

Experiment 28

DIELS-ALDER REACTION

Fig. 28-1, left
Fig. 28-2,
right



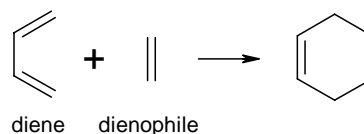
Otto Diels (1876 - 1954) and Kurt Alder (1902 - 1958) received the Nobel Prize in Chemistry in 1950 for their discovery of the Diels-Alder reaction.
<http://nobelprize.org/chemistry/laureates/1950/diels-bio.html>
<http://nobelprize.org/chemistry/laureates/1950/alder-bio.html>

Text Topics

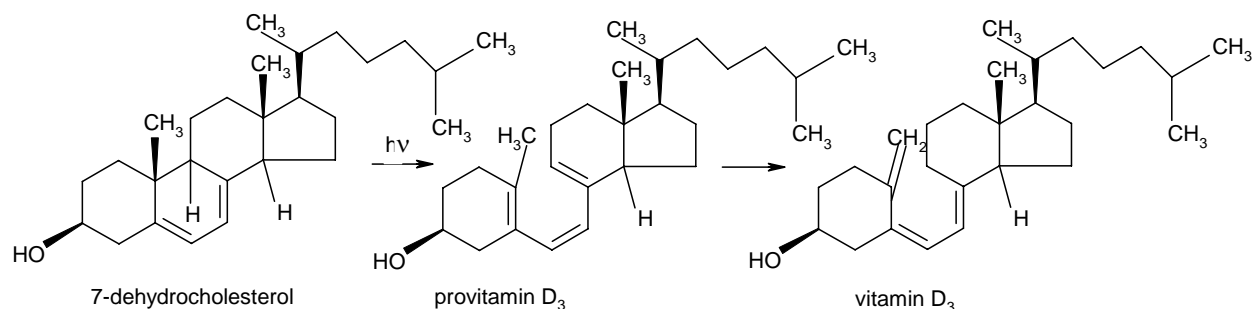
Pericyclic reactions, Diels-Alder reaction, trapping of reactive intermediates.

Discussion

When Otto Diels and his student, Kurt Alder discovered the reaction now called the Diels-Alder reaction, they opened the door to the synthesis of many compounds. Without their very important carbon-carbon bond forming reaction, the preparation of many compounds would have remained extremely difficult and time consuming if not close to impossible. Today, the Diels-Alder reaction is recognized as one type of a broader class of reactions often referred to as pericyclic reactions. Pericyclic reactions differ from most of the reactions you have previously studied as they do not proceed through discrete intermediates such as carbocations, carbanions or radicals. The reactions are said to take place in a concerted fashion or synchronously with all the bond cleavages and formations occurring simultaneously. In fact the Diels-Alder reaction results in the “breaking” of three π bonds and the formation of two new σ bonds and one π bond.



Other examples of pericyclic reactions include two of the steps involved in the synthesis of vitamin D₃. Notice that the first step is a photochemical conversion of a cyclohexadiene to a hexatriene system and the second step is a thermally activated 1,7 hydrogen shift. Because the first step requires light, vitamin D₃ is sometimes referred to as the sunshine vitamin.

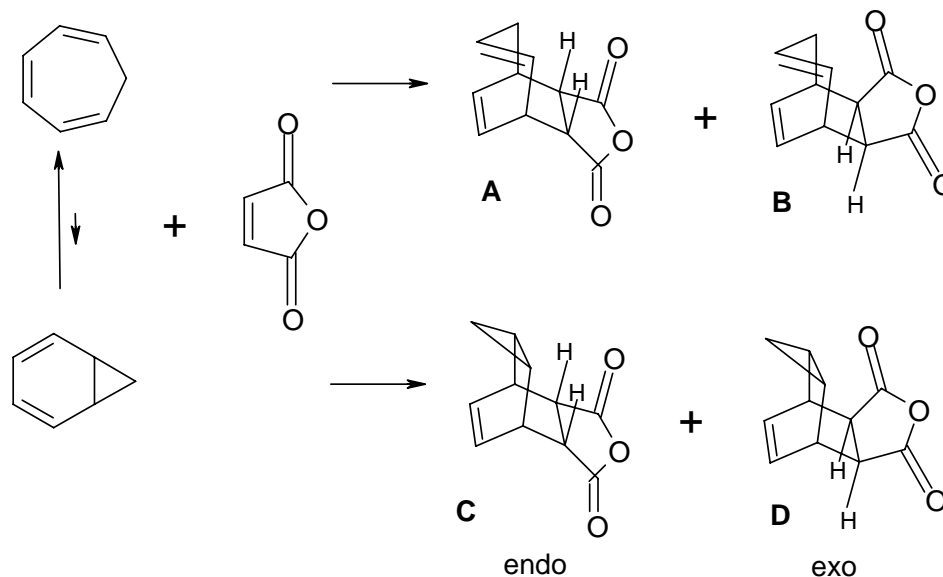


The reaction you will perform today also includes two different kinds of pericyclic reactions. The compound 1,3,5-cycloheptatriene is in equilibrium via a pericyclic reaction or valence isomerization with [4.1.0]hepta-2,4-diene (norcaradiene). The position of equilibrium strongly favors the triene. Norcaradiene is not detectable in the triene solution and it is estimated that the equilibrium mixture contains less than 0.1%

of norcaradiene. Even though norcaradiene is not directly detectable, it is possible to obtain evidence for its existence by demonstrating that a reaction product could only have been formed as a result of the reaction of norcaradiene.

