

that two current trends will correct this situation. The first trend is the increasing availability of crystal structures of macromolecules which are of pharmacological interest and the explosion of molecular biology and protein engineering techniques which help us understand drug-receptor interactions at the molecular level. The second is the increasing availability of modeling tools to experimentalists, a trend which will

no doubt result in a more timely testing of computer-generated models.

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Laser Photolysis of Silylene Precursors

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Introduction

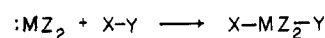
The reactions of compounds containing divalent silicon atoms, generally called silylenes,¹ were of particular interest to us from the beginning of our efforts to employ the mechanistic ideas of organic chemistry beyond the first row of the periodic table. The reactions of divalent carbon compounds—carbenes—are so distinctive² that it seemed possible to address the differences between reactions of silylenes and carbenes even while the mechanisms of carbene reactions were being elucidated.

It has been found that the most important types of transformations of carbenes are shared by silylenes,³ as shown in Scheme I. Since these reactions are both unusual and useful, we were curious about exactly how they occur, and we wanted detailed mechanistic knowledge in order to exercise greater control over them.

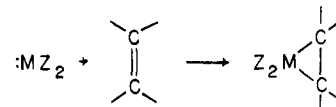
Our knowledge of silylene reaction mechanisms is rather rudimentary.³ Almost every known silylene has

Scheme I. Comparable Reactions of Carbenes and Silylenes

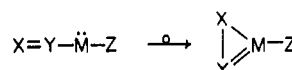
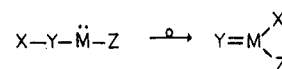
1. Sigma-bond insertion



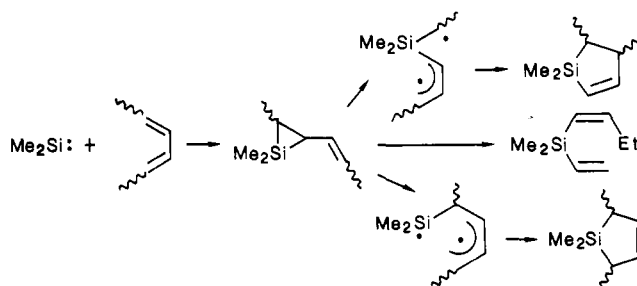
2. Pi-bond addition



3. Rearrangements



Scheme II



a singlet electronic ground state, so that only singlet silylene chemistry is thus far known. Silylenes have been found to readily insert into Si-H, Ge-H, and O-H bonds, and C-H insertion is known as an intramolecular

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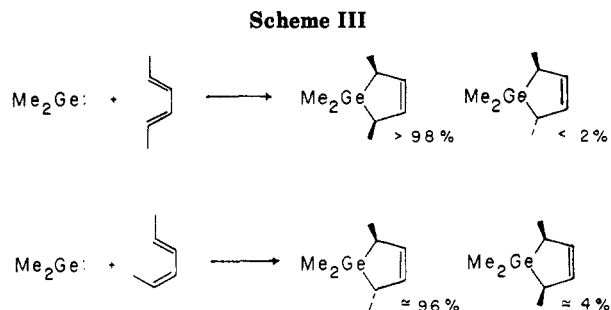
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Peter P. Gaspar was born in Brussels, Belgium. His undergraduate education was received at Caltech. His Ph.D. (1961) in organic chemistry at Yale, under William Doering, was followed by a NATO Fellowship at Heidelberg with Georg Wittig and further postdoctoral work at Caltech under George Hammond. A member of the faculty at Washington University, St. Louis, since 1963 he has been a visiting professor at Princeton (twice) and in Lisbon where he was also a Fulbright Lecturer. With interests in reaction mechanisms of a variety of short-lived electron-deficient species, his work in organosilicon chemistry led to the Frederic Stanley Kipping Award in 1986.

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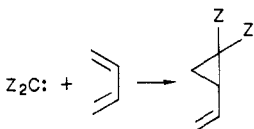
Stanislaw Konieczny is an Associate in Teaching and Research in the Institute of Inorganic Chemistry and Technology of the Technical University, Gdansk, Poland, where he completed his Ph.D. in 1978. His research interests cover a wide range of silicon chemistry.

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process, with a barrier that we have determined to be ca. 16 kcal/mol.⁴ The selectivity of SiH₂ and SiMe₂ insertion between two different Si-H bonds shows no temperature dependence, and from this lack of a difference between activation energies, a small absolute value for the energy barrier has been inferred.⁵ Calculations have predicted a 27.5 kcal/mol barrier for insertion of singlet SiH₂ into CH₄ and no barrier for insertion into SiH₄.⁶ Transition states in which the silicon atom is simultaneously bonded to the H and M (M = C, Si) atoms of the H-M bond being attacked were inferred from the calculations, similar in their triangular geometry to those for ¹CH₂ insertions.

