

- factory elemental analyses, as well as expected spectral properties.
- (13) (a) T. J. Marks and J. R. Kolb, *J. Am. Chem. Soc.*, **97**, 27 (1975); (b) T. J. Marks, W. J. Kennelly, J. R. Kolb, and L. A. Shimp, *Inorg. Chem.*, **11**, 2540 (1972).
- (14) (a) P. J. Davidson, M. F. Lappert, and R. Pearce, *Acc. Chem. Res.*, **7**, 209 (1974); (b) P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, **2**, 271 (1973); (c) A. Tamaki, S. A. Magennis, and J. K. Kochi, *J. Am. Chem. Soc.*, **96**, 6140 (1974); (d) D. G. Morrell and J. K. Kochi, *ibid.*, **97**, 7262 (1975).
- (15) (a) G. Wilkinson, *Science*, **185**, 109 (1974); (b) G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Am. Chem. Soc.*, **94**, 5258 (1972).
- (16) R. D. Ernst and T. J. Marks, experiments in progress.
- (17) Camille and Henry Dreyfus Teacher-Scholar.
- (18) NSF Predoctoral Fellow, 1974-present.
- (19) Fellow of the Alfred P. Sloan Foundation.

Cynthia A. Secaur, Victor W. Day*¹⁷

Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68508

Richard D. Ernst,¹⁸ William J. Kennelly, Tobin J. Marks*^{17,19}

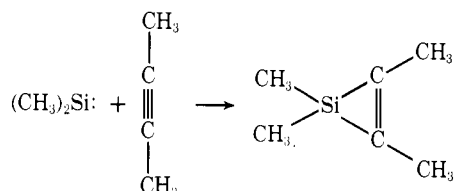
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received February 4, 1976

Tetramethylsilacyclopropene

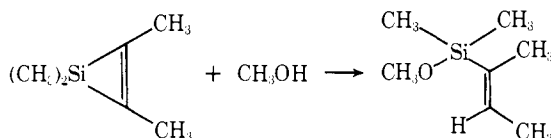
Sir:

In his recent review of the chemistry of silacyclopropanes,¹ Seyferth noted the many attempts which preceded his first successful synthesis of 1972.² There are no recorded failures in the synthesis of silacyclopropenes, for, with the notable exception discussed below, the idea that a silacyclopropene might prove to be stable did not dawn on the chemical world until Seyferth uncovered the unexpected stability of the saturated compound.



We wish to report that tetramethyl-1-silacycloprop-2-ene has been obtained as the addition product of dimethylsilylene $(\text{CH}_3)_2\text{Si}:$ and 2-butyne, and is stable for many weeks at room temperature in the absence of air. Gas-phase flow-pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane at 600 °C and pressures below 100 μ were employed to generate dimethylsilylene³ in the presence of a tenfold excess of 2-butyne.⁴ Absolute yields of ca. 50% were obtained as determined by the methanolysis described below.

Trap-to-trap distillation of the reaction mixture provided solutions containing 10–20% of the silacyclopropene in dimethoxydimethylsilane together with ca. 5% of other compounds.⁵ The proton NMR spectrum of such a solution displays two sharp singlets at δ 0.15 and 1.96 in ratio of peak areas 1:1, and the mass spectrum, obtained by combined gas chromatography-mass spectroscopy indicates a parent peak at m/e 112 and base peak at m/e 97, thus eliminating all alternative structures except $(\text{CH}_3)_2\text{C}=\text{C}=\text{Si}(\text{CH}_3)_2$. This latter structure is not consistent with the evidence afforded by methanolysis of the compound, which proceeds in ca. 80% yield to give *cis*-1,2-dimethylvinyl dimethylmethoxysilane:⁶



The stereochemistry of this reaction was established by independent synthesis of the *cis* and *trans* isomers⁷ and the

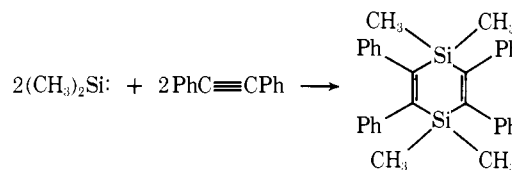
demonstration that the stereoisomers could be distinguished by proton NMR spectroscopy. Use of methanol-OD proved that hydroxyl hydrogen is the source of the vinyl hydrogen in the methanolysis product.

