with an electrocyclic ring opening to **7** which gives rise to **4**, **5**, and **6** (Scheme I). All the observed products are readily accomodated by these two mechanisms.

Acknowledgment. We thank the National Science Foundation, the National Institutes of Health (CA 23488), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Registry No. 1, 65754-71-4; **2**, 2327-56-2; **2** TCNE adduct, 80485-39-8; **3**, 1961-93-9; **3** TCNE adduct, 80502-01-8; **4**, 68367-49-7; **5**, 90-12-0; **6**, 91-57-6; **11**, 276-32-4; **13**, 264-08-4; bicyclo[6.3.0]undeca-1-(8),2,4,6,9-pentaene, 276-33-5.

Silylene to Silene Thermal Rearrangement. Generation and Rearrangement of Cyclopropylsilylene and Vinylsilylene

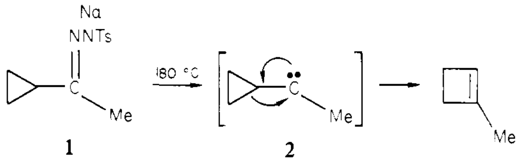
Thomas J. Barton,* Gary T. Burns, William F. Goure, and William D. Wulff

Department of Chemistry
Iowa State University
Ames, Iowa 50011

Received October 26, 1981

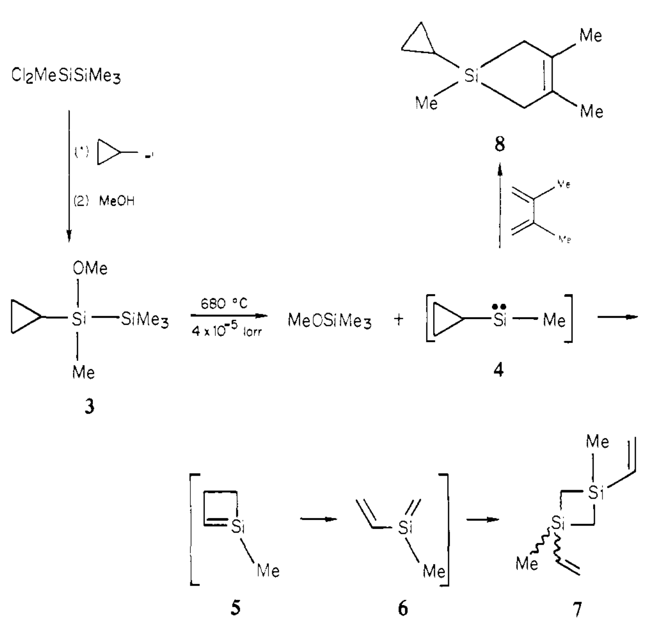
Although the isomerization of carbenes to olefins is a long-established reaction and there are now several documented examples of facile rearrangement of silylcarbenes to silenes ($R_2Si{=}CR'_2$),[1] there exists only a single report[2] of the rearrangement of a silylene (R_2Si:) to a silene.[3] Thus, the photochemically induced isomerization of Me_2Si: to $MeHSi{=}CH_2$[2] is the sole example of a reaction which recent calculations reveal to be essentially thermoneutral.[6]

In an attempt to gain the first definitive evidence for a thermally induced silylene to silene rearrangement, it was decided to generate cyclopropylmethylsilylene (**4**), as thermally generated cyclopropylcarbene (**2**) is known to undergo facile rearrangement via ring expansion. For example, thermolysis of the sodium salt of cyclopropyl methyl ketone tosylhydrazone (**1**) affords 1-methylcyclobutene in 92% yield.[7]