Silylenes, like singlet carbenes, have been shown to undergo stereospecific addition to olefins with the formation of three-membered rings.⁷⁻¹⁰ Silylenes also add to acetylenes, forming silacyclopropenes in a reaction whose product is analogous to that from a carbene, but the mechanism is not known for either species.^{3,11} The addition of silylenes to 1,2-dienes appeared to differ dramatically from that of carbenes, since the latter generally undergo 1,2-addition yielding vinylcyclopropanes.¹²



The major products from many silylene-diene additions are five-membered rings, but a great deal of effort from many groups has established that silylenes, like carbenes, undergo stereospecific 1,2-addition as their primary reaction with 1,3-dienes.¹³⁻¹⁷ The re-

sulting alkenylsilyrane usually reacts further under the high-temperature conditions often employed for silylene generation. Depending on the substituents and their stereochemistry, varying proportions of silicon-carbon and carbon-carbon bond homolysis can occur as shown in Scheme II, leading to the formation of 1-silacyclopent-3-enes and -2-enes.¹⁶ The 3-sila-1,4-hexadiene can also arise from a concerted rearrangement, a retro-homo-ene reaction of the alkenylsilyrane.¹⁷

That 1,2-addition to a 1,3-diene is not the inevitable fate of a carbene analogue was dramatically and surprisingly revealed by the stereospecific addition of dimethylgermylene to isomeric 2,4-hexadienes (Scheme III).¹⁸

One would of course like to know much more about the mechanisms of silylene (and also carbene) reactions. What are the transition-state structures, and what is the balance between electrophilic and nucleophilic character of the attacking species in the transition state? What role do steric and electronic effects have in silylene reactions?

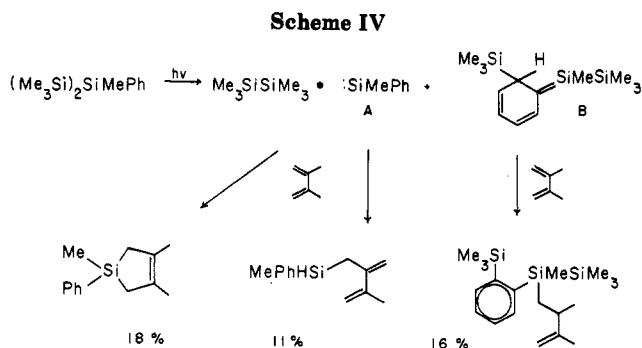
Such questions have been difficult to answer experimentally for carbene reactions,¹¹ but silylenes have several advantages over carbenes for mechanistic studies. The most important is the possibility of studying the intermolecular reactions of substituted silylenes, because their rearrangements are sufficiently slow at moderate temperatures to allow them to undergo other reactions. This is in marked contrast with alkyl-substituted carbenes, which in their singlet states react exclusively by intramolecular C-H insertion and alkyl migration.^{2,11} Thus, electronic and steric effects on silylene reactivity can be conveniently studied. The anticipated lower reaction rates for silylenes vs. carbenes are another advantage, both in the technical sense of easing experimental difficulty and in providing more information through a broader range of rates and activation parameters.

The reversibility of silylene reactions makes their transition states accessible via kinetic studies of the decomposition of stable products, and indeed several groups have utilized this approach. Purnell and co-workers derived the activation parameters for Si-H insertion by SiH₂ from those of the reverse reaction, disilane pyrolysis, together with thermodynamic functions for SiH₂.¹⁹ These activation parameters, extrapolated to 300 K, predict k_2 for SiH₂ + H₂ and SiH₂ + SiH₄ to equal 1.2×10^5 and 5.7×10^8 M⁻¹ s⁻¹, respectively, but a recent kinetic study by Inoue and Suzuki has reported rate constants 2 orders of magnitude faster: 6×10^7 M⁻¹ s⁻¹ for SiH₂ + H₂ and 6.6×10^{10} M⁻¹ s⁻¹ for SiH₂ + SiH₄.²⁰ Jasinski has reported an even larger rate constant, 1.6×10^9 M⁻¹ s⁻¹, for SiH₂ + D₂.²¹

Thus, despite the opportunities for the study of silylene reaction mechanisms via the reverse processes, it is obvious that direct kinetic measurements are needed. We have therefore set out to study the rates

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of reaction of substituted silylenes in solution.

