Synthesis of a Bicyclo[2.2.1]heptene Diels–Alder Adduct

An Organic Chemistry Experiment Utilizing NMR Spectroscopy To Assign Endo Stereochemistry

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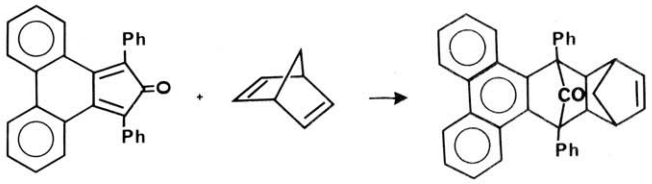
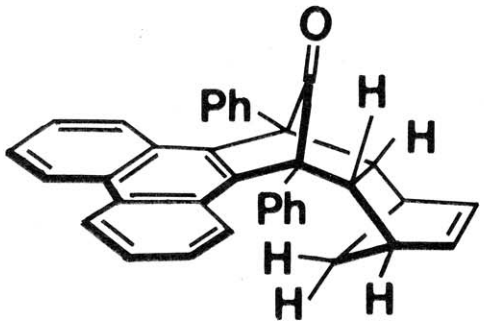
While most contemporary organic chemistry laboratory texts contain statements emphasizing the well-documented preference for endo addition in the Diels–Alder reaction, few (if any) provide experiments that allow students to verify this fact.[1] The experiment described below was developed to rectify this situation by having the students prepare Diels–Alder adduct **3** (*1*, *2*) and determine its stereochemistry by a careful analysis of the NMR spectrum of the compound



1 **2** **3**

As shown in the equation, the synthesis involves the cycloaddition of phencyclone (**1**) with norbornadiene (**2**) to yield adduct **3**. Use of the highly reactive **1**[2] (rather than, say, tetraphenylcyclopentadienone) permits the reaction to be carried out at the boiling point of toluene and insures that the adduct **3** will survive intact. The product (**3**) usually crystallizes out of the reaction mixture and, once in hand, it exhibits the interesting (or mystifying) property of decomposing with (vigorous) gas evolution on heating. The reaction is easily run, requires only a simple setup, and can be completed in one 3-h laboratory period.[3]

In order to establish the endo stereochemistry of **3**, the methylene protons must be correctly identified as the source of the high-field set of doublets in the NMR spectrum. It must also be recognized that the extraordinarily low chemical shifts of these protons (plus 0.43 and *minus* 0.43[4]) strongly suggest that they lie within the shielding cone of the phenanthrene ring (*3*). With this information in hand, an examination of molecular models then becomes a useful exercise that ultimately leads to identification of the endo–exo isomer (figure) as the most likely possibility for the structure of **3**.



Endo–exo **3**.

In addition to the one mentioned above, this experiment has a number of other pedogogical features that make it well-suited for use in the undergraduate laboratory. For example, it lends itself well to a discussion of stereospecificity, the effect of ring strain on the carbonyl stretching frequency in the IR, and the concept of magnetic anisotropy. Also, an exploration of the chemistry behind the observed thermal decomposition of **3** leads very nicely to a consideration of decarbonylation and relief of ring strain as a driving force for reactions.

Experimental

Warning: Toluene is flammable; therefore, ground glass joints should be tight and reflux restricted to the lower third of the condenser.

9,9a,10,13,13a,14-Hexahydro-9,14-diphenyl-9,14:10,13-dimethanobenz[a,c] anthracene-15-one (3)

Phencyclone (**1**)[5] (1.0 g; 2.6 mmol), norbornadiene (**2**) (0.60 g; 6.5 mmol), and toluene (10 mL) were placed in a 100-mL round-bottom flask equipped with a reflux condenser. A boiling stone was added to the mixture, and the whole was then heated at reflux using a heating mantle as the heat source. The progress of the reaction was monitored by TLC (CH_2Cl_2:hexane = 1:1 and Silica-Gel plates[6]) every 15–20 min, and heating was discontinued when the TLC results indicated **1** had been consumed.

At the end of the reflux period (approximately 1 h) the reaction mixture (now light yellow) was cooled to room temperature and filtered to remove the insoluble **3**. Evaporation of the toluene yielded an additional crop of product. The yield, after recrystallization from EtOAc/MeOH, was 0.6 g (50%), mp 222–224 °C (with gas evolution) (lit. (*1*) 224–226 °C (decomp.). IR (paraffin oil, cm^{-1}): 1780 (bridge C=O), 1605 (alkene). NMR ($CDCl_3$, from Me_4Si): 8.7 (d, 2H, H_4 and H_5 of phenanthrene ring), 7.0–8.0 (m, 16H, aromatic), 6.40 (br s, 2H, olefinic), 3.0 (s, 4H, methine), 0.40 (d, 1H, J = 10 Hz, methylene), −0.40 (d, 1H, J = 10 Hz, methylene).

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[1] In some cases the adduct is not isolated (*4*); in others the stereochemistry of the adduct is simply stated (*5*) or ignored (*6*).

[2] Phencyclone is recognized as a more reactive diene (in the Diels–Alder reaction) than other cyclopentadienones (*3*).

[3] We typically have the students first prepare **1** and then convert it into **3**. This requires two laboratory periods to accomplish.

[4] The presence of this signal typically arouses the students' curiosity and this can lead to very productive discussions.

[5] Phencyclone can be purchased from Lancaster Synthesis Ltd. (cat. no. 0108) or synthesized from 1,3-diphenyl-2-propanone and 9,10-phenanthrenequinone. The procedure for the synthesis may be obtained from the author.

[6] Depending on the type of plate used, visualization of the developed plate can be accomplished by either exposing the dried plate to iodine vapors or to an ultraviolet light source.

Acknowledgment

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Literature Cited

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4. See, for example: (a) Fieser, L. F.; Williamson, K. L. *Organic Experiments,* 6th ed.; Heath: Lexington, MA, 1987; p 352. (b) Pavia, D.; Lampman, G. M.; Kriz, G. S. *Introduction to Organic Laboratory Techniques,* 3rd ed.; Saunders: Philadelphia, 1988; p 379.
5. See, for example: Eaton, D. C. *Laboratory Investigations in Organic Chemistry;* McGraw–Hill: New York, 1989; p 400.
6. See, for example: Roberts, R. M.; Gilbert, J. C.; Rodewald, L. B.; Wingrove, A. S. *Modern Experimental Organic Chemistry, 4th ed.; Saunders: Philadelphia, 1985; p 389.*