1 2

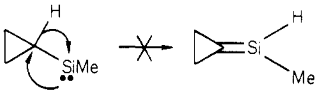
Synthesis of the desired thermal precursor of silylene **4** was accomplished by reaction of 1,1-dichlorotetramethyldisilane and cyclopropyllithium[8] (Et_2O, 0 °C, 160 min) followed by quenching with an equimolar mixture of methanol and pyridine. After distillation [72–75 °C (20 torr)], separation of 1-cyclopropyl-1-methoxytetramethyldisilane (**3**) from 1,1-dicyclopropyltetramethyldisilane was achieved by preparative gas chromatography (GC) [**3**: 30% yield; NMR (CCl_4) δ 0.00 (s, 3H), 0.10 (s, 9H), –0.40 to 0.70 (m, 5H), 3.38 (s, 3H); mass spectrum, *m/e* 188 (14%), 173 (76, 133 (67), 115 (84, 73 (100); calcd for $C_8H_{20}OSi_2$ *m/e* 188.1053, measured *m/e* 188.1055; 30% yield]. Flash vacuum pyrolysis (FVP) of **3** was conducted through a quartz-packed horizontal 36-cm tube at 680 °C (4×10^{-5} torr) with 88% mass balance. The two major products were isolated by preparative GC: trimethylmethoxysilane (99%) and 1,3-dimethyl-1,3-divinyl-1,3-disilacyclobutane (**7**) (42%) as an equal mixture of cis and trans isomers [**7**, NMR (CCl_4) δ 0.14 (apparent t, 4H), 0.28 (s, 3H), 0.30 (s, 3H), 5.35–6.57 (vinyl m, 6H); mass spectrum, *m/e* 168 (24%), 153 (64), 140 (100), 127 (68), 126 (20), 125 (64), 113 (46), 99 (41), 85 (30), 83 (18), 73 (27), 71 (31), 69 (27), 59 (65); calcd for $C_8H_{16}Si_2$ *m/e* 168.0788, measured *m/e* 168.0791].



The most economical mechanistic rationalization for the formation of **7** is α elimination of Me_3SiOMe to form silylene **4**, ring expansion of **4** to 1-methyl-1-silacyclobutene (**5**), ring opening of **5** to vinylsilene **6**, and the usual head-to-tail silene dimerization of **6**. Thus, the conversion of **4** to **5** represents the first example of a thermal silylene to silene rearrangement. Also, the isomerization of **5** to **6** represents the first example of a silene to silene rearrangement.

Evidence that silylene **4** is indeed involved in this remarkably efficient sequence was obtained from the cothermolysis of **3** and 2,3-dimethylbutadiene (500 °C, vertical quartz-packed 36-cm tube, 55-mL/min N_2 flow) to afford 4-cyclopropyl-1,2,4-trimethyl-4-silacyclopentene (**8**), the expected product of addition of **4** to the diene [**8**: 43% yield; NMR (CCl_4) δ -0.44 to 0.70 (m, 5H), 0.07 (s, 3H), 1.20 (br s, 4H), 1.63 (br s, 6H); mass spectrum, *m/e* 166 (56%), 151 (23), 125 (100), 124 (83), 123 (77), 109 (90), 97 (31), 95 (26), 85 (28), 83 (45), 69 (42), 67 (22), 59 (96), 58 (28); calcd for $C_{10}H_{18}Si$ *m/e* 166.1178, measured *m/e* 166.1179].

It is of interest to note that silylene **4** eschews the opportunity for 1,2-hydrogen migration to silicon to form cyclopropylidenesilane **9**. Molecular orbital calculations have revealed that the



4 9

silicon–carbon double bond should be significantly strengthened by d–σ hyperconjugation in the silicon analogue of methylenecyclopropane.[9]

Another carbene that is known to undergo facile rearrangement is vinylcarbene which isomerizes to cyclopropene through intramolecular π addition.[10] Thus, we constructed 1-chloro-1-

---

(1) Barton, T. J.; Hoekman, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 1584.

(2) Drahnek, T. J.; Michl, J.; West, R. *J. Am. Chem.* **1981**, *103*, 1843.

(3) Gaspar[4] has made the interesting suggestion that the origin of 1,3-dimethyl-1,3-disilacyclobutane from generation of Me_2Si: above 600 °C could "in principle" arise from Me_2Si: rearranging to $MeHSi{=}CH_2$ followed by dimerization. However, this mechanism is not demanded.[5]

(4) Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 868.

(5) Wulff, W. D.; Goure, W. F.; Barton, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6236.

(6) Goddard, J. D.; Yoshioka, Y.; Schaeffer, H. F. *J. Am. Chem. Soc. 1980*, *102*, 7644.