Laser Flash Photolysis of Dodecamethylcyclohexasilane

For kinetic measurements to be feasible for highly reactive species like silylenes, they must be formed in a time period brief compared with their chemical lifetimes, and this requires photochemical generation. Unfortunately, there are no clean, efficient photochemical routes to silylenes comparable with the photolysis of diazo compounds, diazirines, or ketenes to carbenes. Polysilanes have been the most frequently employed precursors for the photochemical generation of silylenes.³ Kumada and co-workers demonstrated in product studies that photolysis of dodecamethylcyclohexasilane leads to the formation of dimethylsilylene and the corresponding cyclopentasilane:²² cyclo- $(\text{Me}_2\text{Si})_6 \xrightarrow{h\nu} \text{Me}_2\text{Si} \cdot + \text{cyclo-}(\text{Me}_2\text{Si})_5$.

Our experiments on the laser flash photolysis of silylene precursors were stimulated by the observation by Drahnak, Michl, and West that irradiation of cyclo- $(\text{Me}_2\text{Si})_6$ in a frozen matrix resulted in a species with an electronic absorption spectrum centered at 450 nm and displaying emission with a maximum near 600 nm, which they assigned to matrix-isolated dimethylsilylene.²³ This interpretation was challenged by Griller, Weber, and co-workers, who found, upon photolysis of cyclo- $(\text{Me}_2\text{Si})_6$ in solution at 308 nm, a transient absorption with $\lambda_{\text{max}} = 350$ nm (but none at 450 nm) whose rapid reactions with trimethylsilane ($k_2 = 2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and methanol ($k_2 = 3.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for $[\text{MeOH}] < 0.05 \text{ M}$ and $5.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for higher concentrations) suggested that it was dimethylsilylene.²⁴ Michl and West have vigorously defended their assignment, observing an absorption at $\lambda_{\text{max}} = 450$ nm from seven quite different precursors possessing only the SiMe_2 moiety in common.²⁵

Our laser flash photolysis studies also began with cyclo- $(\text{Me}_2\text{Si})_6$, but we have found this a difficult compound with which to work. In our hands, employing 266-nm photons, only weak absorption was observed, and even this was not uniformly reproducible. We observed absorption at both ca. 350 and 450 nm, with the former transient significantly longer lived.²⁶

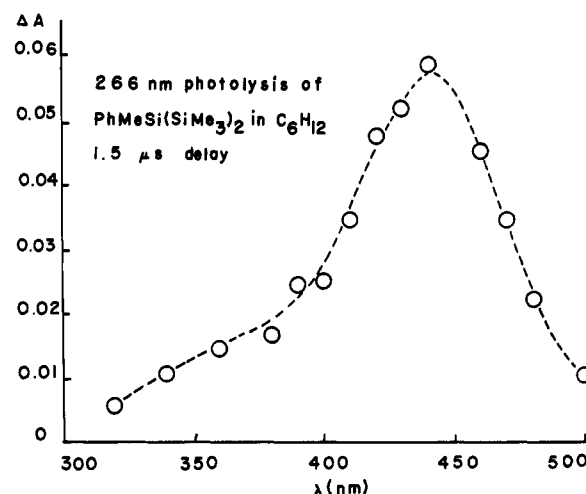


Figure 1. Transient absorption spectrum for the 266-nm photolysis of 2-phenylheptamethyltrisilane (10^{-3} M) in degassed cyclohexane solution, recorded point by point.

Laser Flash Photolysis of 2-Phenylheptamethyltrisilane

In search of a more tractable photochemical reactant, we turned to a trisilane, 2-phenylheptamethyltrisilane $((\text{Me}_3\text{Si})_2\text{SiMePh})$, found by Kumada to yield methylphenylsilylene ($\text{MePhSi} \cdot$): (see Scheme IV).²⁷ The photochemistry is, however, quite complex, and an interesting but undesirable side reaction produces a second type of reactive intermediate, a conjugated silene containing a silicon-carbon double bond.²⁸

With the use of other trapping agents, the silylene product yields rise to about 60%. Nevertheless, it is important to keep in mind that the irradiation of any aryl-substituted di- or polysilane has the potential for forming a *silene* in addition to a *silylene*. While silenes are known to be quite reactive toward oxygen and olefins and hydroxyl groups, and toward each other, there is even less known about their reaction rates than about those of silylenes.²⁹

From our first laser photolysis experiments, it was clear that we had entered a new era in the study of reactive intermediates in organosilicon chemistry under realistic reaction conditions.³⁰ Irradiation at 266 nm of $(\text{Me}_3\text{Si})_2\text{SiMePh}$ in air-saturated cyclohexane solution had produced a transient absorption with $\lambda_{\text{max}} = 440$ nm that disappeared within a few microseconds.³¹ This absorption maximum is shifted ca. 40 nm to the blue from the value attributed to methylphenylsilylene by Michl and West on the basis of a matrix isolation photolysis of the same precursor.³²

