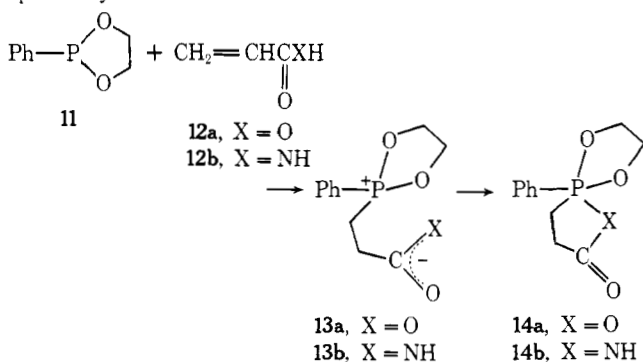


A five-membered cyclic pentaoxyacylphosphorane, which has been considered as a biologically important transient species,² has now become available. Acyloxyphosphoranes, **3a–3d**, are a new class of mixed anhydrides. They can be taken as ortho esters of cyclic acyl phosphate, a high-energy compound in biological metabolism.⁸ The nature of the anhydride bond POC=O is of high energy,^{8b} and therefore, acyloxyphosphoranes such as **3a–d** have a potential for the synthetic application.^{1c}

In reference to the synthesis of the above phosphorane compounds, the reactions of 2-phenyl-1,3,2-dioxaphospholane **11** with acrylic acid **12a** and with acrylamide **12b** are to be mentioned here. Pentavalent acyloxy- (**14a**) and amidophosphoranes (**14b**) are produced via zwitterions **13a** and **13b**, respectively.⁹



Acknowledgment. The authors are indebted to Dr. Y. Chokki, Takeda Pharmaceutical Co., Osaka, Japan, for the ³¹P NMR spectra.

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Takeo Saegusa,* Shiro Kobayashi
Yoshiharu Kimura, Tsunenori Yokoyama

Department of Synthetic Chemistry Faculty of Engineering
Kyoto University Kyoto, Japan

Received June 15, 1976

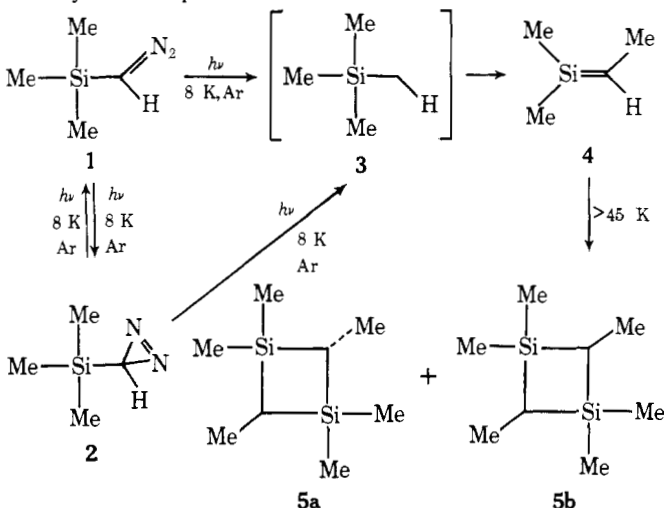
1,1,2-Trimethylsilaethylene

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.¹ In spite of intense interest in silicon-carbon double bonds, only one report of an attempt to observe such a species spectroscopically is available.^{2,3} We wish to describe the first physical and chemical characterization of a silicon-carbon double bond, 1,1,2-trimethylsilaethylene.

Trimethylsilyldiazomethane⁵ provides an attractive precursor for photochemical generation of 1,1,2-trimethylsilaethylene. During the course of our experiments, Kreeger and Shechter⁶ described the room temperature photochemistry and the thermolysis of trimethylsilyldiazomethane and provided evidence for the generation of 1,1,2-trimethylsilaethylene as a transient intermediate.

