g of D-glucose, and [6-^{14}C]glucose (1.74 × 10^8 dpm) in 24.0 mL of distilled water was dispensed equally via a Millex disposable sterile filtration unit to the 24 flasks. After incubation for an additional 42 h, the culture was filtered through Celite. The pH of the filtrate was adjusted to 2.4 with 50% H_2SO_4, and the solution was extracted three times with 500 mL of chloroform. After drying of the extracts over sodium sulfate and evaporation of the solvent, the resulting brown oil (0.34 g) was dissolved in 25 mL of dry ether and filtered. An ethereal solution of distilled benzyl amine was added to the filtrate until no further precipitation was apparent. The mixture was allowed to stand for 15 min at room temperature, the ethereal supernatant was drawn off, and the amorphous benzylammonium salts were washed several times with dry ether. The acids were then regenerated by dissolving the salts in chloroform, shaking with concentrated phosphate buffer, pH 2.75, and then extracting the aqueous phase with two additional portions of chloroform. The combined organic extracts were washed once with saturated sodium chloride, dried over sodium sulfate, and evaporated to give 0.20 g of oil. This mixture of acids was dissolved in 1:1 tetrahydrofuran–ether and methylated at 0 °C for 5 min with diazomethane, freshly generated from *N*-nitrosomethylurea and potassium hydroxide in ether at 0 °C. The reaction was quenched by addition of a small amount of etheral acetic acid, and the solution was washed three times with saturated sodium bicarbonate and once with saturated sodium chloride, dried over sodium sulfate, and evaporated to yield 0.16 g of oil.

Initial separation of this oil into its components was effected by PLC on silica gel (buffered to pH 7, 2:1 benzene–ethyl acetate). Two major zones were eluted, a less polar, R_f 0.65, containing pentalenolactone methyl ester (0.054 g), and a more polar R_f 0.07–0.46, containing pentalenic acid methyl ester, (0.062 g). The less polar fraction was further enriched by a second PLC (2:1 benzene–ethyl acetate) to give two fractions, R_f 0.65 (0.045 g) and R_f 0.55 (0.009 g). The latter was combined with the more polar fraction from the previous separation while the former was subjected to purification on four 20 × 20 cm analytical silica gel plates (19:1 benzene–ethyl acetate, five developments) to yield 18.2 mg of pure pentalenolactone methyl ester[2,3] and 4.6 mg of pentalenolactone E methyl ester.[11]

Labeled pentalenic acid methyl ester was obtained by further purification of the 0.070 mg from the more polar fraction by PLC (2:1 benzene–ethyl acetate), excising the band R_f 0.38–0.44, to give 27.1 mg of oil which was resubmitted to PLC (20:1 benzene–ethyl acetate, four developments) to yield 15.3 mg of **5**-Me. Final purification was effected by high-pressure LC using a 3.9 mm id × 30 cm column of μ-Bondapak CN, eluted with 8:1 hexanes–chloroform (2.5 mL/min, $k' = 4$), yielding finally 13.1 mg of pentalenic acid methyl ester.[10]

Incorporation of D-[6-$^2H_2$]Glucose. A solution of 3.0 g of D[-6-$^2H_2$]-glucose and 4.0 × 10^7 dpm [6-^{14}C]glucose was administered to 2.4 L of a 30-h fermentative culture of *Steptomyces* UC5319 incubated as described above in 24 Delong flasks at 27 °C. After an additional 42 h at 27 °C and 300 rpm, the cultures were extracted and the crude mixture of methyl esters (0.187 g), was isolated as before. Separation into the individual components was achieved by flash column chromatography on 0.040–0.063 mm Merck silica gel 60 (5:1 benzene–ethyl acetate), thick-layer PLC (3:1 benzene–ethyl acetate), and thin-layer PLC (20:1 benzene–ethyl acetate, four developments). Pentalenic acid methyl ester was further purified by high-pressure LC on μ-Bondapak CN, as above: pentalenolactone methyl ester, 8.3 mg; pentalenolactone E methyl ester, 9.6 mg; pentalenic acid methyl ester, 15.5 mg. **6**-Me: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.06 (s, 3 H), 1.07 (s, 3 H) (H-14,15), 1.44 (dd, J = 6.2, 12.8 Hz, 1 H, H-1β), 1.74 (d, J = 13.9 Hz, 1 H, H-3b), 1.89 (dd, J = 9.2, 12.8 Hz, 1 H, H-1α), 2.16 (d, J = 13.9 Hz, 1 H, H-3a), 3.29 (m, 2 H, H-5,8), 3.76 (s, 3 H, H-16), 4.31 (m, 2 H, H-12), 5.57 (s, 1 H, H-10a), 5.91 (s, 1 H, H-10b), 6.85 (bs, 1 H, H-7). Irradiation of the signal at δ 1.89 caused the peaks at δ 1.44 to dollapse to a doublet and changed the shape of the multiplet at δ 3.29.