The ¹³C NMR spectrum of product mixtures has also been obtained. The lone resonance whose ¹³C chemical shift is 152 ppm downfield from tetramethylsilane and which remains a singlet in the absence of proton spin decoupling is assigned to the ring carbons and provides strong evidence for the cyclic structure. The *C*-methyl and *Si*-methyl ¹³C resonances are found at 11.9 and –2.4 ppm downfield from Me₄Si with proton coupling constants 125 ± 2 and 120 ± 2 Hz, respectively.

While tetramethylsilacyclopropene is quite stable in the absence of air and moisture, exposure to the laboratory atmosphere initiates an exothermic reaction which destroys the compound within a minute. When a solution containing 20% of the silacyclopropene was heated at 75 °C for 3 h, no diminution of the characteristic NMR signals was observed. When the temperature was raised to 105° the silacyclopropene was destroyed within an hour. The NMR spectrum indicated only polymeric product and no observable 2-butyne. Thus the mode of thermal decomposition of tetramethylsilacyclopropene in dimethoxydimethylsilane solution is *not* the extrusion of dimethylsilylene observed by Seyferth for hexamethylsilacyclopropene.⁸

There is much indirect evidence for the addition of silylene to carbon-carbon multiple bonds forming three-membered silicon-containing rings.^{9,10} We believe, however, that this is the first report of the direct detection by spectroscopic means and the chromatographic separation of the primary silylene adduct.¹

The addition of silylenes to acetylenes has had a checkered history. The claim of Volpin and co-workers to have isolated 1,1-dimethyl-2,3-diphenyl-1-silacycloprop-2-ene from the addition of the dimethylsilylene to diphenylacetylene¹¹ was soon refuted by the demonstration that the product isolated was dimeric:¹²

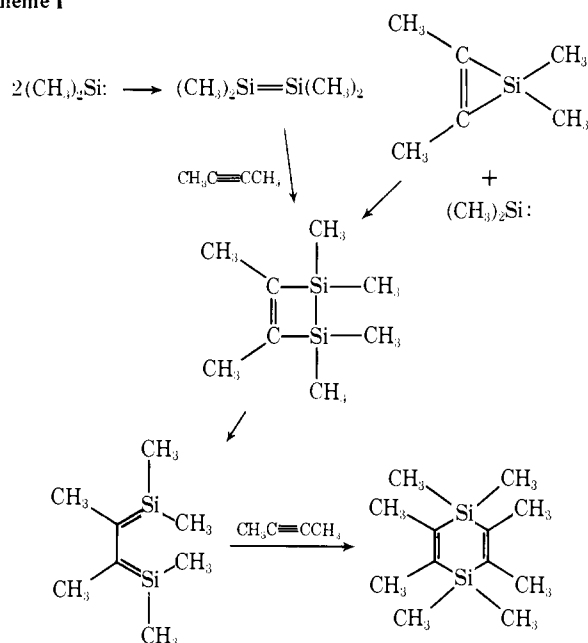


While the proposal that silacyclopropene intermediates may intervene in the formation of disilacyclohexadienes from the reactions of silylenes and acetylene has been widely discussed,¹³ this suggestion has recently been revived¹⁴ to account for the formation of a disilacyclobutene as an isolable product. However, the demonstration by Barton and Kilgour that disilacyclobutenes can act as precursors to disilacyclohexadienes¹⁵ and our recent finding that dimethylsilylene can undergo dimerization^{5b,16} suggest that silacyclopropenes may play no role in the formation of disilacyclohexadienes, if the alternative reaction, Scheme I discussed by Barton¹⁵ proves to be correct.

