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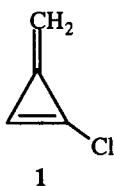
## Synthesis and Characterization of 1-Chloro-3-methylenecyclopropene

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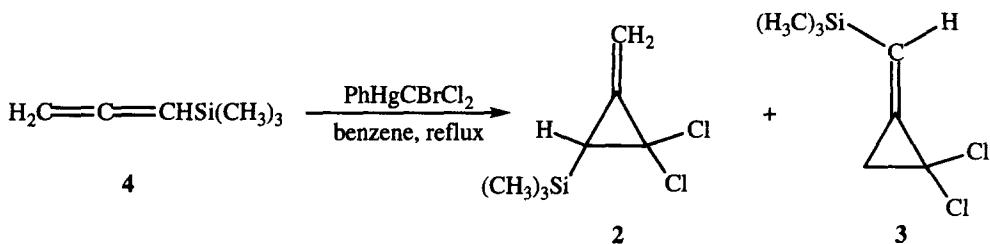
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**Abstract:** 1-Chloro-3-methylenecyclopropene was prepared by vacuum gas-solid elimination of 2,2-dichloro-1-methylene-3-(trimethylsilyl)cyclopropane over solid cesium fluoride and characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy at -103 °C. © 1999 Elsevier Science Ltd. All rights reserved.

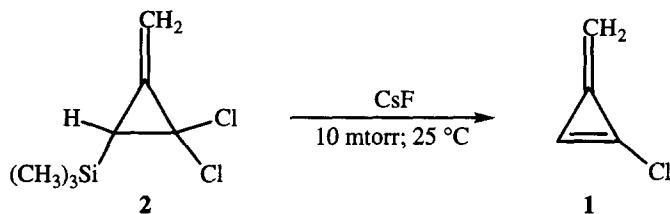
Although moderately stable derivatives of methylenecyclopropene were reported as early as 1964, evidence for the parent hydrocarbon was indirect before 1984 when two syntheses were reported.<sup>1–3</sup> These syntheses relied on the dehydrohalogenation of 1-methylene-2-halocyclopropanes using solid potassium t-butoxide supported on Chromosorb W.<sup>4</sup> More recently, we have found that the vacuum gas-solid reaction procedure (VGSR) using solid fluoride supported on glass helices to eliminate trimethylsilylfluoride from  $\beta$ -halocyclopropylsilanes provides a superior route to strained cycloalkenes.<sup>5</sup> Since these reactions may be carried out at room temperature and without nucleophilic solvents, the method is useful for the synthesis of halogenated reactive intermediates that may be used as synthons. We report here the synthesis of 1-chloro-3-methylenecyclopropene **1**.



2,2-Dichloro-1-methylene-3-(trimethylsilyl)cyclopropane **2** proved to be a satisfactory starting material. This compound could be prepared by the addition of dichlorocarbene to 1-trimethylsilylallene **4**<sup>6</sup> as shown in the equation. Although the desired isomer **2** could only be purified by preparative gas chromatography, the overall yield using phenyl(trihalomethyl)mercury<sup>7</sup> as the carbene source is 78%.



Elimination of trimethylsilylchloride from **2** was achieved using solid CsF adsorbed on glass helices. The cyclopropene is stable below about -60 °C. The <sup>1</sup>H NMR spectrum recorded in tetrahydrofuran-*d*8 exhibits an AB pattern at  $\delta$  3.27 (J = 6.8 Hz, 2H) and a singlet at  $\delta$  8.61 (1H).



The  $^{13}\text{C}$  isotopic chemical shifts were computed using MP2/6-311G(d,p) basis set at the MP2/6-311G(d,p) geometry.<sup>8</sup> The experimental and calculated chemical shifts are presented in Figure 1.

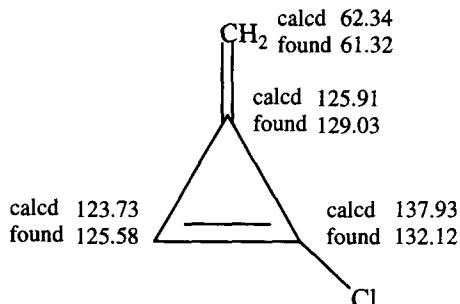
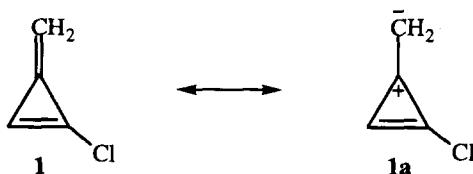


Figure 1. Experimental and Calculated Carbon Chemical Shifts for 1.