In the past 2 years a number of laser flash photolysis experiments have been carried out to characterize the transient species formed upon irradiation of silylene precursors and to learn about their chemistry. The 16-ns flashes from a Nd:YAG laser (Quantel Datachrom 5000 System) are frequency-quadrupled to 266-nm

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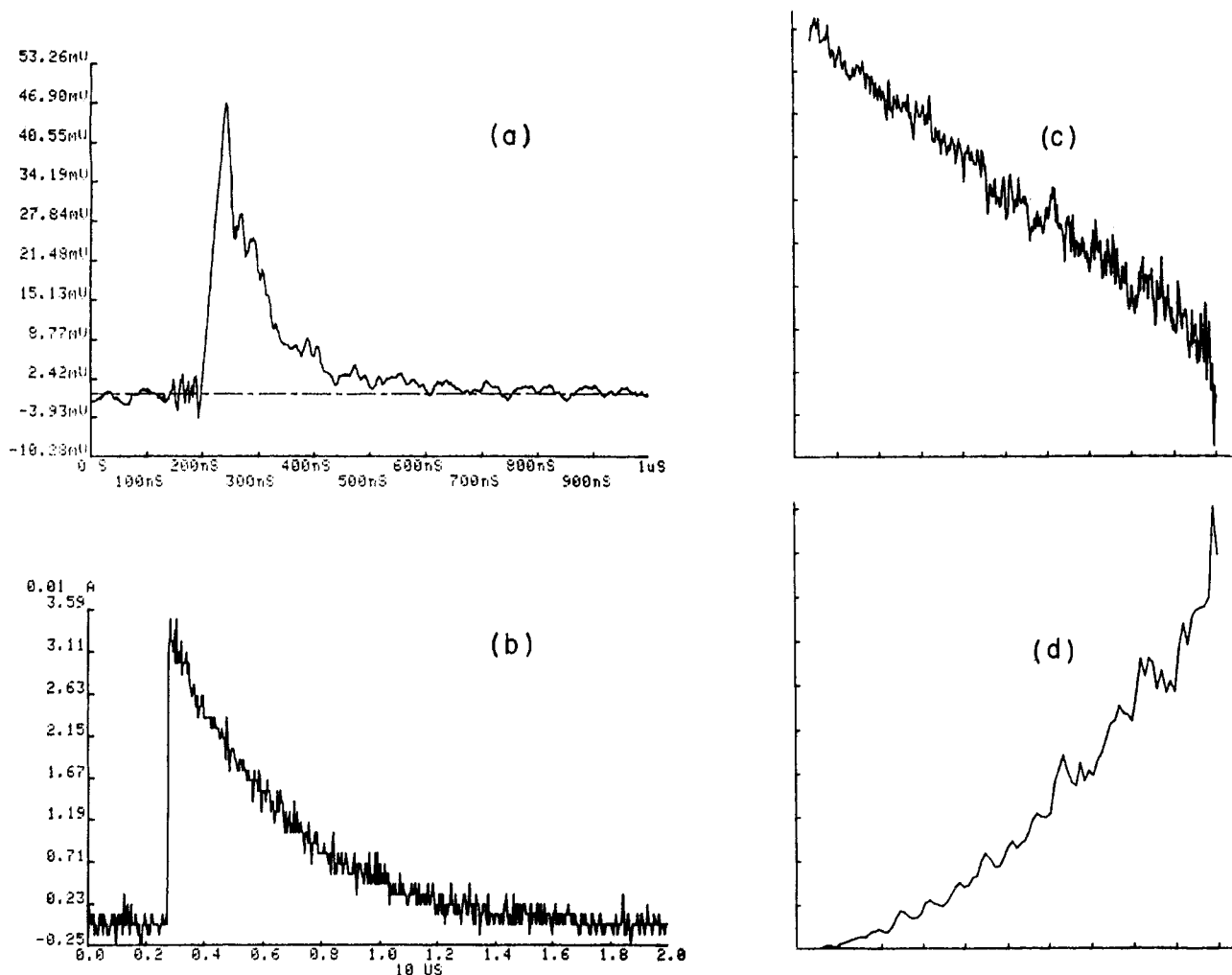


Figure 2. Representative data displays from laser flash photolysis-kinetic spectroscopy experiments: (a) photomultiplier voltage as a function of time upon irradiation of cyclo-(Me_2Si) $_6$, undegassed in cyclohexane monitored at 370 nm; (b) absorbance at 440 nm as a function of time upon irradiation of (Me_3Si) $_2\text{SiMePh}$, undegassed in cyclohexane; (c) \ln absorbance at 440 nm as a function of time upon irradiation of (Me_3Si) $_2\text{SiMePh}$ in degassed cyclohexane containing 0.842 M Et_3SiH ; (d) reciprocal absorbance at 440 nm as a function of time upon irradiation of (Me_3Si) $_2\text{SiMePh}$ in O_2 -saturated cyclohexane.

pulses (10–25 mJ) that are used to generate the reactive intermediates. These are detected by absorption of light from a continuous xenon source with wavelengths selected by entrance and exit monochromators. The photolysis and interrogation beams are at 90° , but both traverse more than 80% of the sample volume, so good overlap is assured. The amplified output of the photomultiplier is fed to a computer (Tektronix 4052A) via a storage oscilloscope (Tektronix 468) or, for very fast decays, by a transient digitizer (Tektronix 7912).