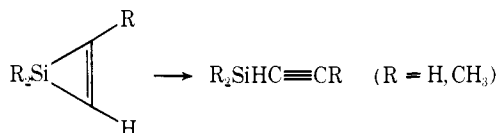
Since the reactions leading to the formation of disilacyclohexadienes are generally carried out as static pyrolyses of the silylene precursors in the liquid phase at temperatures above 150°, conditions under which the lifetime of tetramethylsilacyclopropene is short, the suggestion that the disilacyclobutene arises from silylene addition to a silacyclopropene seems no more likely than the silylene dimerization followed by cycloaddition pictured above.

Nevertheless, evidence has been presented for the formation of silacyclopropenes as fleeting intermediates in the addition of silylenes to acetylenes. The silylacetylenes formed from

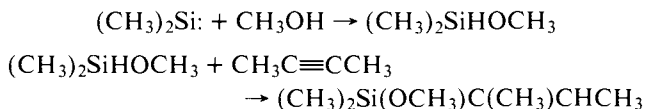
Scheme I



pyrolysis in the gas phase of silylene precursors in the presence of terminal acetylenes have been plausibly attributed to the rearrangement of silacyclopentadiene intermediates.^{17,5b}

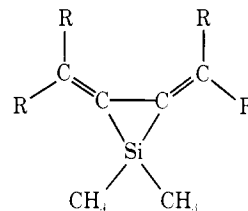


Indeed the subject of this report, tetramethylsilacyclopentadiene, has already been suggested by Atwell and Weyenberg as a transient intermediate responsible for the formation of dimethylvinyl dimethylmethoxysilane when dimethoxytetramethyldisilane is pyrolyzed in the presence of 2-butyne and methanol.¹⁴ Evidence in addition to the product structure was not presented for the intermediacy of a silacyclopentadiene. Since these workers had found that dimethylsilylene reacts with methanol to form dimethylmethoxysilane,¹⁸ addition of this silane to 2-butyne may also occur:



Our finding that tetramethylsilacyclopentadiene does give dimethylvinyl dimethylmethoxysilane upon methanolysis lends support to the intervention of a silacyclopentadiene in the experiments of Atwell and Weyenberg.

Only the barest beginning has been made in the exploration of the chemistry of tetramethylsilacyclopentadiene, but the initial results suggest that this highly strained unsaturated compound possesses unusual chemical stability. The expectation that tetramethylsilacyclopentadiene might be a voracious dienophile is not supported by an experiment in which a fivefold excess of cyclopentadiene was added to a 10% solution of tetramethylsilacyclopentadiene in dimethoxydimethylsilane. After a week at room temperature no reaction occurred. This fact leads us to echo the speculation of Seyferth that $d_{\pi}-p_{\pi}$ bonding may contribute to the stability of an unsaturated three-membered ring containing silicon.¹ A silacyclopentadiene has an added advantage over the di-*exo*-methylene silacyclopentanes discussed by Seyferth in that the endocyclic double bond can form a quasiaromatic system by cyclic interaction with a silicon d orbital.



It is hoped that photoelectron and ²⁹Si spectra will provide additional data which will enable us to determine the electronic structure of tetramethylsilacyclopentadiene and thus define the factors which contribute to its stability. A variety of reactions of tetramethylsilacyclopentadiene is also under investigation. The full exploration of the chemistry of this fascinating compound has now been made feasible by the demonstration that it is stable enough to handle.

Acknowledgment. The authors are grateful to Dr. William R. Sherman and Mr. William Holland for carrying out combined gas chromatography-mass spectrometry in the Department of Psychiatry, Washington University School of Medicine, with financial support from NIH Grant RR-00954. The ¹³C NMR spectra were determined by Dr. Michael Sefcik of the Monsanto Company Corporate Research Department who has also provided valuable experimental and theoretical advice. This work is supported by the United States Energy Research and Development Administration. This is report No. COO-1713-65.

