The infrared spectrum of 1,1,2,trimethylsilaethylene[8] shows several interesting features. The olefinic C–H stretch (3020 cm^{-1}) and the deformation modes (795, 645 cm^{-1}) are typical modes for a trisubstituted ethylene. It is not possible to assign a silicon–carbon double bond stretching vibration in the spectrum.[8] Labeling studies will be necessary to make this assignment. The similarities between the infrared spectra of trimethylethylene and 1,1,2-trimethylsilaethylene strongly suggest that the silaethylene is a planar molecule, i.e., that there is a significant barrier to rotation about the silicon–carbon double bond.

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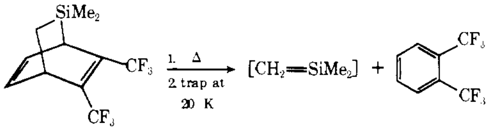
(2) T. J. Barton and C. L. McIntosh, *J. Chem. Soc., Chem. Commun.*, 861 (1972).
(3) The report[2] that thermolysis of 1,1-dimethyl-1-silacyclobutane gives 1,1-dimethyl-1-silaethylene with one observed infrared band at 1407 cm^{-1} (tentatively assigned to the Si═C stretch) suffers from the fact that ethylene (the coproduct) was not observed and that no other identification of the product was obtained. Thermolysis of i[4] gives hexafluoroxylene but no 1407



i

cm^{-1} species. These observations together with the observation that 1,1,2-trimethylsilaethylene reacts with itself above 45 K lead to the conclusion that the previously reported[2] 1407 cm^{-1} species is an artifact of the thermolysis of 1,1-dimethylsilacyclobutane and not 1,1-dimethylsilaethylene.
(4) T. J. Barton and E. Kline, *J. Organomet. Chem.*, **42,** C21 (1972).
(5) Trimethylsilyldiazomethane was prepared by the method of Schöllkopf (personal communication from Professor U. Schöllkopf) and by the method reported in D. Seyferth, H. Menzel, A. W. Dow, and T. C. Flood, *J. Organomet. Chem.*, **44,** 279 (1972).
(6) R. L. Kreeger and H. Shechter, *Tetrahedron Lett.*, 2061 (1975).
(7) T. J. Barton, G. Marquardt, and J. A. Kilgour, *J. Organomet. Chem.*, **85,** 317 (1975).
(8) A theoretical prediction of the infrared spectrum of silaethylene ($H_2Si{=}CH_2$) has been published.[9] Direct correlation of these predictions with the spectrum of 1,1,2-trimethylsilaethylene is not possible.
(9) H. B. Schlegel, S. Wolfe, and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 246 (1975).
(10) The electron spin resonance spectrum of trimethylsilylmethylene has been observed. M. Chedekel and H. Shechter, *J. Am. Chem. Soc.*, following paper in this issue.

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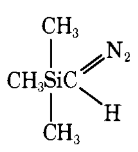
Solid State Chemistry. Discrete Trimethylsilylmethylene

Sir:

Rearrangement and insertion reactions resulting upon pyrolysis and photolysis of diazo compounds are frequently presumed to involve carbene intermediates.[1] Although carbenes have been generated at low temperatures in matrices and their ESR, electronic spectra, spin states, and geometry determined,[2a] the relevance of this information to chemical reactivity, mechanism, and synthesis has yet to be fully established.[2b] We should now like to report the photochemical matrix conversion of trimethylsilyldiazomethane (**1**)[3] to (1) trimethylsilylmethylene (**2**),[4] a ground state triplet, (2) *trans*-1,2-bis(trimethylsilyl)ethylene (**3**),[5] and (3) 2-methyl-2-sila-2-butene (**4**).[4,6] Matrix isolation coupled with ESR and IR techniques[7] allow study of the intimate details of photolytic and thermal transformations of **1** to **2**–**4**.



