CH 242 EXPERIMENT #1

WEEK OF February 11, 2002

A DIELS –ALDER REACTION
(Synthesis of cis—1,2,3,6-tetrahydro-4,5-dimethylphthalic anhydride)

Background

The Diels-Alder reaction is an important, synthetically useful reaction in organic chemistry. It is named after Otto Diels and his student Kurt Alder who were awarded the Nobel Prize in chemistry in 1950 in recognition of the importance of their discovery. An example of the Diels-Alder process is the cycloaddition reaction of a 1,3-π system (a diene) with a π bond (a dienophile) to produce a six-membered ring. The reaction is usually concerted and occurs with great stereoselectivity. The mechanism of the reaction involves the head-to-head overlap of p-orbitals to form new sigma bonds.

![Diene, Dienophile, T.S., D-A Adduct]

In this experiment the diene will be 2,3-dimethyl-1,3-butadiene and the dienophile will be maleic anhydride. These react to form the Diels-Alder adduct, cis—1,2,3,6-tetrahydro-4,5-dimethylphthalic anhydride. After synthesizing the anhydride, you will need to recrystallize it from light petroleum. The product will be then characterized by its melting point, ¹H NMR spectrum, and IR spectrum. You will also need to do a quick calculation of the energy changes accompanying the reaction using the semi-empirical PM3 method in Spartan.

![Chemical Structures]
**Procedure**

Weigh 1.0 g of powdered maleic anhydride into a clean and dry 25 mL Erlenmeyer flask. Then add 1.25 mL of the diene in one portion to the flask. Within a few minutes, the contents of the flask will become warm as the reaction occurs. Gently stir the reaction mixture with a clean and dry glass rod. After the mixture has attained room temperature, add 5 mL of petroleum ether and recrystallize the product. Add more solvent, only if necessary, in small portions. Vacuum filter the recrystallized product and let dry on the funnel for a few minutes. Weigh the product and calculate its percentage yield. Finally, characterize the product using the method you picked.

**Prelab**

(1) Read section 11.15 of your text, The Diels-Alder Reaction of Dienes.
(2) Review the technique of recrystallization by consulting your lab book from last year and the lab manuals available in Olin Library (Rm 142).

**Report**

Your report should contain a brief introduction stating the purpose of this experiment, an experimental section which should be complete enough so that someone else could repeat your experiment using only your write-up, your results including analysis of yield, melting point and spectral data, a discussion-conclusion section including mechanism, stereochemistry and computational data, and answers to the questions below.

**Questions**

1. A commercially important use of the Diels-Alder reaction is in the synthesis of insecticides. Dieldrin and Aldrin, named after Diels and Alder, are used against insect pests of fruits and vegetables, as well as soil insects, termites and moths. What is the structure of Aldrin?

   ![Aldrin Structure]

2. Provide a mechanism for the following synthesis.

   ![Mechanism Diagram]