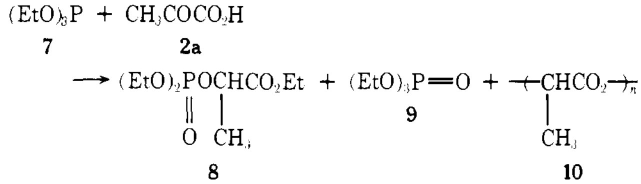
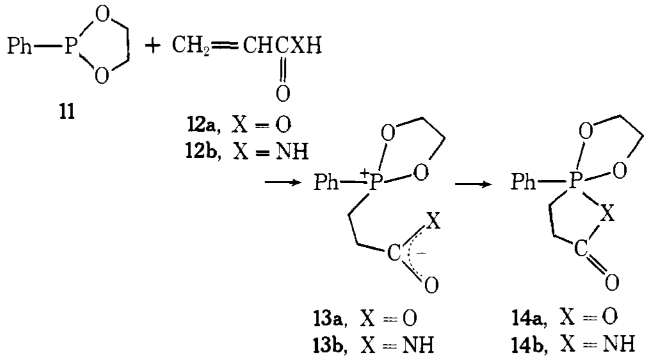


$$\underset{7}{(EtO)_3P} + \underset{2a}{CH_3COCO_2H} \rightarrow \underset{8}{(EtO)_2\overset{\overset{O}{\|}}{P}\underset{\underset{CH_3}{|}}{C}HCO_2Et} + \underset{9}{(EtO)_3P{=}O} + \underset{10}{-\!\!\!\left(\underset{\underset{CH_3}{|}}{C}HCO_2\right)\!\!\!-_n}$$

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.[1e]

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. Pentacovalent 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 ^{31}P NMR spectra.

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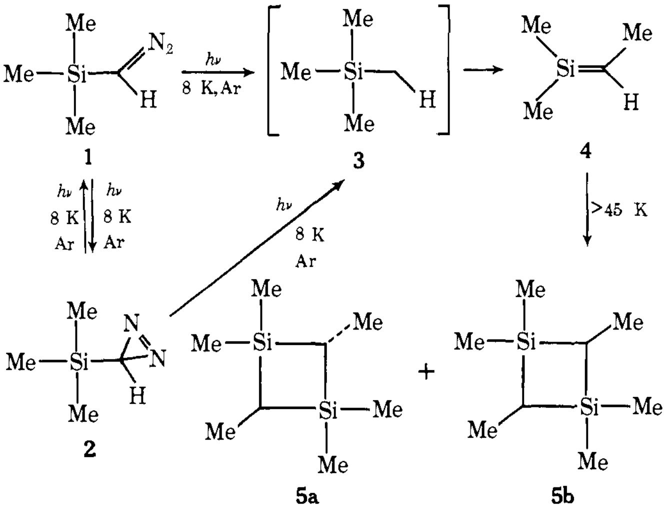
1,1,2-Trimethylsilaethylene

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.

Trimethylsilyldiazomethane[5] provides an attractive precursor for photochemical generation of 1,1,2-trimethylsilaethylene. During the course of our experiments, Kreeger and Shechter[6] 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), $CDCl_3$; $\lambda_{max}^{2MeTHF, 77K}$ 340, 332, 324, 317, and 309 nm, Figure 1). Trimethylsilyldiazirine 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-trimethylsilaethylene (**4**) via the carbene (**3**).[10] The infrared spectrum of 1,1,2-trimethylsilaethylene



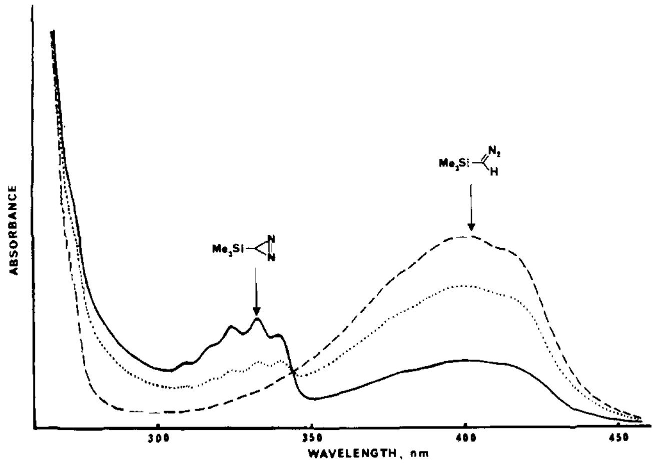


Figure 1. Ultraviolet spectrum of trimethylsilydiazomethane (**1**) in 3-methylpentane at 77 K: before irradiation (- - -), after 50 min of irradiation (· · ·), and after 190 min of irradiation (λ >355 nm) (—).