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Communications to the Editor

Evidence for the Isomerization of 1-Methylsilene to Dimethylsilylene

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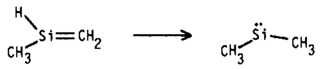
Among the most convenient methods employed to generate simple silaethylenes (silenes) is the thermal fragmentation of appropriately substituted alkylsilacyclobutanes.[1] For example, the formation of 1,1-dimethylsilene and ethylene from the gas-phase pyrolysis of 1,1-dimethylsilacyclobutane has been firmly established by direct detection (mass spectrometry[2] and matrix isolation)[3]and kinetic[4] and chemical trapping studies.[5] Nevertheless, it is surprising that similar attempts to characterize silenes bearing a hydrogen on silicon by using chemical trapping and matrix-isloation techniques have met with only limited success.[6] We now wish to report evidence that such a silene, 1-methylsilaethylene, rapidly isomerizes to dimethylsilylene in the gas phase.



Low-pressure pyrolysis[7] of 1-methylsilacyclobutane[8] at 625 °C

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[1] L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.* **79**, 529 (1979).

[2] L. E. Gusel'nikov, K. S. Konobeevskii, V. M. Vdovin, and N. S. Nametkin, *Dokl. Akad. Nauk SSSR*, **235**, 1086 (1977); W. J. Pietro, S. K. Pollack, and W. J. Hehre, *J. Am. Chem. Soc.*, **101** 7126 (1979); S. Basu, I. M. T. Davidson, R. Laupert, and P. Potzinger, *Ber. Bunsenges. Phys. Chem.*, **83**, 1282 (1979).

[3] A. K. Mal'Tsev, V. N. Khabashesky, and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1193 (1976); O. L. Chapman, C. C. Chang, J. Kolc, M. E. Jung, J. A. Lowe, T. J. Barton, and M. L. Tumey, *J. Am. Chem. Soc.*, **98**, 7844 (1976); M. R. Chedekel, M. Skoglund, R. L. Kreeger, and H. Shechter, *ibid.*, **98**, 7846 (1976).

[4] M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968).

[5] N. S. Nametkin, L. E. Gusel'nikov, R. L. Ushakova, and V. M. Vdovin, *Dokl. Akad. Nauk SSSR*, **201**, 1365 (1971); R. D. Bush, C. M. Golino, G. D. Homer, and L. H. Sommer, *J. Organomet. Chem.*, **80**, 37 (1974).

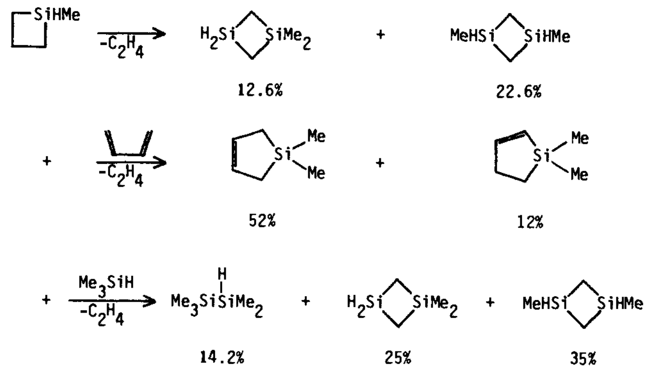
[6] C. M. Golino, R. D. Bush, and L. H. Sommer, *J. Am. Chem. Soc.*, **97**, 7371 (1975); A. K. Mal'tsev, V. N. Khabashesku, and O. M. Nefedov, *Dokl. Akad. Nauk SSSR*, **247**, 383 (1979); N. Auner and J. Grobe, *J. Organomet. Chem.*, **188**, 151 (1980).