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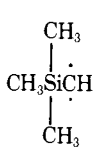

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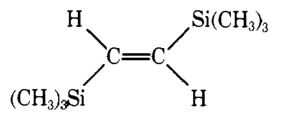

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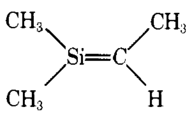

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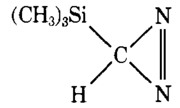
A dilute mixture of **1** and argon, matrix isolated and cooled to 8 K, was irradiated with filtered light of wavelengths greater than 3600 Å.[8] The IR bands of **1** (Figure 1) gradually disappear and are replaced by absorptions (Figure 2) assigned to trimethylsilyldiazirine (**5**).[9] Continued irradiation through the



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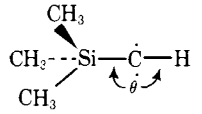
same filter produces no further spectral changes. The ESR spectra of this matrix indicate the presence of a second species with $\Delta m = \pm 1$ transitions typical of a ground state triplet carbene.[10,11] The signals persist for at least 6 h at 4 °C in the absence of light. The zero field splitting parameters, D and E,[11] are 0.613 and 0.00145 cm^{-1}, respectively. Hyperfine structure is observable for several of the transitions and $A_\perp$ is measured to be 25.0 G.

The ESR spectra are interpreted to arise from triplet trimethylsilylmethylene (**2**) in which the carbenic moiety is essentially linear (**6**, $\theta = \sim 180°$). The low E value indicates the high molecular symmetry of **6**. The hyperfine splitting is demonstrated to be due to hydrogen bonded to the divalent carbon of **6** upon determination of the ESR spectrum of α-deuteriotrimethylsilylmethylene (**7**) generated by irradiation of α-deuteriotrimethylsilyldiazomethane, $(CH_3)_3SiCDN_2$. Photolyses of dimethylsilyldiazomethane, $(CH_3)_2SiHCHN_2$, and bis(trimethylsilyl)diazomethane, $[(CH_3)_3Si]_2CN_2$, in matrix yield dimethylsilylmethylene (**8**; $D = 0.628$ cm^{-1}, $E = 0$; $A_{\perp\alpha H} = 24.8$ G; $A_{\perp\beta H} = 11.9$ G) and bis(trimethylsilyl)methylene (**9**; $D = 0.614$ cm^{-1}, $E = 0.002\,52$ cm^{-1}), respectively, for which the ESR parameters reveal to be linear ground state triplets. Preliminary study also indicates that there is a strong angular dependence on the hyperfine of triplet



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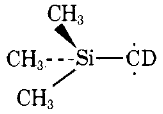

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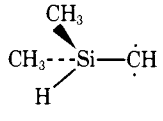

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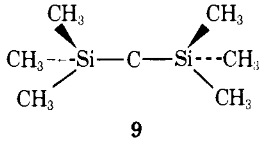

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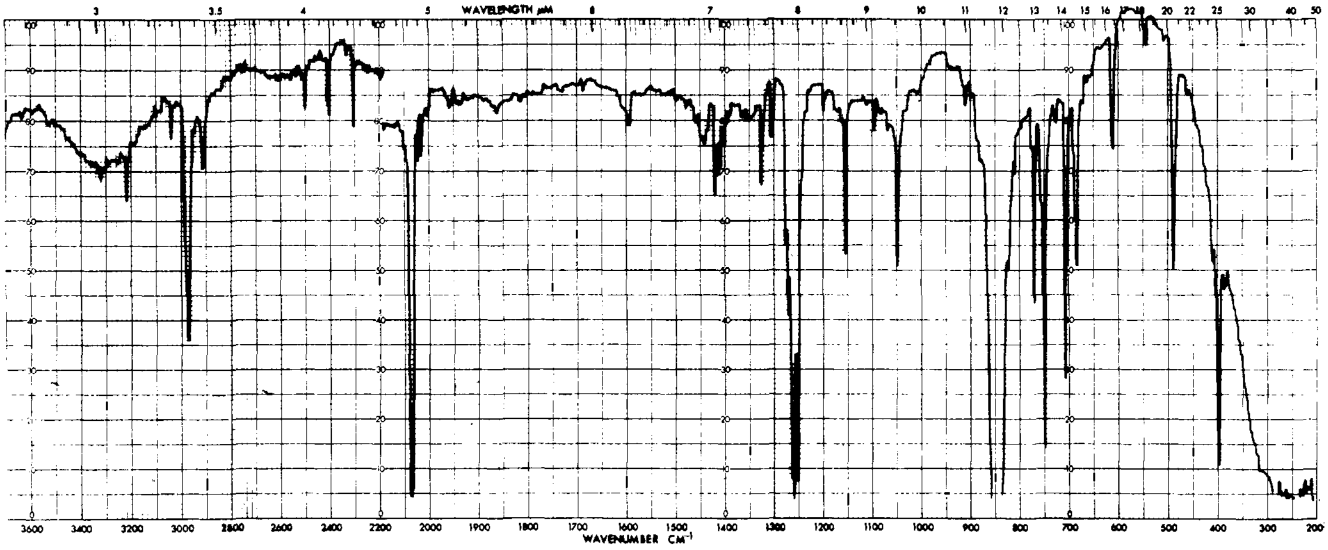


Figure 1. Matrix infrared spectrum of **1**.