References and Notes

- (1) D. Seyferth, *J. Organomet. Chem.*, **100**, 237 (1975).
- (2) R. L. Lambert, Jr., and D. Seyferth, *J. Am. Chem. Soc.*, **94**, 9246 (1972).
- (3) (a) W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969); (b) P. P. Gaspar and B. J. Herold, "Carbene Chemistry", 2d ed, W. Kirmse, Ed., Academic Press, New York, N.Y., 1971, p 504.
- (4) All pyrolyses employed a seasoned hot zone consisting of a 10 mm i.d. X 12 cm quartz tube. Temperatures are measured at the outer surface of the tube. Products are condensed at 77 K within 2 cm of the hot zone. The disilane vapor flowed into the hot zone at a rate of ca. 200 mg/h. and a total of 400 mg was pyrolyzed in each experiment.
- (5) (a) These include a small residue of unreacted 2-butyne and di- and trimethylsilacyclobutanes which are rearranged products of the dimethylsilylene dimer, tetramethyldisilene $(\text{CH}_3)_2\text{Si}=\text{Si}(\text{CH}_3)_2$. (b) See R. T. Conlin and P. P. Gaspar, *J. Am. Chem. Soc.*, **98**, 868 (1976).
- (6) Upon addition of methanol the two peaks in the proton NMR spectrum which are attributed to tetramethylsilacyclopentadiene are the only ones to disappear and are replaced by the peaks which correspond to authentic *cis*-dimethylvinyl dimethylmethoxysilane.
- (7) Chloroplatinic acid-catalyzed addition of chlorodimethylsilane to 2-butyne followed by methanolysis gave the *cis* isomer while use of benzoyl peroxide catalyst yielded a mixture of the *cis* and *trans* isomers. See R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *J. Am. Chem. Soc.*, **83**, 4385 (1961).
- (8) D. Seyferth and D. C. Annarelli, *J. Am. Chem. Soc.*, **97**, 7162 (1975).
- (9) M. Ishikawa and M. Kumada, *J. Organomet. Chem.*, **83**, C3 (1974).
- (10) M. Ishikawa, F. Ohi, and M. Kumada, *ibid.*, **86**, C23 (1975); R.-J. Hwang, R. T. Conlin, and P. P. Gaspar, *ibid.*, **94**, C39 (1975).
- (11) M. E. Volpin, Yu. D. Koreshkov, V. G. Dulova, and D. N. Kursanov, *Tetrahedron*, **18**, 107 (1962).
- (12) (a) R. West and R. E. Bailey, *J. Am. Chem. Soc.*, **85**, 2871 (1963); (b) F. Johnson, R. S. Gohlke, and W. H. Nasutavicus, *J. Organomet. Chem.*, **3**, 233 (1965); (c) N. G. Bokii and Yu. T. Stuchow, *J. Struct. Chem. (USSR)*, **6**, 548 (1965).
- (13) (a) H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Am. Chem. Soc.*, **86**, 1596 (1964); (b) W. H. Atwell and D. R. Weyenberg, *ibid.*, **90**, 3438 (1968).
- (14) (a) W. H. Atwell and J. G. Uhlmann, *J. Organomet. Chem.*, **52**, C21 (1973); (b) W. H. Atwell and D. R. Weyenberg, *Intra-Sci. Chem. Rep.*, **7**, 139 (1973).
- (15) T. J. Barton and J. A. Kilgour, *J. Am. Chem. Soc.*, **96**, 7150 (1974).
- (16) At low pressures in the gas phase rearrangement of tetramethyldisilene to dimethylsilacyclobutanes is so rapid that cycloaddition to acetylenes does not occur. See ref 5b.
- (17) C. H. Haas and M. A. Ring, *Inorg. Chem.*, **14**, 2253 (1975).
- (18) U.S. Patent No. 3 478 078, "Thermolysis of Alkoxy Disilanes in the Presence of Alcohols to Provide Hydrogen-Substituted Alkoxy monosilanes", Nov 11, 1969.

Robert T. Conlin, Peter P. Gaspar*

Department of Chemistry, Washington University
Saint Louis, Missouri 63130
Received February 23, 1976