[7] All pyrolyses were carried out at pressures of 1–5 torr employing a seasoned hot zone consisting of a 10 mm i.d. x 30 cm quartz tube. Residence time in the hot zone was on the order of tenths of a second and was controlled by $^1/_{32}$-in. constriction placed at the end of the hot zone. Yields were determined relative to the C_2H_4 product or with hexane as an inert internal standard.

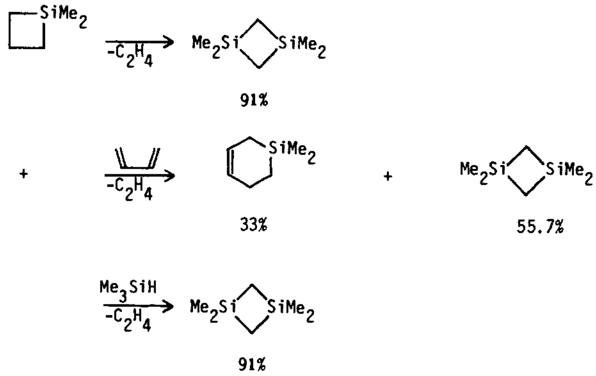
[8] D. Seyferth, R. Damrauer, S. B. Andrews, and S. S. Washburne, *J. Am. Chem. Soc.*, **93**, 3709 (1971).

[9] All compounds reported were fully characterized by their IR, NMR, and mass spectra.

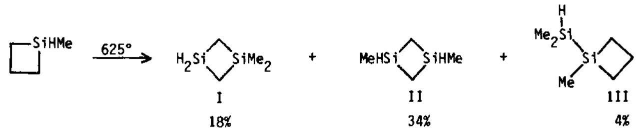
Scheme I. Pyrolysis of 1-Methylsilacyclobutane at 652 °C (~75% Decomposition)



Scheme II. Pyrolysis of 1,1-Dimethylsilacyclobutane at 652 °C (~75% Decomposition)



in a flow system produces chiefly ethylene and small amounts of propylene among the gaseous products. In addition to the two major silicon-containing products, 1,1-dimethyl-1,3-disilacyclobutane (18%) and 1,3-dimethyl-1,3-disilacyclobutane (34%), a small amount of 1-methyl-1-(dimethylsilyl)silacyclobutane (4%) is produced.



Both disilacyclobutane products have previously been reported to be the major products resulting from the gas-phase dimerization of dimethylsilylene.[10] The third product is suggestive of dimethylsilylene insertion into the silicon–hydrogen bond of unreacted 1-methylsilacyclobutane. When the pyrolysis temperature is raised from 625 to 652 °C, both disilacyclobutanes I (12.6%) and II (22.6%) are again formed; however, no III is produced.

In order to elucidate the role played by 1-methylsilene or its isomer dimethylsilylene in the formation of the two disilacyclobutanes and the silylsilacyclobutane in the neat pyrolysis, we have examined the pyrolysis of 1-methylsilacyclobutane in the presence of 1,3-butadiene or trimethylsilane (Scheme I). For comparison we also report our results of the thermal decomposition of 1,1-dimethylsilacyclobutane in the absence of a trapping agent and the presence of butadiene or trimethylsilane (Scheme II) under identical reaction conditions.

Butadiene was selected as a trapping agent since it is well-known to undergo efficient but fundamentally different reactions with silaethylenes[5,11] and silylenes.[12] Thus, decomposition of 1,1-dimethylsilacyclobutane in an eightfold excess of butadiene yields the expected [2 + 4] adduct, 1,1-dimethyl-1-silacyclohex-3-ene (33%), along with the dimethylsilene dimer, 1,1,3,3-tetramethyl-1,3-disilacyclobutane (55.7%). Under otherwise identical conditions, decomposition of 1-methylsilacyclobutane in excess butadiene produces no [2 + 4] adduct but instead two isomers, 1,1-dimethyl-1-silacyclopent-3-ene (52%) and 1,1-dimethyl-1-silacyclopent-2-ene (12%), plus trace amounts of disilacyclobutanes. Dimethylsilacyclopentenes are precisely those products previously observed from the addition of dimethylsilylene to butadiene by Atwell and Weyenberg.[13]

