minutes to remove any remaining liquids and impurities.

Test for impurities

I measured the melting point and compared it to the literature value. A prolonged melting period occurred where an initial melting of the solid was observed without any further change happening until after an increase in temperature of 10.0°C. Also, IR spectroscopy was used to make additional observations about the products by using a KBr pellet. The pellet was created by mixing 0.157g of KBr into a very small amount of carefully ground product and inserting this into a die. Extreme pressure was applied to the die for two minutes within a Carver machine. This produced a clear pellet with white flecks that was about the size of a penny, which was then used to obtain an IR spectrum.

Results

Yield, melting point and appearance

Table 1. Data for the reaction of Cyclopentadiene with Maleic anhydride

| Product | Yield (g) | Yield (%) | Experimental Melting Point | Literature Melting Point | Appearance |
|---|-----------|-----------|----------------------------|--------------------------|--------------------|
| <i>cis</i> -Norbornene-5,6- <i>endo</i> -dicarboxylic anhydride | 1.171g | 69.74% | 155.5°C – 165.5°C | 164°C [†] | White clumpy solid |

[†] (Pavia 420)

HNMR and IR Data Summary

Both IR and HNMR spectra did not indicate the presence of contaminants (see Figures 3 and 4). For HNMR, only three different signals appeared for eight hydrogen atoms, as was expected for the product.

Discussion and Conclusion

Given the straightforwardness of this reaction, very little can be said about the results. The Diels-Alder Cycloaddition reaction occurred as expected. Very little contamination appears to have been present in the final product, although the drawn out melting temperature reading is of some concern. The percent yield was acceptable, but probably could have been improved with better handling techniques.

References

McMurry, J. *Organic Chemistry*. 7th ed. Belmont, CA: Brooks/Cole, 2008.

Pavia, D.L., Lampman, et al. *Introduction to Organic Laboratory Techniques, A Small Scale Approach*. 2nd ed. Belmont, CA: Brooks/Cole, 2005.

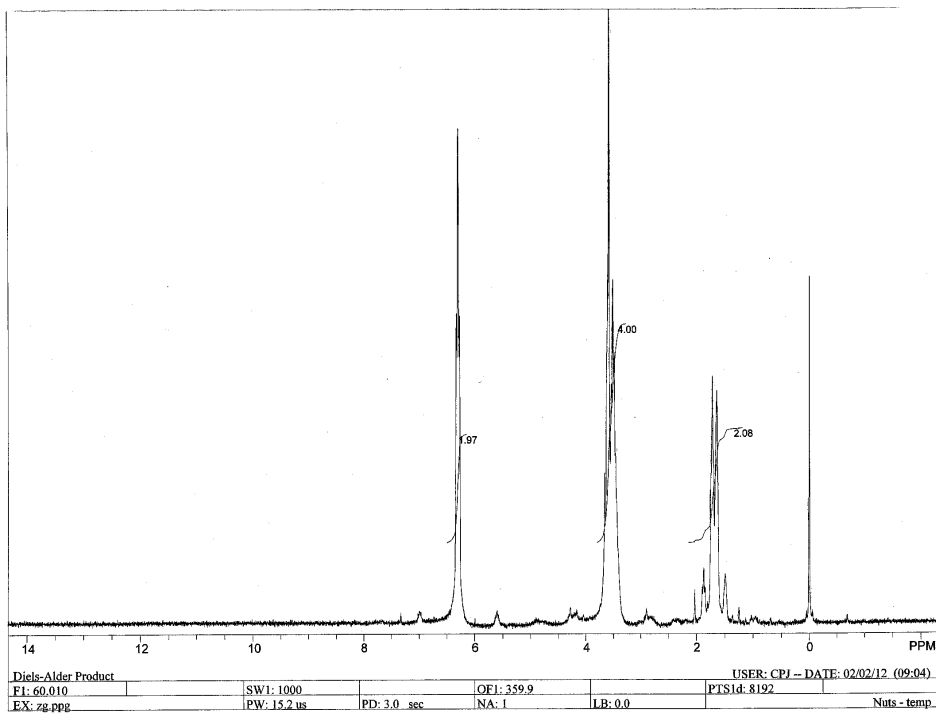


Figure 3. HNMR spectrum for *cis*-Norbornene-5,6-*endo*-dicarboxylic anhydride

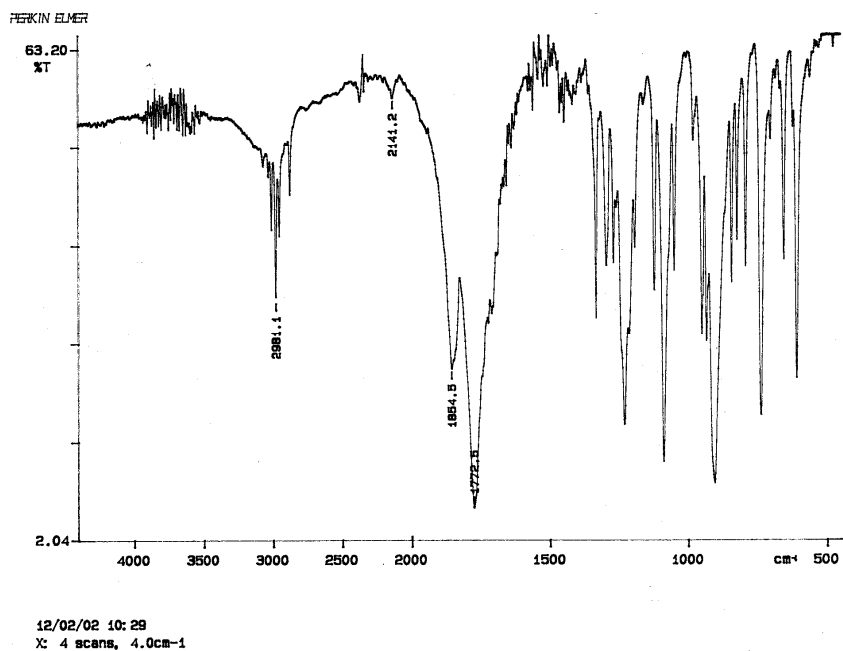


Figure 4. IR spectrum for *cis*-Norbornene-5,6-*endo*-dicarboxylic anhydride