The trapping of an intermediate using a chemical reaction is frequently used to demonstrate the temporary existence of short lived intermediates in a reaction. In *Experiment 26*, evidence for the formation of the reactive intermediate, dichlorocarbene was provided by the determination of the structure of the product (cyclopropyl group) of the reaction. It would have been very difficult to write a mechanism to the product without invoking the presence of dichlorocarbene as an intermediate. The temporary formation of other important intermediates in organic chemistry such as benzyne and cyclobutadiene have also been demonstrated using trapping experiments. For this experiment, 1,3,5-cycloheptatriene will be heated in the presence of maleic anhydride. If the 1,3,5-cycloheptatriene behaves as a diene in a straightforward Diels-Alder reaction, the product should be one or both of the top two products on the right in the scheme below. If, on the other hand, the 1,3,5-cycloheptatriene undergoes a valence isomerization to norcaradiene and the norcaradiene behaves as a diene in a reaction with maleic anhydride, then one or both of the bottom two products should be formed.

Assuming that one of the four possible products predominates in the reaction, the challenge after running the reaction will be to determine which one of the isomers was formed. Fortunately, three of the four possible products have been previously characterized. This means that if you are able to isolate a single compound, you should be able to determine from melting points and an ^1H -nmr which product was formed. If it is one of the bottom two, you will have provided evidence for the temporary formation of norcaradiene during the course of the reaction.



Techniques

According to reference 2, the melting points of compounds A, C and D are 112 - 113°C, 101°C and 112 - 113°C respectively. For the analysis, cyclopropyl hydrogens usually resonate at high field between 0.2 and 0.8 ppm where few other types of hydrogens give signals. For the purposes of this experiment, it will only be necessary to determine if there are cyclopropyl hydrogens in the nmr. If you are able to isolate a fairly pure product, by using a combination of melting points and ^1H -nmr, it should be possible to determine if the product is A, C or D.

Procedure

This reaction is best run with microscale glassware but can be scaled up or down as desired. If it is scaled up significantly, the reflux time should be increased. Set up a reflux system with a 10 mL round bottom reaction flask containing a couple of boiling chips, 0.50 g of cycloheptatriene, 0.50 g of finely powdered maleic anhydride (as maleic anhydride is hazardous, if grinding is necessary to make it powdered, the grinding should be carefully performed by a lab supervisor) and 5 mL of mixed xylenes. Reflux the mixture for a minimum of 30 minutes. Reset the condenser for vacuum distillation and under vacuum, distill off as much of the xylenes as possible. When the reaction mixture has been decreased to about 1 mL, allow it to cool and then add a mixture of 1 mL of ethyl acetate and 4 mL of hexane. Cool the mixture in an ice bath and collect the solid product that should result using vacuum filtration with a Hirsch funnel. Determine the percent yield, the melting point and the ^1H -nmr spectrum (in CDCl_3). Also, dissolve a small amount of the product in a small amount of p-xylene and run a gc at about 200°C .

References

1. Kurtz, D. W.; Johnson, R. P. *J. Chem. Educ.*, **1989**, *66*, 873.
2. Ishitobi, H.; Tanida, H.; Tori, K.; Tsuji, T. *Bull. Chem. Soc. Japan*, **1971**, *44*, 2293.

Prelaboratory Preparation - *Experiment 28*

First, be sure to list all the goals of the experiment. The carbon - hydrogen bonds in a cyclopropane contain more s character than would be predicted by sp^3 hybridization. Consider why this is so and why it leads to high field resonance for the cyclopropyl hydrogens. Explain how a combination of melting points and ^1H -nmr should enable you to distinguish between A, C and D. Prepare a table for insertion of useful and observed data such as molecular mass, mass, moles, melting points and percent yields and recoveries. Locate this type of reaction on the *Reaction-Map of Organic Chemistry* in **Appendix C** and include the reaction number in your report.

Observations

Report all relevant observations including masses and melting ranges, ^1H -nmr and gc results.

Conclusions

This section should include the following:

1. Were the goals of the experiment achieved? Explain your answer.
2. What was the identity of your product? Explain your evidence.
3. Did the product structure provide any evidence for the existence of norcaradiene?
4. How could the percent yield and recoveries have been improved?
5. Suggest a reason for formation of the major product in this reaction.

