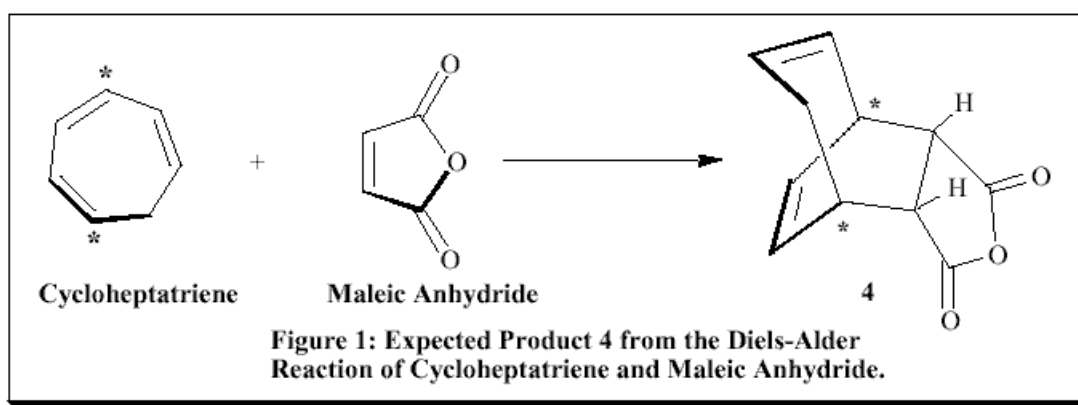


# Introduction

1,3-Cyclopentadiene and 1,3-Cyclohexadiene undergo Diels-Alder reactions with a variety of dienophiles roughly one million times as fast as acyclic dienes. The reason for this is that the molecules are constrained into the S-cis conformation instead of being allowed to adopt the lower energy S-trans conformation. Because the Diels-Alder adducts of monocyclic dienes are bicyclic systems, which are difficult to obtain in other ways, Diels-Alder reactions of cyclic dienes and even trienes have been studied closely. One of the most interesting of these reactions is that of cycloheptatriene (**2**) with maleic anhydride (**3**), the product of which is the title compound(**1**).



This reaction was first studied by Kohler and co-workers in 1939, 2 a decade after Diels and Alder published the first article on their reaction. Kohler and his colleagues were smart enough to realize that the adduct they obtained from the reaction was not the expected structure (**4**), but rather an isomer of it (**Figure 1**).

Although Kohler and his co-workers were working before the availability of infrared and NMR spectrometry, they suggested that (**1**) was the most likely structure of the adduct. Structure was confirmed by chemical degradation more than a decade later,<sup>3</sup> although its formation from reactants **2** and **3** was still unexplained. This unusual reaction was studied once again in 1971 (after NMR was available) and the assignment of structure **1** as the major product was confirmed.<sup>4</sup> The research group also detected about 10% of the exo,exo isomer of **1** and less than 1% of the expected adduct **4**. In this lab you will prepare and recrystallize compound **1** and study the reaction that produces it.

## Procedure:

Cycloheptatriene (75.0 mmole, 7.75 mL), finely powdered maleic anhydride (75.0 mmole, 7.35g) were refluxed in 50 mL of mixed xylenes in a 100 mL round bottom flask for two hours (for this simulation reflux for about 5 minutes).

The solution was allowed to cool briefly followed by resetting the condenser for distillation and 25-35 mL of the solvent was distilled off. After allowing the mixture to cool briefly, the pot mixture was then poured into a small beaker, the flask rinsed with 15 mL of ethyl acetate, and the rinses were added to the beaker. Hexane (50 mL) was then added to the solution which was then chilled in an ice bath for 15 minutes. To create a cold water bath add a 600 ml beaker then use the water menu option to add 300 ml of ice water to beaker.

Large needles of product were then isolated in a buchner funnel to afford cream colored crystals (m.p.= 98.5° - 99.5° C).

To isolate using a buchner funnel first add a 100 ml Erlenmeyer flask to lab then select flask and press the buchner funnel button (or menu). To remove contents from buchner funnel select the flask and press the buchner funnel button again (or menu). A dialog will indicate that the funnel has some contents, place contents in a watch glass.

The product can be further purified via recrystallization from ethyl acetate / hexanes to afford pure product (lit. m.p. =101° C) .

## Questions:

1. Cycloheptatriene does not add to maleic anhydride in a normal Diels-Alder fashion. From your knowledge of how a Diels-Alder reaction works, use the structure of the actual adduct **1** to deduce the structure of the diene which actually added to the maleic anhydride. This is, work backward from the adduct **1** to the structure of the actual diene reactant by detaching the skeleton of maleic anhydride.
2. The actual diene reactant whose structure you have deduced is called Norcaradiene. Write its structure next to the that of cycloheptatriene. Next, use mechanistic arrows to suggest how cycloheptatriene might isomerize to form norcaradiene.

3. Isomerizations such as the one hinted at in Question 2 are called Valence Tautomerizations. Two structures related like cycloheptatriene and norcaradiene are referred to as valence tautomers. It is not necessary to shift hydrogens to turn one valence tautomer into another. However, valence tautomers are not resonance forms of the same molecule either, since bond lengths and angles are different between the two. Write an equation which shows the interconversion of cycloheptatriene and norcaradiene as an equilibrium.

4. The equation you wrote for Question 3 expresses the fact that a bottle of cycloheptatriene always contains some of the norcaradiene tautomer. However, norcaradiene is much less stable than cycloheptatriene and comprises less than 1% of the equilibrium mixture. For every molecule of norcaradiene present, there are 99 or more molecules of cycloheptatriene. Proving the existence of an unstable molecule by causing it to react selectively with some other compound is called trapping. In this lab we used maleic anhydride as a trap to react with norcaradiene. Try to suggest a reason that the norcaradiene, rather than cycloheptatriene is trapped by maleic anhydride.

### **Typical Experimental Results**

The yield of product (1) from the reaction is typically about 70%.