

Experiment 3: Diels-Alder exo or endo?

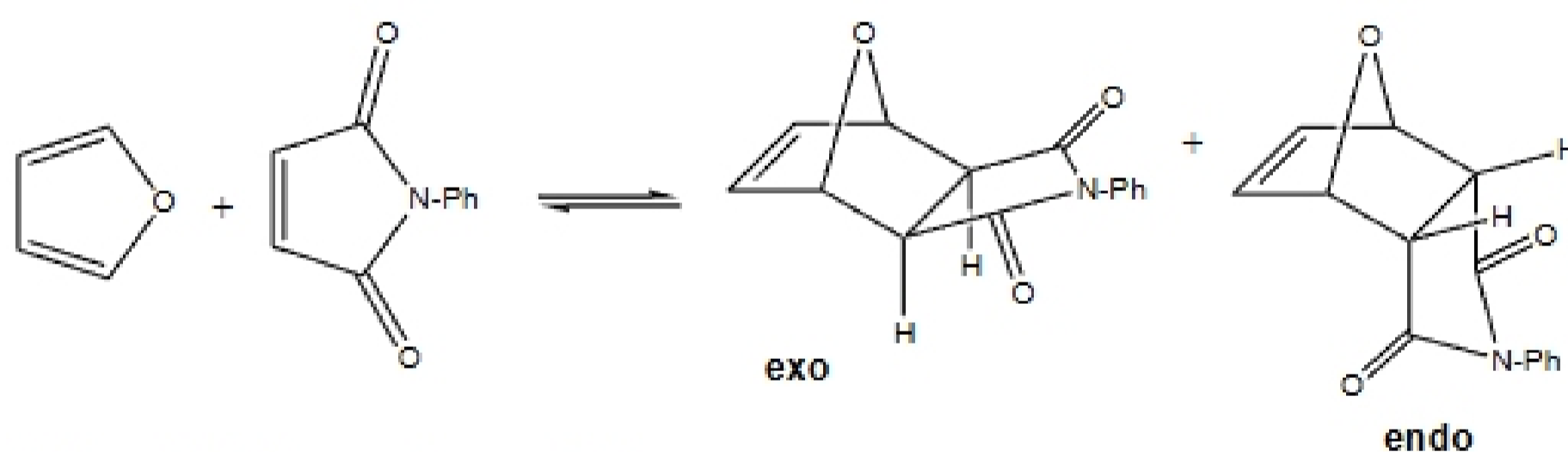
Background

A Diels-Alder cycloaddition can result in either and/or both endo and exo- products. Does the neat Diels-Alder reaction of furan with N-phenyl maleimide produce exo and/or endo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxy-N-phenylimide? Once the reaction has taken place, you will separate and characterize the products to determine what product/s are made, in what ratio, and if starting material is fully reacted.

Experimental

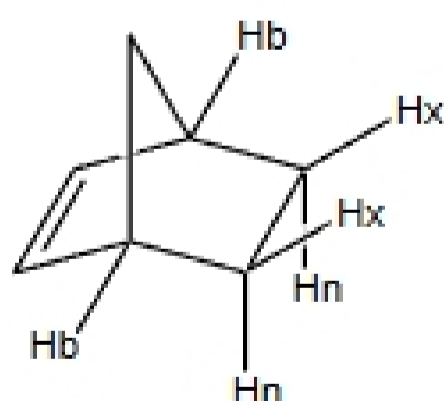
N-Phenylmaleimide (56mg) was dissolved in 0.5 mL of furan. The mixture was allowed to stand for at least 20 h. The white, solid product was separated by filtration and washed with 2 mL of ether. (If no solid is present, a stirring rod was used to evaporate some of the solution and then the solid reintroduced to seed the crystallization.) The number of products was determined through TLC using 1:1 EtOAc-hexane. A 52 mg portion of the product/s was dissolved in 1 mL of hot EtOAc and chromatographed on 5.5 g of silica gel using a 10 mm i.d. chromatographic column (aka buret). The eluent was monitored by TLC, the appropriate fractions combined and the solvent removed.

If your glassware seems to be too large for say filtering this reaction, be creative. Try removing the solvent from the solid via pipet, then wash with 1mL ether and remove the solvent by pipet; repeat and dry under a gentle stream of nitrogen or air.



Differentiating exo from endo.

Stumped on how you will identify the exo from the endo product? Consider the following data and the links below it.



$$J(\text{Hb}, \text{Hx}) = 3.66 \text{ Hz}$$
$$J(\text{Hb}, \text{Hn}) = 0.55 \text{ Hz}$$

<http://pubs.acs.org/cen/science/8151/8151karplus.html>

<http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/nmr/nmr2.htm>

Discussion to be addressed in your report

The following data was also obtained. Fill in your observations and explain all of the data using the concepts of thermodynamic and kinetic control. Be sure to include an energy diagram.

Time	Temp	% exo	% endo	%N-phenyl-maleimide
7 days	0°C	36	49	14
7 days, then 5 h	0°C, 60°C	43	21	36
7 days	ambient			
20 days*	ambient	68	23	9

*Equilibrium ratio