The second type of trapping agent, trimethylsilane, is known to intercept silylenes[12] but does not react with silenes.[14] Accordingly, pyrolysis of dimethylsilacyclobutane with an eightfold excess of trimethylsilane affords a single product, the dimethylsilene dimer (91%), in the same yield as the neat pyrolysis of starting material. When methylsilacyclobutane is thermally decomposed in excess trimethylsilane, 1,1,1,2,2-pentamethyldisilane (14.2%) is produced in addition to the disilacyclobutanes I (25%) and II (35.9%) also found in the neat pyrolysis.

Thus, isolation of products characteristic of dimethylsilylene reactions, pentamethyldisilane, dimethylsilacyclopentenes, and dimethyldisilacyclobutanes, from the pyrolysis of the methylsilene precursor, methylsilacyclobutane, provides compelling evidence for silene to silylene isomerization. Furthermore, all products originating from methylsilacyclobutane decomposition are those expected from dimethylsilylene insertions, cycloadditions, and dimerizations. While formation of 1,3-dimethyl-1,3-disilacyclobutane may suggest the apparent dimerization of methylsilene, previous studies have shown that it is the major product resulting from inital dimerization of dimethylsilylene followed by rearrangement of tetramethyldisilene.[10] To date, we have observed no reaction other than isomerization which can be unambiguously attributed to methylsilene.

Our experimental findings lend support to the theoretical results of Gordon[15] and Schaefer[16] on a similar system, namely, the relative thermodynamic stabilities of silaethylene and methylsilylene. Gordon using STO-4G SCF calculations has predicted the singlet state of methylsilylene to be more stable than singlet silaethylene by ~7 kcal/mol, while Schaefer employing SCF–CI–DZ calculations has reported the methylsilylene to lie only slightly below silaethylene. On a more intuitive level it is reasonable to expect that replacement of a methyl group by a hydrogen atom on the partially positive silicon center of silenes[17] may lead to a significant decrease in the π bond energy. For example, the π bond energy in formaldehyde is nearly 7 kcal/mol less than in acetone.[18] To the extent this analogy between silene and carbonyl π bonds is valid, we might expect silaethylene to be even more prone to isomerization than 1-methylsilaethylene.[19] Experiments are in progress to examine this prediction and to provide thermodynamic information concerning this interesting transformation.

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(10) R. T. Conlin and P. P. Gaspar, *J. Am. Chem. Soc.*, **98**, 868 (1976); for a discussion of the mechanism of the tetramethyldisilene rearrangement, see W. D. Wulff, W. F. Goure, and T. J. Barton, *ibid.*, **100**, 6236 (1978).

(11) P. R. Jones, T. F. O. Lim, and R. A. Pierce, *J. Am. Chem. Soc.*, **102**, 4970 (1980).

(12) For recent review of the reactions of silylenes, see P. P. Gaspar in *React. Intermed.*, **1**, 229–277 (1978).

(13) W. H. Atwell and D. R. Weyenberg. *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969); U.S. Patent No. 3 509 191, "Silacyclopentenes and a Method for Making Some", April 28, 1970.

(14) M. Elsheikh, N. R. Pearson, and L. H. Sommer, *J. Am. Chem. Soc.*, **101**, 2491 (1979).

(15) M. S. Gordon, *Chem. Phys. Lett.*, **54**, 9 (1978).

(16) H. F. Schaefer, *Acc. Chem. Res.*, **12**, 288 (1979).

(17) C. M. Golino, R. D. Bush, D. N. Roark, and L. H. Sommer, *J. Organomet. Chem.*, **66**, 29 (1974).

(18) R. Walsh and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 3480 (1968).

(19) We are aware that our results are in serious disagreement with the report of Auner and Grobe[20] who claim spectral observation of both silaethylene and methylsilaethylene at −196 °C.

(20) N. Auner and J. Grobe, *Z. Anorg. Allg. Chem.*, **459**, 15 (1979).