With this apparatus, transient absorption spectra, as for the photolysis of (Me_2Si) $_2\text{SiMePh}$ shown in Figure 1, are recorded point by point. The shoulder at 380 nm is due to a longer lived species whose identity is still not known.³¹ For kinetic studies the photomultiplier output voltage as a function of time (Figure 2a) is transformed into absorbance units (Figure 2b). The computer can fit such a curve to a kinetic model and can display a first-order (Figure 2c) or second-order (Figure 2d) kinetic plot. For trapping experiments, a large excess of reaction substrate is employed, and under these conditions the slopes of linear plots of log absorbance vs. time are pseudo-first-order rate constants. When these are plotted against substrate concentrations (Figure 3), the slopes of linear plots are second-order rate constants for decay of the transient absorption due to interactions

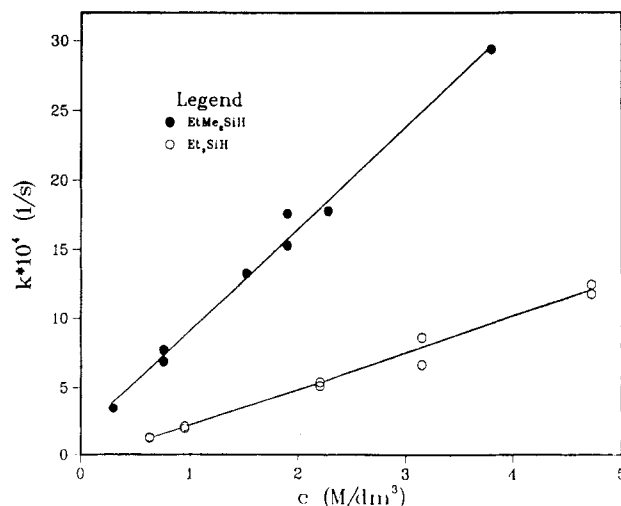






Figure 3. Pseudo-first-order rate constants for the decay of the 440-nm transient formed in the 266-nm irradiation of (Me_3Si) $_2\text{SiMePh}$ in the presence of EtMe_2SiH and Et_3SiH plotted against substrate concentration.

of its carrier with the reaction substrate.

Table I gives the second-order rate constants for disappearance of the major transient, $\lambda_{\text{max}} = 440$ nm, formed upon 266-nm irradiation of (Me_3Si) $_2\text{SiMePh}$.

Table I.
Second-Order Rate Constants for Disappearance of the Transients in the 266-nm Photolysis of $(\text{Me}_3\text{Si})_2\text{SiMePh}$, $(\text{PhMe}_2\text{Si})_2\text{SiMe}_2$, and $\text{PhSiMe}_2\text{SiMe}_3$ in Cyclohexane^a

trapping agent	$k_2, \text{M}^{-1} \text{s}^{-1}$		
	$(\text{Me}_3\text{Si})_2\text{SiMePh}$	$(\text{PhMe}_2\text{Si})_2\text{SiMe}_2$	$\text{PhSiMe}_2\text{SiMe}_3$
O_2	$(3.03 \pm 0.10) \times 10^8$	$(2.25 \pm 0.16) \times 10^9$	2.50×10^9
EtMe_2SiH	$(7.35 \pm 0.31) \times 10^4$	$(8.82 \pm 0.20) \times 10^5$	
Et_3SiH	$(2.59 \pm 0.05) \times 10^4$	$(2.12 \pm 0.07) \times 10^5$	$\tau_{1/2} = 4.4 \mu\text{s}$
	$(8.62 \pm 0.40) \times 10^5$	$(12.09 \pm 0.51) \times 10^7$	
	$(3.61 \pm 0.27) \times 10^5$	$(9.57 \pm 0.55) \times 10^7$	
	$(3.15 \pm 0.20) \times 10^5$	$(8.58 \pm 0.47) \times 10^7$	
	$(1.14 \pm 0.08) \times 10^5$	$(7.02 \pm 0.43) \times 10^7$	9.55×10^7
MeOH	$(5.44 \pm 0.38) \times 10^7$	$(2.43 \pm 0.07) \times 10^8$	
EtOH	$(4.93 \pm 0.54) \times 10^7$	$(3.00 \pm 0.14) \times 10^8$	2.50×10^8
<i>t</i> -BuBr	$(3.57 \pm 0.23) \times 10^5$		
none	$\tau_{1/2} = 63 \pm 4 \mu\text{s}^b$	$\tau_{1/2} = 6 \mu\text{s}^b$	$\tau_{1/2} = 4.1 \mu\text{s}$
$\text{ClCH}_2\text{CH}_2\text{Cl}$	$\tau_{1/2} = 66 \pm 5 \mu\text{s}^{b,c}$	$\tau_{1/2} = 6 \mu\text{s}^{b,d}$	

