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Spiro[2.4]hepta-1,4,6-triene

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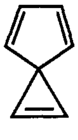
The possibility that double bonds arranged perpendicularly in space might interact by conjugation has generated considerable interest in the synthesis of molecules with geometry suitable for this interaction.[1-6] Spiro[2.4]hepta-1,4,6-triene (**1**) is of interest in this regard since ground state stabilization through spiroconjugation has been predicted on the basis of theoretical calculations.[2-6] Although the syntheses of simple derivatives of spiro[2.4]hepta-1,4,6-triene have been reported,[7] the parent hydrocarbon has not been synthesized.[8] We present here the synthesis and some of the spectral properties of this compound. The starting material **2** was synthesized by photolysis of **3**[7] in the presence of (2-bromovinyl)trimethylsilane.[9] The predominant formation of the *trans* isomer probably reflects the isomeric composition (mostly *trans*) of the starting alkene. Compound **2** can be purified with considerable difficulty by column chromatography. The cyclopropyl protons of the *trans* isomer appear at δ 1.73 ($CHSiMe_3$, d, J = 8 Hz) and 3.85 (CHBr, d, J = 8 Hz) whereas the corresponding signals for the *cis* isomer appear at δ 1.21 (d, J = 10 Hz) and 4.20 (d, J = 10 Hz).



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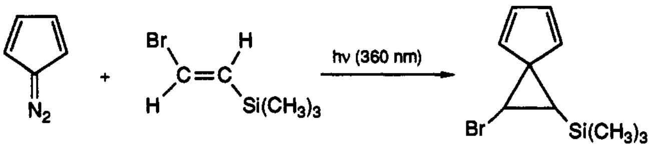


3 **2**

We were surprised to find that **1** can be synthesized readily by treating **2** with CsF in DMSO and that it is remarkably stable. Thus addition of **2** to a solution of CsF in d_6-DMSO at room temperature led to the rapid disappearance of the NMR signals arising from **2** with the concomitant formation of new signals assigned to **1**[10] at δ = 6.01 (narrow multiplet, 2 H), 6.49 (narrow multiplet, 2 H), and a sharp singlet at 7.82 (cyclopropenyl, s, 2 H) (Figure 1). The ^{13}C NMR signals appear at 117.8, 130.9, and 141.4 ppm. A weak signal at 42.0 ppm can be assigned provisionally to the quaternary carbon. ^1H NMR signals could be observed for several hours at room temperature, emphasizing the stability of **1**. A prominent infrared band (cyclopropenyl stretching mode) was observed at 1718 cm^{-1}.

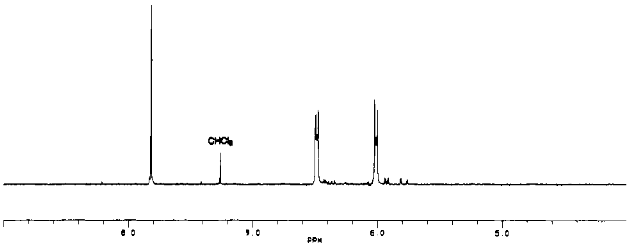
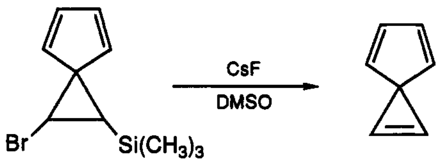
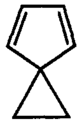


Figure 1. 300-MHz NMR spectrum of spiro[2.4]hepta-1,4,6-triene recorded in $CDCl_3$.



2 **1**

Dürr, Ruge, and Schmidt[7] have compared the UV spectra of model compounds such as **4**, where spiroconjugation is not possible, with those of simple alkyl derivatives of **1** and found that the λ_{max} is shifted by 12–15 nm. This shift is in agreement with earlier theoretically predicted hypsochromic shifts[2-3,5] and was taken as evidence for spiroconjugation. The UV spectrum of **1** recorded in methanol has λ_{max} = 254 nm, identical to λ_{max} exhibited by **4**. Thus the use of the UV spectral data to evaluate spiroconjugation, at least in the case of the parent compound, is inconclusive.



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Studies on the PE spectrum[11] and the X-ray crystal structure of **1** are planned.

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Supplementary Material Available: Detailed experimental procedures describing the synthesis of all compounds (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(7) Dürr, H.; Ruge, B.; Schmidt, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 577. See also: Mitsuhashi, T.; Jones, W. M. *J. Chem. Soc., Chem. Commun.* **1974**, 103.

(8) A previous attempt to synthesize **1** via the elimination of HCl from 1-chlorospiro[2.4]hepta-1,5-diene using potassium *tert*-butoxide in dimethyl sulfoxide led to products arising from cyclopentadienyl anion intermediates. See: Amaro, A. H.; Grohmann, K. *J. Am. Chem. Soc.* **1975**, *97*, 5946.

(9) Commercially available from Aldrich Chemical Company.

(10) Nearly pure **1** could be removed *in vacuo* from the reaction medium.

(11) The PE spectrum of the diethyl derivative of **1** has been reported. In this case a dominant $\pi(b_2)$–$\sigma^*(b_2)$ interaction appears to override any effect of spiroconjugation. See: Bischof, P.; Gleiter, R.; Dürr, H.; Ruge, B.; Herbst, P. *Chem. Ber.* **1976**, *109*, 1412. Computational interpretation of the salient features of the PE spectrum of **1** has also been reported. See: Galasso, V. *J. Mol. Struct.* (THEOCHEM) **1992**, *257*, 181.

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