Irradiation of trimethylsilyldiazomethane (**1**) matrix isolated in argon at 8 K produces a photostationary state involving a new species, trimethylsilyldiazirine (**2**). Trimethylsilyldiazirine 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; λ_{max} ^{2MeTHF, 77K} 340, 332, 324, 317, and 309 nm, Figure 1). Trimethylsilyldiazirine can be isolated and is remarkably stable at room temperature. Continued irradiation of the photostationary mixture produced from either **1** or **2** matrix isolated



in argon gives 1,1,2-trimethylsilaethylene (**4**) via the carbene (**3**).¹⁰ The infrared spectrum of 1,1,2-trimethylsilaethylene

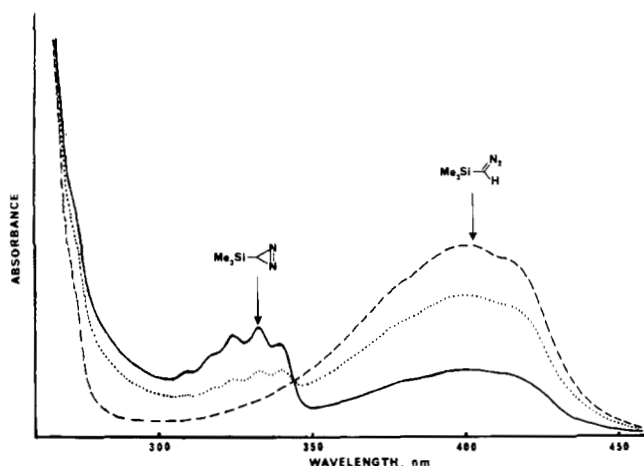


Figure 1. Ultraviolet spectrum of trimethylsilyldiazomethane (**1**) in 3-methylpentane at 77 K: before irradiation (···), after 50 min of irradiation (---), and after 190 min of irradiation ($\lambda > 355$ nm) (—).