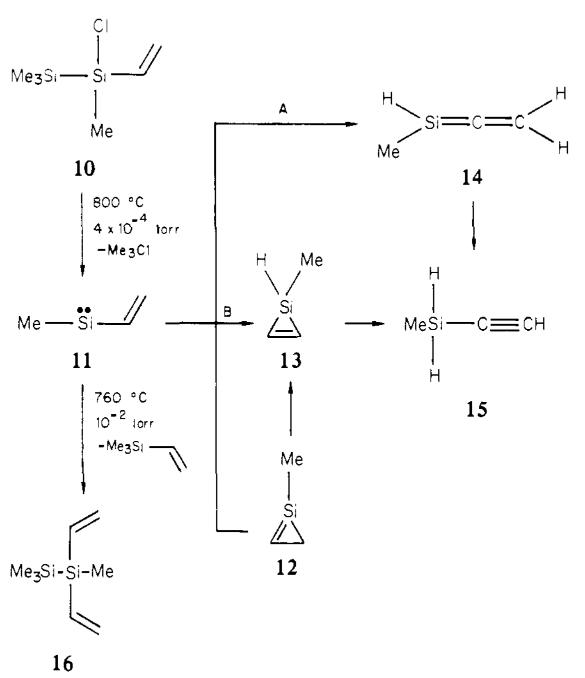
(7) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002.

(8) Seyferth, D.; Cohen, H. M. *J. Organomet. Chem.* **1963**, *1*, 15.

(9) Mollère, P. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 3680.

0002-7863/82/1504-1149$01.25/0

vinyltetramethyldisilane (**10**) by reaction of 1,1-dichlorotetramethyldisilane and 1 equiv of vinylmagnesium chloride in THF [**10**: 42% by NMR, 17% GC isolated; NMR δ 0.17 (s, 9H), 0.5 (s, 3H), 6.08 (m, 3H); mass spectrum, *m/e* 180 (0.9%), 178 (2.4), 165 (2.2), 163 (4.6), 155 (38), 85 (69), 73 (1 00); calcd for $C_6H_{15}Si_2Cl$ *m/e* 178.0401, measured *m/e* 178.0401].



FVP of **10** [800 °C 4 × 10^{-4} torr)] afforded two products of α elimination, trimethylchlorosilane (30%) and trimethylvinylsilane (11.5%), along with a surprising third major product, ethynylmethylsilane [**15**: 11.9% (39% based on Me_3SiCl); NMR of SiMe obscured by impurity absorbtions, δ 2.27 (t, 1H, J = 1 Hz, collapses to s with $h\nu$ at δ 4.05, C≡CH), 4.05 (d of q, 2H, J = 4.5 and 1 Hz, $h\nu$ at δ 2.27 collapses to q; mass spectrum, *m/e* 70 (27%), 69 (24), 68 (7), 55 (100), 54 (17), 53 (42); both NMR and mass spectrum matched those of an authentic sample of **15** prepared from LAH reduction of dichloroethynylsilane]. Ethynylsilane (**15**) was also observed (by NMR spectrometry among the products from the FVP [760 °C (10^{-2} torr)] of 1,1-divinyltetramethyldisilane (**16**). The major product of this pyrolysis is trimethyl vinylsilane arising from α elimination to afford vinylsilylene **11**. Thus, it seems likely that ethynylsilane (**15**) arises from isomerization of silylene **11**. It is reasonable to suggest that the isomerization is initiated by intramolecular π addition to form 1-silacyclopropene **12** (the known carbene mechanism)[10] followed by (disallowed) hydrogen migration to silicon.

Indeed, the formation of silylacetylenes from the gas-phase copyrolyses of silylene precursors and terminal acetylenes has previously been argued to involve rearrangement of intermediate silacyclopropenes.[4,11] Two other routes are possible: (A) α-C–H insertion to form silaallene **14** followed by 1,3-hydrogen migration; (B) β-C–H insertion to directly form silirene **13**. Neither of these paths has ever been observed for vinylcarbenes.[12] Thus, it is likely, but not demanded, that the isomerization of **11** to **15** involves the intermediacy of silirene **12** and represents another silylene to silene rearrangement. Labeling experiments and alternant methods for generation of **11** must now be performed to clear up the admittedly speculative route for the **11** to **15** isomerization.

Currently we are attempting extensions of these rearrangements, including the obvious cyclopropenylsilylene to silacyclobutadiene isomerization.

Acknowledgment. The support of this research by the National Science Foundation is gratefully acknowledged.