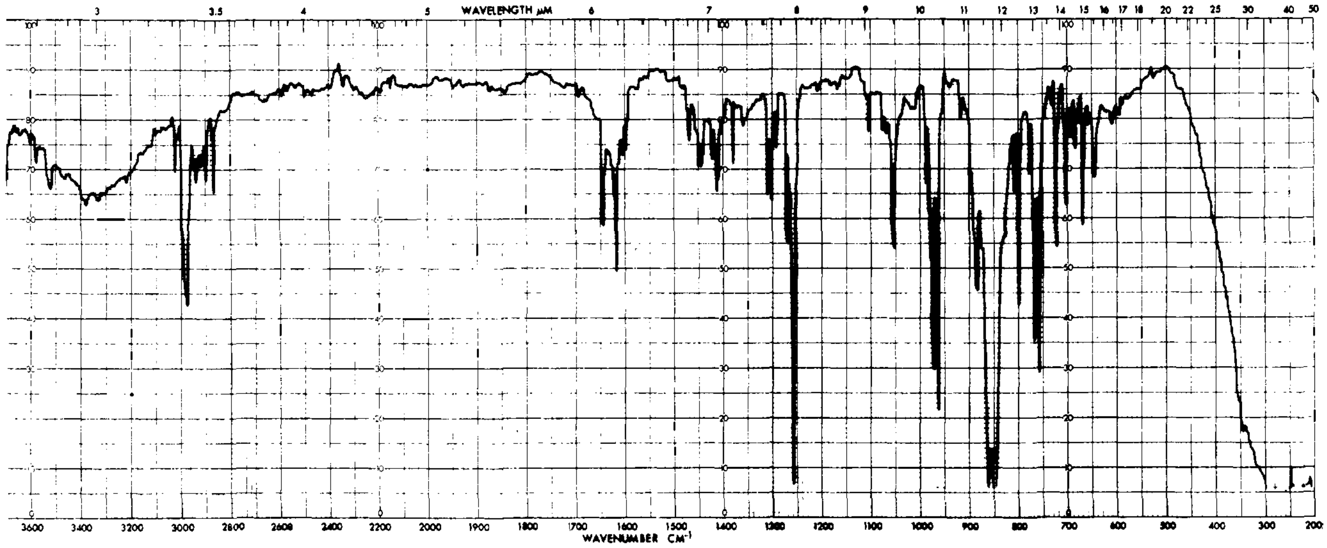


Figure 2. Matrix infrared spectrum of **5**.

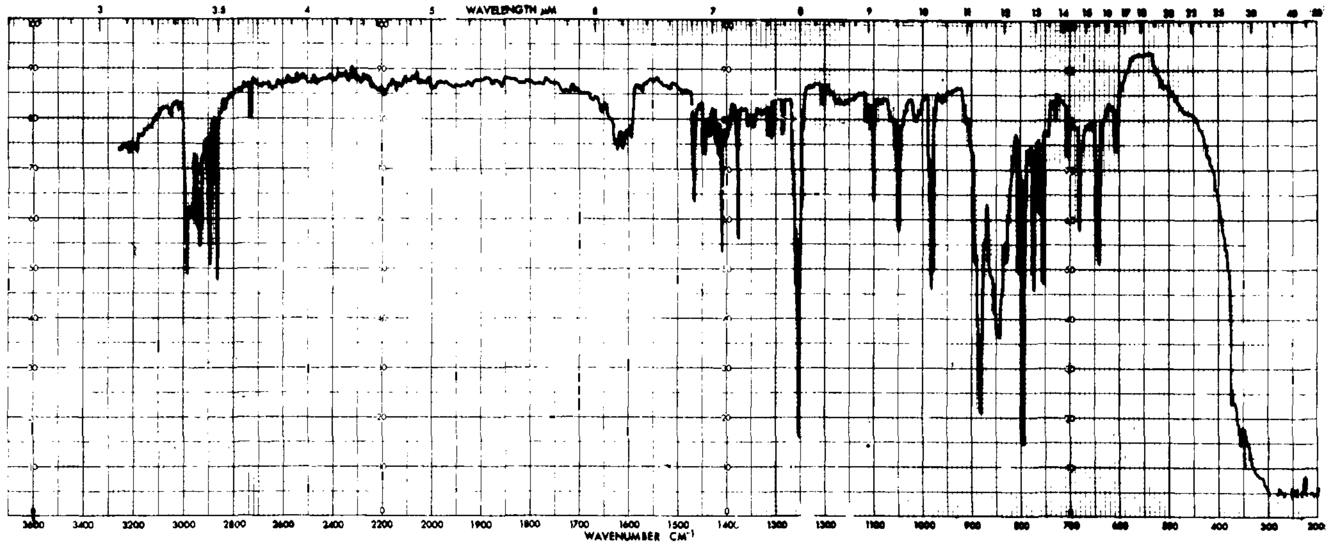
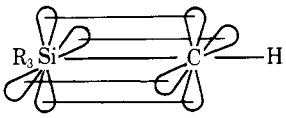
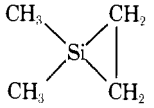


