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Pyramidalized Olefins: The Stereospecific Conjugate Reduction of a Bicyclo[2.2.2]octadiene.

Richard Vaughan Williams,* Vijay R. Gadgil, Gary G. Garner, John D. Williams and Ashwani Vij

Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, USA

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Abstract

Structure determination on 2-benzenesulphonyl-3-trimethylsilylbicyclo[2.2.2]octa-2,5-diene (**3**) demonstrates that the double bonds are pyramidalized in the *exo* direction. Nucleophilic attack (conjugate reduction) on **3** parallels this pyramidalization and occurs exclusively from the *endo* face.

Keywords: Bicyclic aliphatic compounds; Reduction; Stereospecificity; Sulfones

In contrast with the *exo* stereoselectivities of norbornenes [1], the few stereoselectivities examined on bicyclo[2.2.2]octadienes show a preference for *endo* attack [2-5]. We recently showed that the double bonds of some bicyclo[2.2.2]octadienes are pyramidal (substituents bent *exo*) [6]. The observed stereoselectivities in norbornenes have been rationalized in a variety of ways [7] including alkene pyramidalization (substituents bent *endo*) [8,9]. In pyramidalized olefins the π-facial selectivity generally parallels the pyramidalization [9-11].

As an example of the utility of **1** as an acetylene equivalent for the Diels-Alder reaction, we converted 1,3-cyclohexadiene to **2** *via* **3** and **4** [12]. We reported that the conjugate reduction of **3** with lithium aluminum hydride (LAH) was stereospecific giving a single product in 94% isolated yield. ^{1}H NMR established a *trans* relationship between the $PhSO_2$ and TMS groups. However, it was not possible to assign which group was *endo* and which *exo*. Based on the above mentioned preference for *endo* attack in the bicyclo[2.2.2]octadienes, we speculated that **4a** was probably the observed product. It is thus of considerable interest to firmly establish the identity of the reduction product and confirm the generality of attack from the *endo* face.

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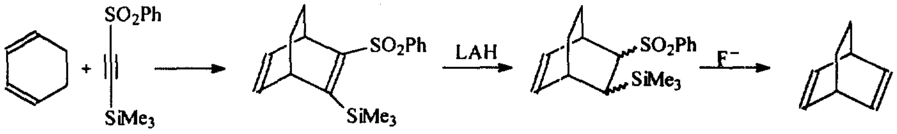
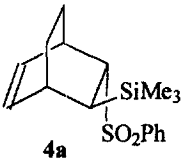
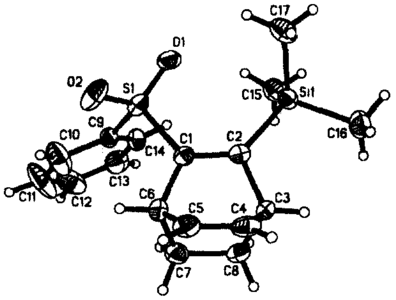


1 **3** **4** **2**

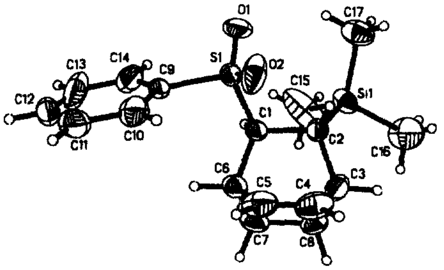
We have now succeeded in growing good crystals of the diene **3** and its reduction product **4** and in obtaining the single crystal X-ray structures of **3** and **4**. As anticipated, the double bonds in **3** are pyramidal with the H, TMS and $PhSO_2$ groups bent in the *exo* direction. The Si-C2-C1-C6 torsion angle is 179.41° (0.25) and the corresponding S-C1-C2-C3 torsion angle is -176.51° (0.24) with the least-squares planes, Si-C2-C1-S and C3-C2-C1-C6, inclined by 2.11° (0.25). The conjugate reduction of **3** proceeds with *endo* attack in complete accord with the stereoselectivity observed in other reactions on the bicyclo[2.2.2]octadiene nucleus [2-5]. Once more, the direction of attack parallels the pyramidalization of the double bond and it would appear that *endo* attack on bicyclo[2.2.2]octadienes is a general phenomenon.



4a



ORTEP drawing of **3**



ORTEP drawing of **4a**

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