Registry No. 1, 80631-65-8; **3**, 80631-66-9; **5**, 80631-67-0; **6**, 80631-68-1; *cis*-**7**, 74045-33-3; *trans*-**7**, 74045-45-7; **8**, 80631-69-2; **10**, 80631-70-5; **12**, 80631-71-6; **15**, 16689-89-7; **16**, 70745-07-2; 1-methylcyclobutene, 1489-60-7; 1,1-dichlorotetramethyldisilane, 4518-99-4; trimethylmethoxysilane, 1825-61-2; cyclopropyllithium, 3002-94-6; 2,3-dimethylbutadiene, 513-81-5; vinyl chloride, 75-01-4; trimethylchlorosilane, 75-77-4; trimethylvinylsilane, 754-05-2.

---

(10) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1971; pp 328–332.

(11) Haas, C. H.; Ring, M. A. *Inorg. Chem.* **1975**, *14*, 2553.

(12) See ref 10. The π-addition mechanism is obvious from the fact that cyclopropenes are best formed from β,β-disubstituted vinylcarbenes.

Cyclotrisilane $(R_2Si)_3$ and Disilene $(R_2Si{=}SiR_2)$ Systems: Synthesis and Characterization

Satoru Masamune,*[†] Yuji Hanzawa, Shu Murakami,
Thomas Bally,[‡] and John F. Blount*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
and Hoffmann-La Roche
Nutley, New Jersey 07110

Received December 7, 1981

Recent renewed activities in cyclopolysilane chemistry[1] concern the nature of silicon–silicon bonding in small ring systems.[1,2] Thus, the degree of electron delocalization in the yet unknown cyclotrisilane (trisilacyclopropane) system (**1**) attracts special interest.[3] Its physical and chemical properties would be unique in many ways. While a large number of cyclopolysilanes $(CR_2Si)_n$ with $n \geq 4$ are available through the reaction of a dichlorosilane with an appropriate electron donor,[1,4] the thus far unsuccessful construction of this smallest ring system has been attributed (tacitly) to the expected high instability and/or reactivity owing to the ring strain intrinsic to **1**.[5] Apparently, the careful selection of both the silicon substituents (R's) and the electron donor is of vital importance in the synthesis. Using an approach similar, in principle, to that adopted earlier in the synthesis of an isolable cyclobutadiene derivative,[6] we have now achieved the first synthesis of a crystalline derivative, hexa-2,6-dimethylphenylcyclotrisilane (**1a**). We present herein not only unequivocal evidence for the structure of this new compound, but also we describe its remarkable reaction, a near-quantitative photochemical conversion into the corresponding disilene (Si=Si) derivative (**2**),[7,8] yet an-

---

[†] To whom correspondence should be addressed at the Massachusetts Institute of Technology.

[‡] Institut de Chimie Physique, Universite de Fribourg Suisse.

(1) For the synthesis of peralkylpolycyclosilanes, see: (a) Watanabe, H.; Muraoka, T.; Kageyama, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, C45. (b) Watanabe, H.; Muraoka, T.; Kohara, Y.; Nagai, Y. *Chem. Lett.* **1980**, 735. (c) Carlson, C. W.; Matsumura, K.; West, R. *J. Organomet. Chem.* **1980**, *194*, C5. (d) Biernbaum, M.; West, R. *Ibid.* **1977**, *131*, 179 and references quoted therein. (e) For a review of perarylpolycyclosilanes, see: Gilman, H.; Schwebke, G. L. *Adv. Organomet. Chem.* **1964**, *1*, 89.

(2) For the properties of peralkylpolycyclosilanes, see: (a) West, R.; Carberry, E.; *Science* **1975**, *189*, 179. (b) Brough, L. F.; West, R. *J. Organomet. Chem.* **1980**, *194*, 139 and the preceding articles of this series.

(3) The system is mentioned from time to time in the literature. For instance, see: Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51.

(4) The method was originated by: Kipping, F. S. *Proc. Chem. Soc.* **1911**, *27*, 143.

(5) Even cyclotetrasilanes $(R_2Si)_4$ react readily with oxygen if the substituents are small, e.g., R = CH_3. See: Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325.

(6) (a) Masamune, S.; Nakamura, N.; Suda, M. Ona, H. *J. Am. Chem. Soc.* **1973**, *95*, 8481. (b) Delbaere, L. T. J.; James, M. N. G.; Nakamura, N.; Masamune, S. *Ibid.* **1975**, *97*, 1973. (c) Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343.