Cycloaddition of Cycloheptatriene with Maleic Anhydride

CHEM HELP *ASAP*

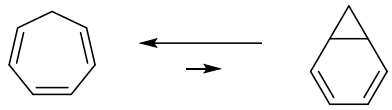
experiment video: https://youtu.be/mUSGMEYHbQY

Purpose

The purpose of this experiment is to perform a Diels-Alder reaction with a valence isomer of cycloheptatriene and maleic anhydride. The crude cycloadduct will be isolated by simple filtration after precipitation and is pure enough to be characterized in its crude form.

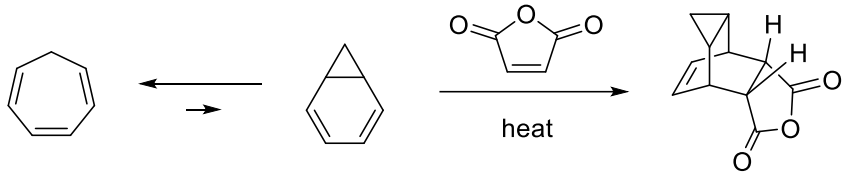
Background

Cycloheptatriene is a fluctional molecule that exists in two forms, which are examples of valence isomers. The major form is cycloheptatriene, and the minor form is a cyclohexadiene (Scheme 1). The equilibrium strongly favors the cycloheptatriene form, but the cyclohexadiene is distinctive as it is a relatively reactive diene for Diels-Alder cycloaddition reactions. In the presence of a suitable dienophile, the cyclohexadiene form of cycloheptatriene readily undergoes cycloadditions to form complex polycyclic products.



Scheme 1. Valence isomerism in cycloheptatriene

In a specific reaction, cycloheptatriene, in the form of its cyclohexadiene valence isomer, undergoes a Diels-Alder cycloaddition with maleic anhydride upon heating. The resulting cycloadduct has *endo* stereochemistry.



Scheme 2. Today's reaction – cycloaddition of cycloheptatriene and maleic anhydride

Procedure – *anti*-tricyclo[3.2.2.0^{2,4}]non-6-*endo*-8,*endo*-9-dicarboxylic anhydride

(adapted from Mohammad, H. J.; Alsamarrai, A. S. H.; Mahmood, R. T. *J. Pharm. Sci. & Res.* **2019,** *11,* 1073-1077.)

In a small test tube combine maleic anhydride (2.00 mmol) and cycloheptatriene (2.00 mmol). Heat the mixture in a hot sand bath to the approximate boiling point of cycloheptatriene (116 °C) for 2 h. At the end of the heating, allow the mixture to cool to room temperature to afford a solid. Add approximately 1 mL of ethyl acetate and mix the product with the solvent until the solid has completely dissolved. Transfer the solution to a 20 mL scintillation vial or a 20 mL beaker with a minimal amount of ethyl acetate to complete the transfer. Add dropwise approximately 6 mL of hexane to the solution with mixing, and cool the resulting solution on ice. After the solution has cooled and solid has formed, filter the solid with a small Buchner funnel and a side-arm Erlenmeyer flask. Rinse the vial and recovered solid with a minimal amount of cold 3:1 hexane:ethyl acetate. Allow the product to dry. Record the mass of the product, determine the percent yield, record a TLC of the product (mobile phase: 20% EtOAc:80% hexane & visualization with I_2), determine the melting range, and analyze the ^{1}H NMR spectrum.