Figure 3. Matrix infrared spectrum of **4**.

methylene (CH_2) itself in that the coupling constants calculated, $A_\perp$, for $\theta = 180$ and 120° are 23.8 and 48.6 G, respectively.[12] The linear stereochemistry and the stabilities of triplet α-silylcarbenes are rationalizable on the basis of advantageous overlap of the mutually perpendicular p orbitals of the carbenes with the vacant d orbitals of adjacent silicon as in **10**.



Carbene **2** is thermally stable between 4 and 40 K. To determine the behavior of **2** at higher temperatures, the matrix was warmed slowly to room temperature and the volatile product pumped away, trapped in liquid nitrogen, and subjected to GLC mass spectral analysis. Ethylene **3** was isolated and there is no evidence for formation of **4** or the intramolecular insertion product, 1,1-dimethyl-1-silacyclopropane (**11**).[13] Silyldiazomethane **1** is not altered even upon storage at >25 °C and thus **3** may be derived by capture of **2** by **1** outside of the matrix photolysis zone or/and by diazirine **5** with evolution of nitrogen.[14]



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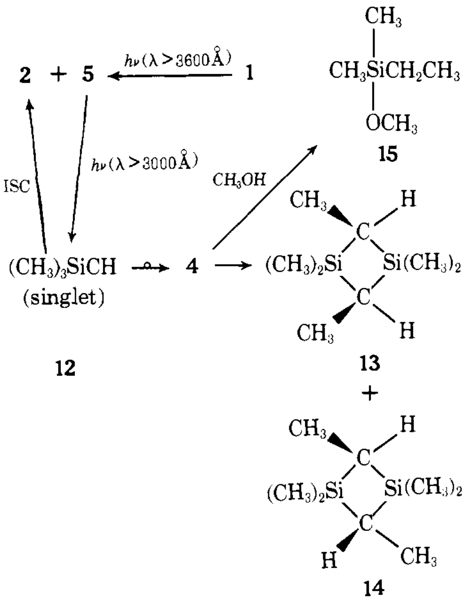
Photolysis of **1** or **5** at 4 °C with light of shorter wavelengths (λ >3000 Å) results in rapid destruction of the IR bands of **1** and/or **5** with formation of at least one set of new bands (Figure 3) assignable to silabutene **4**.[15,16] The infrared spectrum of the matrix product of photolysis of α-deuteriotrimethylsilyldiazomethane, presumably 3-deuterio-2-methyl-2-sila-2-butene, was determined in an attempt to assign the out-of-plane deformation for carbon-hydrogen in **4**. The weak absorption above 3000 cm^{-1} in 3-deuterio-2-methyl-2-sila-2-butene is not changed from that of **4** and therefore is not due to the carbon-hydrogen stretch. The strong band at 641 cm^{-1} in Figure 3 is shifted to 510 cm^{-1} in the spectrum of 3-deuterio-2-methyl-2-sila-2-butene and is thus assigned to the out-of-plane deformation for the lone hydrogen attached to the silicon-carbon double bond. Of significance is that the photolysis products exhibit a sharp band of medium intensity at 1377 cm^{-1} presumably for a *C*-methyl group. Such absorption is absent in **1** or **5** and is indicative of a methyl shift from silicon to carbon. The photolysis product exhibits a weak band at 1466 cm^{-1} but there is no compelling reason to assign it to the stretch of the silicon carbon double bond.[17]

To characterize silabutene **4** further, the matrix was slowly warmed to 20 °C and the volatile products were isolated. Upon comparison with authentic samples,[4b] *cis*- and *trans*-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes (**13** and **14**) were identified, as produced by dimerization of **4** upon destruction of the matrix. If prior to warming the matrix methanol is introduced, dimerization of **4** is suppressed and the major product is ethyldimethylmethoxysilane (**15**).