^a $[(\text{Me}_3\text{Si})_2\text{SiMePh}] = 10^{-3} \text{ M}$; $[(\text{PhMe}_2\text{Si})_2\text{SiMe}_2] = 3 \times 10^{-4} \text{ M}$; $[\text{PhSiMe}_2\text{SiMe}_3] = 10^{-3} \text{ M}$. ^b Second-order decay. ^c At $[\text{ClCH}_2\text{CH}_2\text{Cl}] = 0.63 \text{ M}$; $\tau_{1/2}$ increases to $146 \pm 11 \mu\text{s}$ at $[\text{ClCH}_2\text{CH}_2\text{Cl}] = 6.43 \text{ M}$. ^d At $[\text{ClCH}_2\text{CH}_2\text{Cl}] = 3.17 \text{ M}$.

These can be summarized as follows: The transient reacts very rapidly with oxygen—within 2 orders of magnitude of the diffusion-controlled rate. With alcohols reaction is nearly as rapid, but with such well-known silylene trapping agents as Si-H bonds and 1,3-dienes the reactions are several orders of magnitude slower, corresponding to chemical half-lives of microseconds to hundreds of microseconds under preparative reaction conditions.

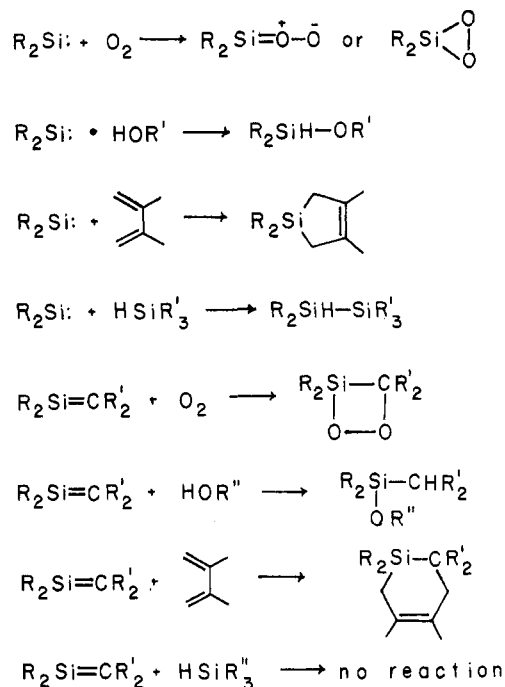
What is the identity of this transient? A likely candidate was methylphenylsilylene (MePhSi:), which is known from product studies to be formed by irradiation of 2-phenylheptamethyltrisilane. The transient, however, could also be the silene found in chemical trapping experiments, or an excited triplet state of $(\text{Me}_3\text{Si})_2\text{SiMePh}$, or perhaps even a silicon-centered free radical.

A silyl radical would be expected to react rapidly with oxygen and with dienes, as is observed for the 440-nm transient. The rapid reaction of the transient with alcohols is unexpected, however, for a trivalent silicon free radical, and the lack of observed reactivity toward $\text{ClCH}_2\text{CH}_2\text{Cl}$ for the transient is also inconsistent with a silicon-centered radical. The absorption maximum at 440 nm is at too long a wavelength for $\text{C}_6\text{H}_5\text{SiMeSiMe}_3$, λ_{max} for $\text{C}_6\text{H}_5\text{SiMe}_2$ having been reported as 320 nm.³³ Thus, a silyl radical structure appears to be excluded for the 440-nm transient.

A triplet excited state of the aromatic ring of $(\text{Me}_3\text{Si})_2\text{SiMePh}$ is excluded as the structure of the 440-nm transient by the sluggishness of its reactions with dienes, which would be expected to quench aromatic excited triplets at nearly the diffusion-controlled rate.³⁴

That leaves MePhSi: (A of Scheme IV) and the silene (B of Scheme IV) as the most likely structures for the carrier of the observed transient. Both should react rapidly with oxygen and alcohols, and both should react with dienes. Some reactions of silylenes and silenes with the substrates employed are shown in Scheme V. Silenes are *not* known to react with silanes,³⁵ and on

Scheme V



this basis the reactivity profile for the transient points toward a silylene structure.