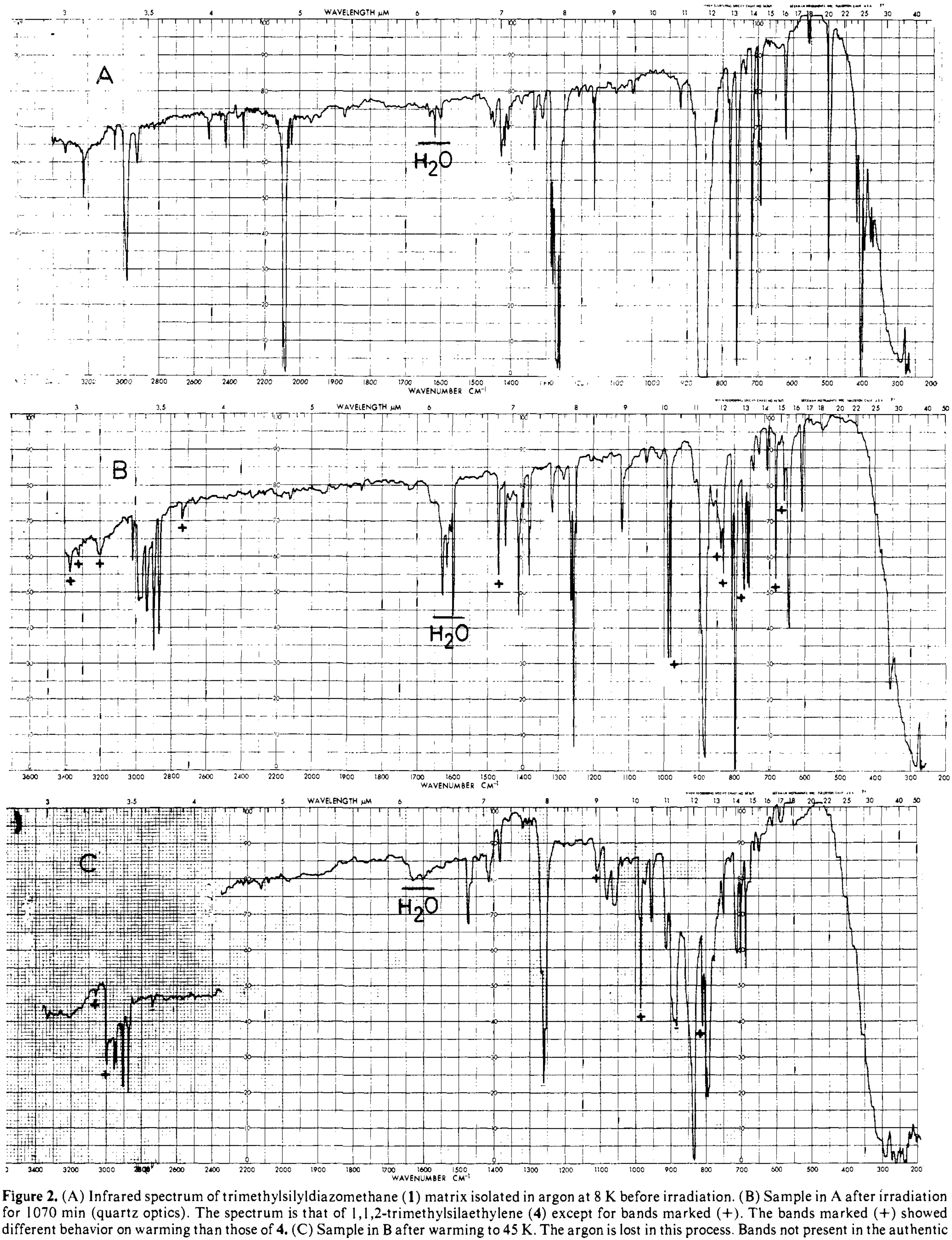


Figure 2. (A) Infrared spectrum of trimethylsilyldiazomethane (**1**) matrix isolated in argon at 8 K before irradiation. (B) Sample in A after irradiation for 1070 min (quartz optics). The spectrum is that of 1,1,2-trimethylsilaethylene (**4**) except for bands marked (+). The bands marked (+) showed 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,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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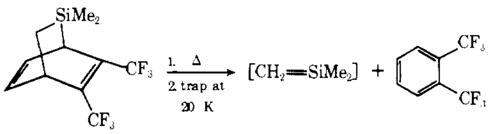
(3) The report[2] that thermolysis of 1,1-dimethyl-1-silacyclobutane gives 1,1-dimethyl-1-silaethylene with one observed infrared band at 1407 cm^{-1} (tentatively assigned to the Si═C stretch) suffers from the fact that ethylene (the coproduct) was not observed and that no other identification of the product was obtained. Thermolysis of i[4] gives hexafluoroxylene but no 1407 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.



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(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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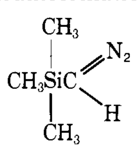
Solid State Chemistry. Discrete Trimethylsilylmethylene

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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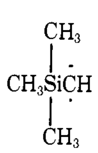
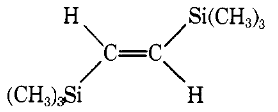


$$CH_3\overset{CH_3}{\underset{CH_3}{Si}}\dot{C}H$$

2



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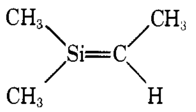

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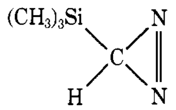
A dilute mixture of **1** and argon, matrix isolated and cooled to 8 K, was irradiated with filtered light of wavelengths greater than 3600 Å.[8] The IR bands of **1** (Figure 1) gradually disappear and are replaced by absorptions (Figure 2) assigned to trimethylsilyldiazirine (**5**).[9] Continued irradiation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



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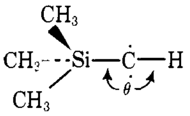
The ESR spectra are interpreted to arise from triplet trimethylsilylmethylene (**2**) in which the carbenic moiety is essentially linear (**6**, $\theta = \sim 180°$). The low E value indicates the high molecular symmetry of **6**. The hyperfine splitting is demonstrated to be due to hydrogen bonded 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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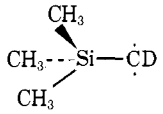

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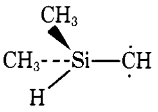

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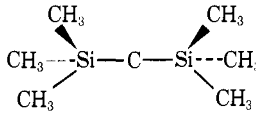

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