

Diels-Alder Cycloaddition on a Furan Ring

CHEM HELP *ASAP*

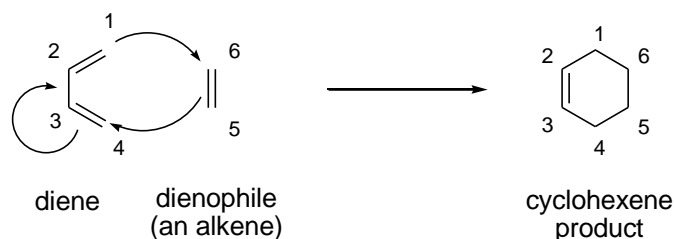
experiment video: <https://youtu.be/xYVWS5WmKgw>

Purpose

The purpose of this experiment is to perform a Diels-Alder cycloaddition. The crude product will be isolated by simple filtration and is pure enough to be used in the next step without further purification.

Background

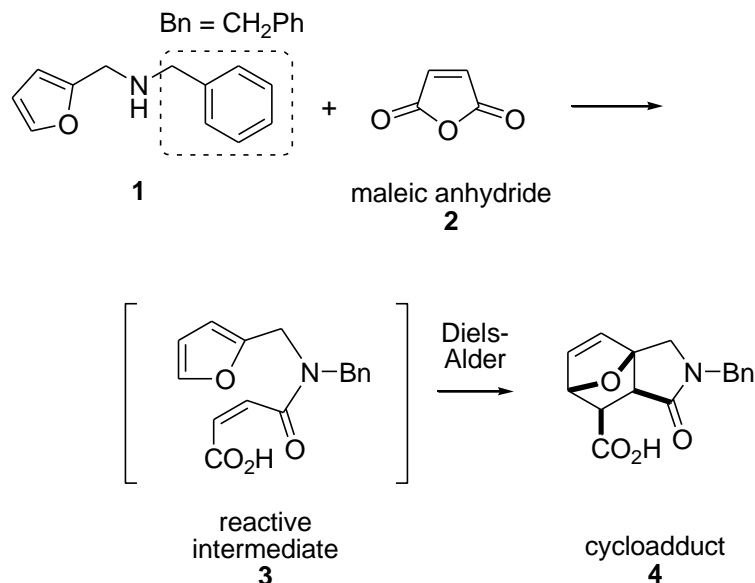
The Diels-Alder reaction combines a diene and a dienophile (Scheme 1). Since the reaction is both an addition (loss of π -bonds for σ -bonds) and forms a ring, the Diels-Alder reaction is classified as a *cycloaddition*. Mechanistically, the reaction occurs in one step with all the electrons moving at the same time and is therefore considered to be a *concerted* reaction. The driving force behind the Diels-Alder reaction is the formation of two new C-C σ -bonds in place of two C-C π -bonds. This favors the product by approximately 40 kcal/mol.



Scheme 1. A simple Diels-Alder reaction

The Diels-Alder cycloaddition requires the diene and dienophile to approach each other in a very specific manner, and this organization between the diene and dienophile causes the reaction to be somewhat slow. One way to make the reaction faster is to connect the diene and dienophile so that the rate of collisions between the two groups is faster. The resulting reaction, an intramolecular Diels-Alder cycloaddition, is much faster. Our reaction today is an intramolecular Diels-Alder.

The reaction begins with amine **1** (Scheme 2). Amine **1** reacts with maleic anhydride (**2**) to form an intermediate compound (**3**) with two interesting features. First, the alkene from maleic anhydride bears two electron-withdrawing groups and is therefore an excellent potential dienophile. Second, the furan contains two alkenes with an oxygen (electron-donating group), so the furan is a potential diene. These two groups are connected so that they can undergo a Diels-Alder reaction in a reasonable manner. The Diels-Alder cycloaddition forms a stable, crystalline cycloadduct (**4**) that precipitates from the reaction under our conditions. The product can be filtered directly from the reaction.



Scheme 2. Intramolecular cycloaddition of **1** and **2**

Procedure – (3a*R*,6*S*,7*R*,7a*S*)-*rel*-1,2,3,6,7,7a-hexahydro-1-oxo-2-(phenylmethyl)-3a,6-epoxy-3a*H*-isoindole-7-carboxylic acid

modified from Zubkov, F. I.; Airiyan, I. K.; Ershova, J. D.; Galeev, T. R.; Zaytsev, V. P.; Nikitina, E. V.; Varlamov, A. V. *RSC Adv.* **2012**, *2*, 4103-4109.

In a 20-mL scintillation vial dissolve *N*-(phenylmethyl)-2-furanmethanamine (**1**) (2.5 mmol) in 5 mL toluene with stirring. Add maleic anhydride (2.5 mmol). Record any relevant appearance changes. Once the reaction has generated a thick precipitate, allow the reaction to stir for an additional 30 min. Cool the mixture on an ice bath for 5 min. Filter the reaction on a Buchner funnel. Use toluene to both complete the transfer from the reaction vial and rinse the solid in the funnel. Spread the solid on a tared watch to air dry. Dispose of the filtrate waste in the organic waste. Once the solid has dried, record a recovered mass and determine the crude percent yield. Determine the melting point of the product and interpret the provided NMR spectrum.