Scheme I



The present study of **1** as summarized in Scheme I illustrates the potential of solid state methods for investigating reactions of carbenes and for advantageous synthesis of highly reactive species.

Acknowledgment. We acknowledge support of this research by the Research Corporation, the National Science Foundation, The Ohio State University Graduate School, and the mass spectral contributions by R. Weisenberger.

References and Notes

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(2) (a) A. M. Trozzolo and E. Wasserman in ref 1a, Vol. II, p 185; (b) A. M. Trozzolo, *Acc. Chem. Res.*, **1,** 329 (1968).

(3) D. Seyferth, H. Menzel, A. W. Dow, and T. C. Flood, *J. Organomet. Chem.*, **44,** 279 (1972).

(4) (a) Thermolysis (~420 °C) and photolyses (25 °C) of 1 to give products apparently derived from **4** are presumed to involve trimethylsilylmethylene as a singlet (**12**). (b) R. L. Kreeger and H. Shechter, *Tetrahedron Lett.*, 2061 (1975). (c) For decomposition of other α-siladiazo compounds, see T. J. Barton, J. A. Kilgour, R. R. Gallucci, A. J. Rothschild, J. Slutsky, A. D. Wolf, and M. Jones, Jr., *J. Am. Chem. Soc.*, **97,** 657 (1975), and references therein.

(5) (a) Copper-catalyzed decomposition of **1** gives **3** and *cis*-1,2-bis(trimethylsilyl)ethylene;[3,5b] (b) M. F. Lappert and J. Lorbeth, *Chem. Commun.*, 836 (1967); R. N. Haszeldine, D. L. Scott, and A. E. Tipping, *J. Chem. Soc., Perkin Trans. 1*, 1440 (1974).

(6) Methods for generating silaolefins are summarized by C. H. Golino, R. D. Bush, and L. H. Sommer, *J. Am. Chem. Soc.*, **97,** 1957 (1976), and ref 1 therein.

(7) H. E. Hallam, "Vibrational Spectroscopy of Trapped Species", Wiley, New York, N.Y., 1973.

(8) (a) A cutoff filter transmitting light greater than 3600 Å and a Hanovia 1000-W high-pressure Hg–Xe light source were used.

(9) We thank Professor O. L. Chapman, while visiting our laboratory, for pointing out that **5** is the major early product of photolysis of **1**.

(10) P. H. Kasai, *Acc. Chem. Res.*, **4,** 329 (1971).

(11) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41,** 1763 (1964).

(12) R. M. Pitzer and M. R. Chedekel, unpublished results.

(13) (a) In decompositions of 1 in ref 4b, there was no evidence for 11. Pyrolysis of **1** in cetane at 270 °C has since been found to give ethylene (~2%, and possibly dimethylsilylene) as apparently produced by collapse of **11**.[13b] At 440 °C **1** yields ethylene and 3,3,4-trimethyl-3,4-disila-1-pentene along with the products previously reported.[4b] The disilapentene is presumably formed by insertion of dimethylsilylene from **11** into dimethylvinylsilane. (b) D. Seyferth and D. C. Annarelli, *J. Am. Chem. Soc.*, **97,** 7162 (1975).

(14) Reference 1a, p 415–417.

(15) Figure 3 contains absorptions other than for **4**. Hexamethyldisiloxane is an impurity in **1** and its absorption along with that of other trace products is present in Figure 3. Detailed vibrational analysis of the spectrum of **4** is not yet feasible and comparison of present data with that calculated for silaethene[16] is not very revealing.

(16) H. B. Schlegel, S. Wolfe, and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 246 (1975).

(17) T. J. Barton and C. L. McIntosh, *J. Chem. Soc., Chem. Commun.*, 861 (1972), report absorption for a silicon–carbon double bond at 1407 cm^{-1}. Recently this assignment has been retracted; O. L. Chapman and T. J. Barton, private communication.

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Wavelength Dependent Carbonium Ion Formation by Photosolvolysis of Benzoates

Sir:

Benzyl alcohol **1** undergoes photochemical heterolytic C–O bond cleavage by a sequence of electron transfer processes initiated by transfer from the donor *N*,*N*-dimethylaminophenyl group (eq 1).[1] We report here on studies to relocate the