A five-membered cyclic pentoxyacylphosphorane, which has been considered as a biologically important transient species, has now become available. Acyloxyphosphoranes, 3a–3d, are a new class of mixed anhydrides. They can be taken as ortho esters of cyclic acyl phosphate, a high-energy compound in biological metabolism. The nature of the anhydride bond PO₂ is of high energy, and therefore, acyloxyphosphoranes such as 3a–d have a potential for the synthetic application.

In reference to the synthesis of the abovephosphorane compounds, the reactions of 2-phenyl-1,3,2-dioxaphosphorane 11 with acrylic acid 12a and with acrylamide 12b are to be mentioned here. Pentacovalent acyloxy- (14a) and amidophosphoranes (14b) are produced via zwitterions 13a and 13b, respectively.

\[
\begin{align*}
\text{Ph-P=O} + \text{CH}=\text{CHCH}=\text{CH} & \rightarrow \text{Ph-P}=\text{O}
\end{align*}
\]

1,1,2-Trimethylsilalaethylene

Sir:

A variety of presumptive evidence based on chemical trapping suggests that it is possible to generate reactive intermediates containing a formal silicon–carbon double bond. In spite of intense interest in silicon–carbon double bonds, only one report of an attempt to observe such a species spectroscopically is available. We wish to describe the first physical and chemical characterization of a silicon–carbon double bond, 1,1,2-trimethylsilalaethylene.

Trimethylsilidiazomethane provides an attractive precursor for photochemical generation of 1,1,2-trimethylsilalaethylene. During the course of our experiments, Kreeger and Shechter described the room temperature photochemistry and the thermolysis of trimethylsilidiazomethane and provided evidence for the generation of 1,1,2-trimethylsilalaethylene as a transient intermediate.

Irradiation of trimethylsilidiazomethane (1) matrix isolated in argon at 8 K produces a photostationary state involving a new species, trimethylsilidiazirine (2). Trimethylsilidiazirine is also formed on irradiation in a variety of solvents at room temperature (δ = 0.03 (s, 9 H), δ = 0.53 (s, 1 H), CDCl₃; \( \lambda_{max} \text{MeTHF,77K} = 340, 332, 324, 317, \) and 309 nm, Figure 1) of trimethylsilidiazirine can be isolated and is reasonably stable at room temperature. Continued irradiation of the photostationary mixture produced from either 1 or 2 matrix isolated in argon gives 1,1,2-trimethylsilalaethylene (4) via the carbene (3). The infrared spectrum of 1,1,2-trimethylsilalaethylene

[Diagram and additional text regarding the experiments and results]
Figure 2. (A) Infrared spectrum of trimethylsilyldiazomethane (1) matrix isolated in argon at 8 K before irradiation. (B) Sample in A after irradiation for 1070 min (quartz optics). The spectrum is that of 1,1,2-trimethylsilylethylene (4) except for bands marked (+). The bands marked (+) showed different behavior on warming than those of 4. (C) Sample in B after warming to 45 K. The argon is lost in this process. Bands not present in the authentic dimers (5a, b) are marked (+).

matrix isolated in argon at 8 K (3020, 2980, 2965, 2940, 2900, 2870, 1450, 1410, 1370, 1315, 1255, 1120, 978, 883, 808, 795, 712, 708, 645, 608, and 358 cm⁻¹) is shown in Figure 2. The identity of 1,1,2-trimethylsilylethylene (4) is established unambiguously by the thermal dimerization of 4 to the cis- and trans-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes (5a, b)⁷ on warming above 45 K. In this transformation, the disappearance of the infrared bands of 1,1,2-trimethylsilylethylene is concurrent with the appearance of the bands of the dimers (5a, b).

Communications to the Editor
The infrared spectrum of 1,1,2-trimethylsilylethane 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.\(^5\) Labeling studies will be necessary to make this assignment. The similarities between the infrared spectra of trimethylethylene and 1,1,2-trimethylsilylethane 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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References and Notes


(3) The report\(^2\) that thermolysis of 1,1-dimethyl-1-silacyclobutane gives 1,1-dimethyl-1-silacyclobutane 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 \(CH_3\) gives hexafluorocyclohexene but no 1407 cm\(^{-1}\) species. These observations together with the observation that 1,1,2-trimethylsilylethane 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-dimethylsilylethane.


(5) Trimethylsilyldiazomethane was prepared by the method of Scholikopf (personal communication from Professor U. Scholikopf) and by the method reported in D. Seyferth, H. Menzel, A. W. Dow, and T. C. Flood, J. Organomet. Chem., 44, 279 (1972).


(8) A theoretical prediction of the infrared spectrum of silacyclobutane (\(h_2\)Si=CH\(_2\)) has been published.\(^5\) Direct correlation of these predictions with the spectrum of 1,1,2-trimethylsilylethane is not possible.


(10) The electron spin resonance spectrum of trimethylsilylethane has been observed. M. Chedekel and H. Shechter, J. Am. Chem. Soc., following paper in this issue.

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Solid State Chemistry. DiscreteTrimethylsilylmethylene

Sir:

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

A dilute mixture of 1 and argon, matrix isolated and cooled to 8 K, was irradiated with filtered light of wavelengths greater than 3600 \(\AA\).\(^7\) The IR bands of 1 (Figure 1) gradually disappear and are replaced by absorptions (Figure 2) assigned to trimethylsilyldiazirine (5).\(^8\) Continued irradiation through the 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.\(^9\)\(^10\) The signals persist for at least 6 h at 4 \(^\circ\)C in the absence of light. The zero field splitting parameters, \(D\) and \(E\),\(^1\) are 0.613 and 0.00145 cm\(^{-1}\), respectively. Hyperfine structure is observable for several of the transitions and \(A_1\) is measured to be 25.0 G.

The ESR spectra are interpreted to arise from triplet trimethylsilylmethylene (2) in which the carbene moiety is essentially linear (6, \(\theta \approx 180^\circ\)). 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 \(\alpha\)-deuteriotrimethylsilylmethylene (7) generated by irradiation of \(\alpha\)-deuteriotrimethylsilyldiazomethane, (\(CH_3\))\(_3\)SiCD\(_2\)N. Photolyses of dimethylsilyldiazomethane, (\(CH_3\))\(_2\)SiHCHN\(_2\), and bis(trimethylsilyldiazomethane, [(\(CH_3\))\(_3\)Si]C=CN, in matrix yield dimethylsilylmethylene (8; \(D = 0.628 \text{ cm}^{-1}\), \(E = 0\); \(A_\text{CH} = 24.8 \text{ G}\); \(A_\text{CH,CH} = 11.9 \text{ G}\)) and bis(trimethylsilyl)methylene (9; \(D = 0.614 \text{ cm}^{-1}\), \(E = 0.00252 \text{ cm}^{-1}\)), re-