Quantitative Comparison of Transient Reactivity with That of Silylenes

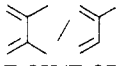
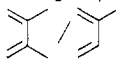
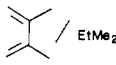
The ratio of the second-order rate constants for the disappearance of the 440-nm transient in the laser photolysis of $(\text{Me}_3\text{Si})_2\text{SiMePh}$ in two separate kinetic experiments with two different substrates like ethyldimethylsilane (HSiMe_2Et) and triethylsilane (HSiEt_3) gives a quantitative measure of the relative reactivity of the carrier of the transient toward the substrate pair. The relative reactivity of $:\text{SiMePh}$ toward the same substrate pair can be obtained from a static photolysis competition experiment in which the silylene precursor is photolyzed in a solution containing both substrates.

(33) Chatagililoglu, C.; Scaiano, J. C.; Ingold, K. U. *Organometallics* 1982, 1, 466-9.

(34) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; pp 58-9.

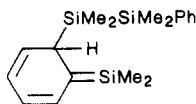
(35) Irradiation of $\text{C}_6\text{H}_5\text{SiMe}_2\text{SiMe}_3$ in cyclohexane solutions in the presence of excess HSiMe_2Et does *not* lead to products incorporating an SiMe_2Et group (Wang, T.; Gaspar, P. P.; Griller, D.; Weber, W. P., to be published).

Table II.
Summary of Competition Experiments

postulated intermediates	reagent pairs	relative reactivity from	
		laser photolysis rate constant ratios	static photolysis product ratios
:SiMe ₂	EtMe ₂ SiH/Et ₃ SiH 	4.11 0.75	4.40 0.77
	EtOH/EtOD	1.01	?
	Et ₃ SiH/Et ₃ SiD	1.37	1.30
	MeOH/Et ₃ SiH	10 ³	2
:SiMePh	EtMe ₂ SiH/Et ₃ SiH 	2.84 3.17	2.63 3.25
	EtOH/EtOD	1.44	?
	Et ₃ SiH/Et ₃ SiD	1.45	1.39
	 EtMe ₂ SiH	1.55	1.38
	EtOH/Et ₃ SiH	10 ³	3

The ratio of the silylene product yields normalized for the substrate concentration ratio gives the relative reactivity of the silylene toward that substrate pair, if several assumptions are valid, including that the silylene is the sole species responsible for the formation of the indicated products and that the reaction of the silylene is a single-step irreversible process.

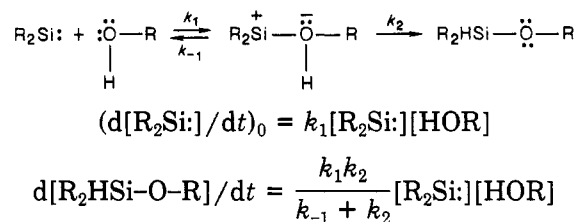
In Table II are collected the results of a series of competition experiments, compared with the ratios of laser photolysis rate constants, for the photolysis of (Me₃Si)₂SiMePh and 1,3-diphenylhexamethyltrisilane ((PhMe₂Si)₂SiMe₂). This photochemical precursor of Me₂Si: was found by Michl and West to produce a yellow species with an absorption spectrum λ_{max} = 450 nm, identical with that obtained from cyclo-(Me₂Si)₆ and five other dimethylsilylene precursors.²⁵ In cyclohexane solution, we have found that 266-nm photolysis of (PhMe₂Si)₂SiMe₂ produces a transient at λ_{max} = 450 nm with no indication of a second absorption at lower wavelength. In Table I rate constants are reported for reactions of this 450-nm transient with the same substrates employed with the 440-nm transient from (Me₃Si)₂SiMePh. The reactivity profile for the transient from (PhMe₂Si)₂SiMe₂ resembles that for the transient from (Me₃Si)₂SiMePh: very rapid reactions with oxygen and alcohols, somewhat slower reactions with 1,3-dienes and silanes, and no reaction with ClC-H₂CH₂Cl. The rate constants for the transient that we believe to be Me₂Si: are at least an order of magnitude greater than those for the transient we suggest is :Si-MePh. Again, however, the question must be asked whether the transient might be a silene.



