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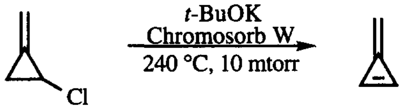
# A New Methylenecyclopropene Synthesis and the Isolation of a Novel Methylenecyclopropene Dimer

**W. E. Billups,* Christoph Gesenberg, and Roger Cole**
Department of Chemistry, Rice University, Houston, TX 77005

**Abstract**: The elimination of trimethylsilylbromide from either *cis* or *trans*-1-methylene-2-bromo-3-trimethylsilylcyclopropane over solid cesium fluoride using the vacuum gas-solid reaction procedure yields methylenecyclopropene. © 1997, Elsevier Science Ltd. All rights reserved.

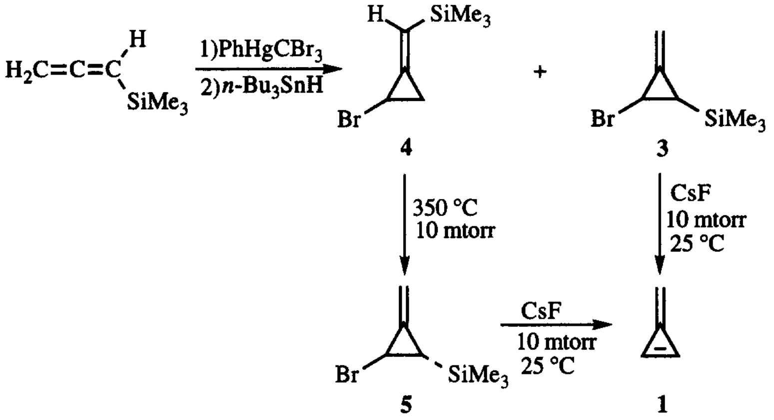
As a member of the $C_4H_4$ family of hydrocarbons, and as the simplest cross-conjugated cyclic hydrocarbon, methylenecyclopropene **1** has been the object of considerable interest.[1] Although moderately stable derivatives of methylenecyclopropene were reported as early as 1964, evidence for the parent hydrocarbon was indirect before 1984 when two independent syntheses were reported.[2-4] These syntheses relied on the dehydrohalogenation[5-7] of 1-methylene-2-halocyclopropanes using solid potassium *t*-butoxide supported on Chromosorb W (vacuum gas-solid reaction procedure)[5] as illustrated for **2** in the equation shown below. We have found that the vacuum gas-solid reaction procedure using solid fluoride supported on glass helices to eliminate trimethylsilylhalide from β-halocyclopropylsilanes provides a more convenient route to many cyclopropenes and we report here the synthesis of methylenecyclopropene using either *cis* or *trans*-1-methylene-2-bromo-3-trimethylsilylcyclopropane as the starting material.



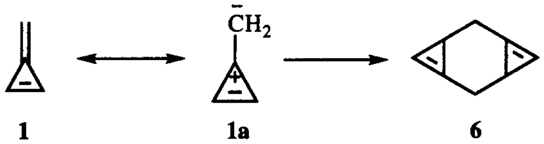
**2** **1**

*cis*-1-Methylene-2-bromo-3-trimethylsilylcyclopropane **3** could be prepared along with the isomer **4** by treating trimethylsilylallene[8] with phenyltribromomethylmercury followed by reduction of the resulting mixture of dibromomethylenecyclopropanes with tri-*n*-butyltin hydride. Thermolysis of **4** at 350°C yielded a mixture of products from which the *trans* isomer **5** could be isolated by preparative gas chromatrography.

Elimination of either **4** or **5** over solid tetra-*n*-butylammonium fluoride (10 mtorr; 25 °C) gave methylenecyclopropene contaminated with methacrolein, suggesting that traces of water remain with the fluoride even after exhaustive pumping. Fortunately, when the elimination was carried over solid cesium fluoride methylenecyclopropene free of the aldehyde could be obtained. These results are summarized in the scheme.



Above -75 °C, the $^1$H NMR signals of methylenecyclopropene began to diminish with the concomitant formation of new signals arising from the head-to-tail dimer **6**. The dipolar structure **1a** undoubtedly leads to this unexpected compound. Although neat **6** decomposed rapidly, $^1$H NMR signals[9] could be observed in tetrahydrofuran for several days at -20 °C.



Studies on the x-ray crystal structure of both methylenecyclopropene and **6** are planned.

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### *References*

1. Billups, W. E.; Moorehead, A. W. In Rappoport, Z. (ed) *The Chemistry of the Cyclopropyl Group*, Wiley: Chichester, 1987, Chapter 24.
2. Billups, W. E.; Lin, L.-J.; Casserly, E. W. *J. Am. Chem. Soc.* **1984**, *106*, 3698.
3. Staley, S. W.; Norden, T. D. *J. Am. Chem. Soc.* **1984**, *106*, 3699.
4. Maier, G.; Hoppe, M.; Lanz, K.; Reisenauer, P. *Tetrahedron Lett.* **1984**, *25*, 5645.
5. Pelletrin, B.; Denis, J. M.; Pfister-Guillouzo, G. *J. Am. Chem. Soc.* **1988**, *110*, 6964.
6. Billups, W. E.; McCord, D. J. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1332.
7. Billups, W. E.; Lin, L.-J. *Tetrahedron* **1986**, *42*, 1575.
8. Hopf, H.; Naujoks, E. *Tetrahedron Lett.* **1978**, *43*, 2739.
9. $^1$H NMR signals were observed at $\delta$ 6.75 (s, 1H), 2.9 (m, 2H), and 1.6 (m, 4H); $^{13}$C signals were observed at 127.7 (quaternary), 105.2 (tertiary), 34.8 (tertiary), and 16.7 (secondary) ppm.

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