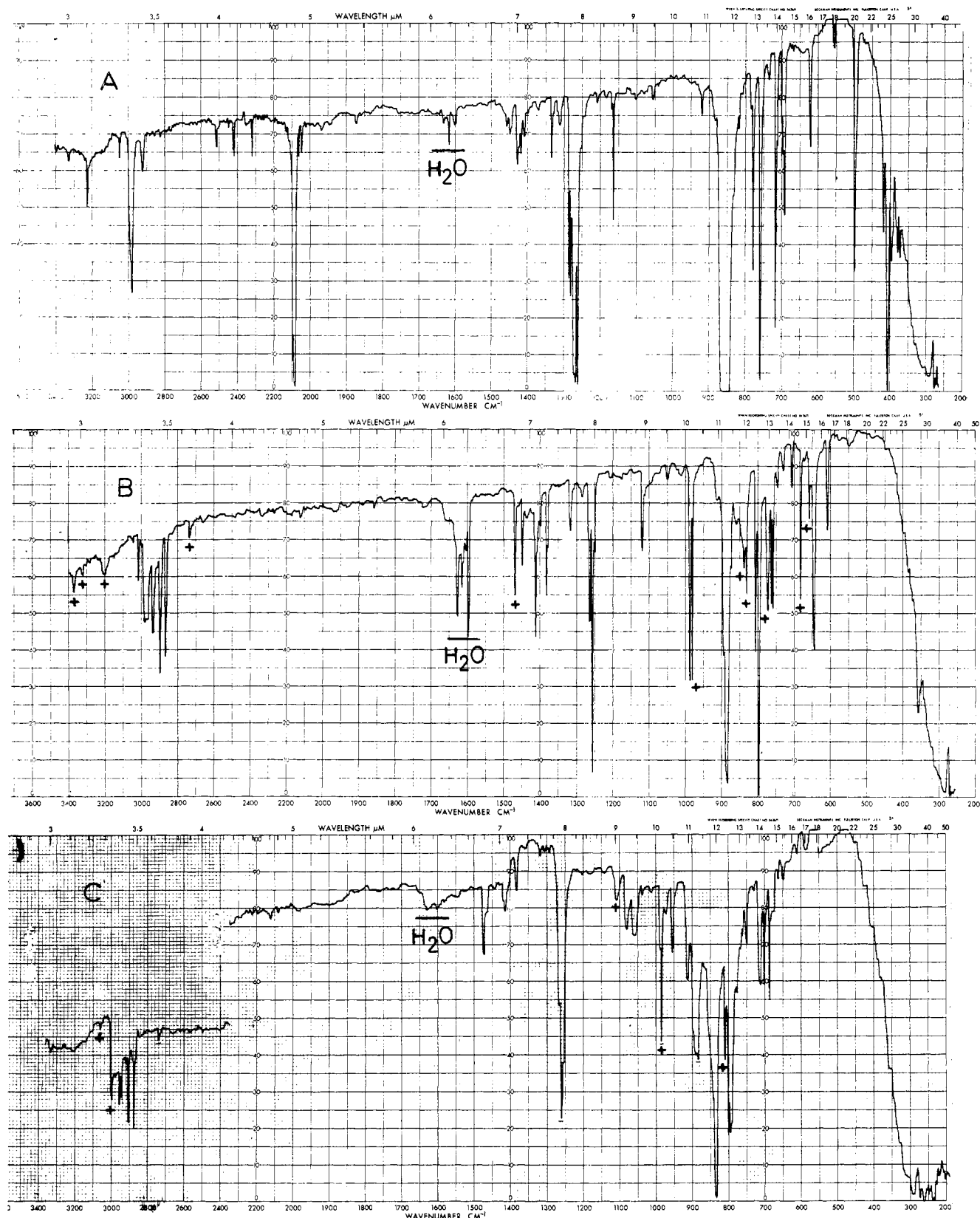


Figure 2. (A) Infrared spectrum of trimethylsilyldiazomethane (**1**) matrix isolated in argon at 8 K before irradiation. (B) Sample in A after irradiation for 1070 min (quartz optics). The spectrum is that of 1,1,2-trimethylsilaethylene (**4**) except for bands marked (+). The bands marked (+) showed 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-trimethylsilaethylene (**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-trimethylsilaethylene is concurrent with the appearance of the bands of the dimers (**5a**, **b**).

The infrared spectrum of 1,1,2-trimethylsilaethylene⁸ shows several interesting features. The olefinic C-H stretch (3020 cm^{-1}) and the deformation modes ($795, 645\text{ cm}^{-1}$) 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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O. L. Chapman,* C.-C. Chang, J. Kolc
M. E. Jung,* J. A. Lowe

Contribution No. 3716, Department of Chemistry
University of California
Los Angeles, California 90024

T. J. Barton,* M. L. Tumej

Department of Chemistry, Iowa State University
Ames, Iowa 50011

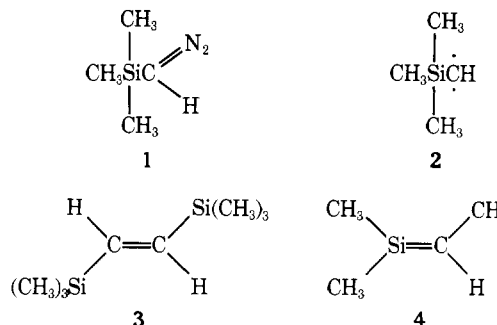
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Solid State Chemistry. Discrete Trimethylsilylmethylene

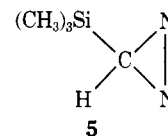
Sir:

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 techniques⁷ allow study of the intimate details of photolytic and thermal transformations of **1** to **2-4**.

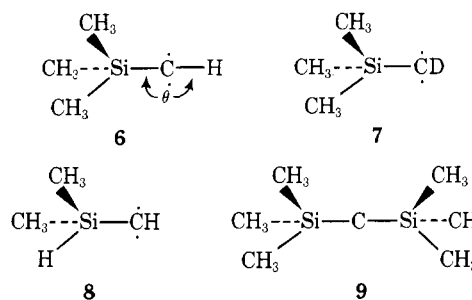


A dilute mixture of **1** and argon, matrix isolated and cooled to 8 K, was irradiated with filtered light of wavelengths greater than 3600 \AA .⁸ The IR bands of **1** (Figure 1) gradually disappear and are replaced by absorptions (Figure 2) assigned to trimethylsilyldiazirine (**5**).⁹ Continued irradiation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



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**, $\theta = \sim 180^\circ$). 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 α -deuteriotrimethylsilylmethylene (**7**) generated by irradiation of α -deuteriotrimethylsilyldiazomethane, $(\text{CH}_3)_3\text{SiCDN}_2$. Photolyses of dimethylsilyldiazomethane, $(\text{CH}_3)_2\text{SiHCHN}_2$, and bis(trimethylsilyl)diazomethane, $[(\text{CH}_3)_3\text{Si}]_2\text{CN}_2$, in matrix yield dimethylsilylmethylene (**8**; $D = 0.628\text{ cm}^{-1}$, $E = 0$; $A_{\perp\alpha\text{H}} = 24.8\text{ G}$; $A_{\perp\beta\text{H}} = 11.9\text{ G}$) and bis(trimethylsilyl)methylene (**9**; $D = 0.614\text{ cm}^{-1}$, $E = 0.00252\text{ cm}^{-1}$), re-



spectively, 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