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Synthesis and Characterization of 1,4-Dichlorospiropentadiene

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Abstract: 1,4-Dichlorospiropentadiene was prepared by vacuum gas-solid elimination of compound 3 over solid $(n\text{-Bu})_4N^+ F^-$ and characterized by ^1H and ^{13}C NMR spectroscopy at -103 °C.

The possibility that double bonds arranged perpendicularly in space might interact by conjugation has generated considerable interest in molecules with geometry suitable for this interaction.[1,2] Spiropentadiene **1** is of interest in this regard and although the parent hydrocarbon has been reported recently,[3] simple derivatives of this ring system have not been reported. Recent theoretical calculations lead to a standard heat of formation of 157.4 kcal/mole for **1**.[4] This is more than twice the experimental heat of formation of 66.2 kcal/mole for cyclopropene. We present here the synthesis and some of the properties of 1,4-dichlorospiropentadiene **2**.

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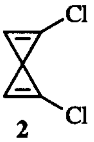

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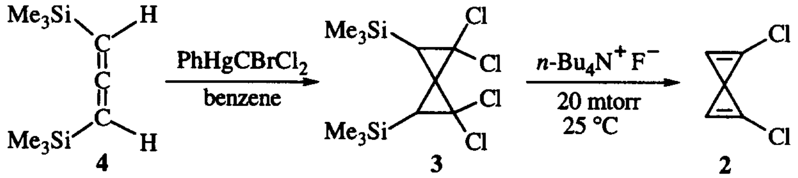
The starting material, compound **3**,[5] was prepared in 75% yield by refluxing a solution of 1,3-trimethylsilylallene[3] **4** and $PhHgCBrCl_2$[6] in benzene for 48 hours. Elimination of trimethylsilylchloride from **3** to yield **2** using solid $n\text{-}Bu_4N^+ F^-$ adsorbed on glass helices as described previously for **1** could be effected *in vacuo* at 25 °C. A ^1H NMR (tetrahydrofuran-*d8*) signal at δ 7.72 could be observed for several minutes at -103 °C. However, this signal disappeared rapidly as the temperature was raised. ^{13}C NMR signals at 54.55 (51.26), 113.84 (112.2), and 123.62 (122.0) ppm are in agreement with chemical shifts calculated (shown in



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parentheses) using MP2/6-311G(d,p) basis set at the MP2/6-311G(d,p) geometry.[7] Optimized bond lengths for **2** calculated at the same level of theory are presented in Figure 1.

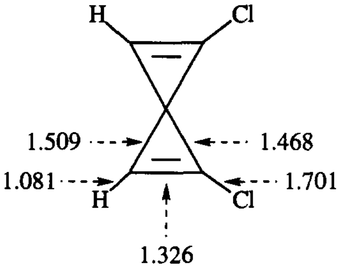
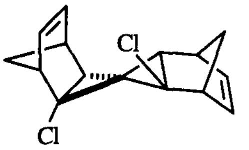


Figure 1. MP2/6-311G(d,p) geometry optimized bond lengths (Å) for **2**.

A mixture of products was formed when the spirene was condensed onto a cold surface coated with cyclopentadiene.[3] Two adducts in which both double bonds of the spirene had reacted (HRMS) were isolated in 8% combined yield by preparative TLC. Although assignment of stereochemistry was not possible, each compound exhibited a simple ^{13}C NMR spectrum consisting of eight lines. Since cyclopropenes normally yield *endo* addition products with cyclopentadiene, the ^{13}C NMR spectra can be rationalized in terms of compounds **5** and **6**. Structural assignments by x-ray crystallography are planned.



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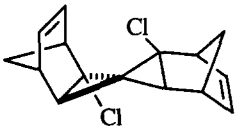

6

Acknowledgment

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References and Notes

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5. ^{1}H NMR ($CDCl_3$): δ 0.25 (s, 18H), 1.49 (s, 2H); ^{13}C NMR: -0.89, 28.45, 43.95, and 66.42 ppm. Anal. Calcd. for $C_{11}H_{20}Cl_4Si_2$: C, 37.72; H, 5.76; Cl, 40.49. Found: C, 37.90; H, 5.48; Cl, 40.28.
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