The impressive chemical shifts observed for **1** emphasize the polarity of the  $\pi$  electron system, which has been estimated to contribute about one-fifth of the ground state character of methylenecyclopropene.<sup>9</sup>



The optimized bond lengths for **1** have also been calculated using MP2/6-311G(d,p) basis set at the MP2/6-311G(d,p) geometry. These parameters are presented in Figure 2.

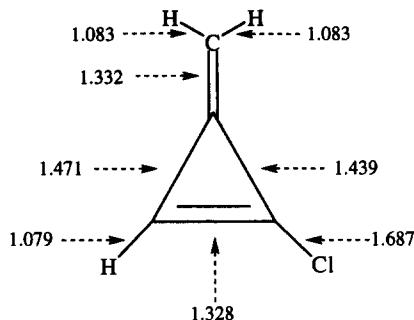
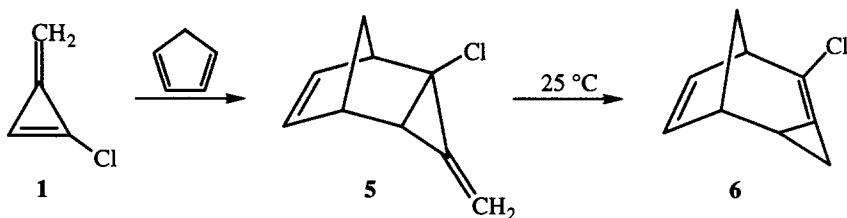
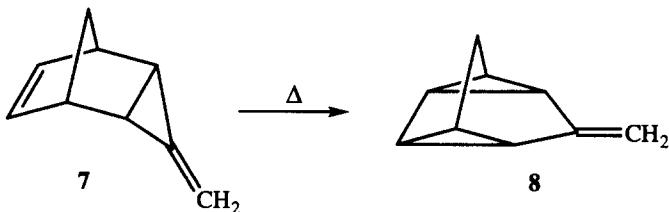


Figure 2. MP2/6-311G(d,p) geometry-optimized bond lengths (Å) for **1**.

1-Chloro-3-methylenecyclopropene can also be generated in solution and trapped with cyclopentadiene. Thus when **2** was added to a solution of cesium fluoride dissolved in dry dimethyl sulfoxide containing freshly distilled cyclopentadiene, a 1:1 adduct was isolated in nearly quantitative yield. HRMS calcd for C9H9<sup>35</sup>Cl m/e 152.0392, found 152.0393; calcd for C9H9<sup>37</sup>Cl m/e 154.0365, found 154.0362. We were surprised to find that this product was not the expected Diels-Alder adduct **5**, but the product **6** resulting from a methylenecyclopropane rearrangement. The <sup>1</sup>H NMR spectrum of **6** exhibits signals at  $\delta$  1.65 (m, 1H), 1.92 (d,  $J$  = 7.6 Hz, 1H), 1.97 (d,  $J$  = 7.6 Hz, 1H), 2.48 (m, 1H), 2.95 (m, 1H), 3.16 (m, 2H) and 6.05 (m, 2H). <sup>13</sup>C signals were observed at 144.8, 136.5, 135.1, 63.1, 54.8, 45.8, 32.4, 29.8 ppm. The quaternary carbon bearing the chlorine substituent was not observed.



The formation of **6** can be explained in terms of the initial Diels-Alder product **5** undergoing a methylenecyclopropane rearrangement. This was somewhat unexpected since thermolysis of **7** has been shown to rearrange to **8**.<sup>10</sup>



Trapping experiments also established that 1-bromo-3-methylenecyclopropene can be generated in solution. When **9** was added to a solution of CsF dissolved in dry DMSO containing freshly distilled cyclopentadiene as described above for **2**, adduct **10** was formed. HRMS calcd for  $C_9H_9^{79}Br$  m/e 195.9888, found 195.9887; calcd for  $C_9H_9^{81}Br$  m/e 197.9868, found 197.9866. The  $^1H$  NMR spectrum of **10** exhibits signals at  $\delta$  1.91 (dd,  $J = 3.2, 6.8$  Hz, 2H), 2.15 (m, 1H), 2.31 (m, 1H), 2.51 (m, 1H), 3.17 (s, 1H), 3.29 (s, 1H) and 6.04 (m, 2H).  $^{13}C$  signals were observed at 143.5, 136.7, 135.8, 63.9, 56.6, 46.6, 35.2, and 32.5 ppm. The quaternary carbon bearing the halogen substituent was not observed.



#### Acknowledgement

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