The competition experiments reported in Table II indicate that, for pairs of substrates of the same class, the results are in clear accord with our identification of the transients observed by kinetic spectroscopy as silylenes. We see that for a pair of silanes the transients from both (Me₃Si)₂SiMePh and (PhMe₂Si)₂SiMe₂ display the same selectivity as the silylenes :SiMePh and Me₂Si: display in Si-H insertion. Again, for pairs of

dienes to which the silylenes add with formation of five-membered rings, the selectivity of the transients and the silylenes is the same. For both :SiMePh and :SiMe₂ we also have a comparison of an isotope effect for insertion of the silylene into Si-H vs. Si-D bonds of triethylsilane. The congruence of the observed isotope effects is important because of the clear evidence that the reaction of the transient is at the Si-H bond. This is a significant observation in light of the absence of any indication that the alternative structure for the transient, a silene, can react with Si-H bonds.³⁵ Even for a pair of substrates that differ in structure, 2,3-dimethylbutadiene and ethyldimethylsilane, there is good agreement between the selectivity of the transient observed in the laser photolysis of (Me₃Si)₂SiMePh and the selectivity of :SiMePh deduced from product yields in a static photolysis competition experiment.

For both silylene precursors, however, a discordant note is struck by the results of competition between two quite different substrates, an alcohol and a silane. Here there is total disagreement between the laser photolysis rate constant ratios of ca. 10³ and the static photolysis product ratios giving relative reactivities of only two or three! What is the explanation for this discrepancy, noted also by Griller? Are the transients, despite the evidence of the other competition experiments, something other than the postulated silylenes? This remains a possibility, although we believe a remote one. If the transients were silenes, a large reactivity difference between an O-H and an Si-H bond, favoring O-H, is readily understandable. There is another explanation, however. If the reaction of a silylene with an alcohol is a two-step sequence with a reversible first step, the spectroscopic studies would measure a different rate (that of the first step in the forward direction) than that sampled by the product studies.³⁶ Then the discrepancy between product ratios and absolute rate measurements would be understandable.


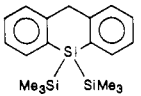
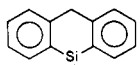
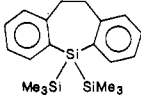
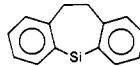
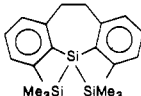
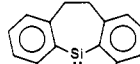
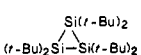
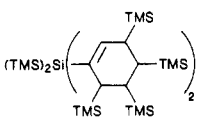
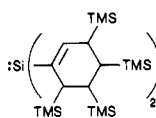


Laser Flash Photolysis of Other Silylene Precursors

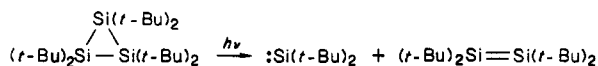
Recently, we have investigated the laser photolysis of a number of other silylene precursors, all of which give transient absorption with absorption maxima between 400 and 490 nm upon irradiation at 266 nm. The structures of the precursors and the silylenes derived from them are displayed in Table III, together with the absorption maxima for the observed transients and their first half-lives with respect to second-order decay in degassed cyclohexane solutions without added trapping agents. They are presented in order of increasing lifetimes, which span 3 orders of magnitude, from 6 μs to 20 ms. The lifetimes parallel the steric encumbrance of the divalent silicon atom in the silylene. It is of

(36) Zwitterionic complexes of silylenes with alcohols and ethers have been inferred frequently, e.g.; Steele, K. P.; Weber, W. P. *J. Am. Chem. Soc.* 1980, 102, 6095-7. Gu, T.-Y. Y.; Weber, W. P. *Ibid.* 1980, 102, 1641-4. Tzeng, D.; Weber, W. P. *Ibid.* 1980, 102, 1451.

Table III.
266-nm Photolysis of Silylene Precursors in Cyclohexane Solution

precursor	silylene	λ_{\max} , nm	$\tau_{1/2}$ (degassed), μs	$k_2, \text{M}^{-1} \text{s}^{-1}$			
				O ₂	Et ₃ SiH		MeOH
(PhMe ₂ Si) ₂ SiMe ₂	:SiMe ₂	450	6	2.3×10^9	2.1×10^5	7.0×10^7	2.4×10^8
(Me ₃ Si) ₂ SiMePh	:SiMePh	440	75	3.0×10^8	2.6×10^4	1.1×10^5	5.4×10^7
		490	1000	1.94×10^8	8.2×10^3	5.9×10^4	1.3×10^7
		485	2100	4.5×10^7	3.7×10^3	1.6×10^4	2.5×10^6
		485	10500	2.3×10^6	1.7×10^1	4.1×10^2	1.7×10^4
	:Si(<i>t</i> -Bu) ₂	440	12000	7.1×10^7	slow	6.4×10^2	7.5×10^4
		400	20000	7.6×10^4			3.5×10^2

course possible that in some of these cases the observed transient is due to a silene, rather than a silylene. All but one of these precursors is unsaturated and could undergo a formal 1,3-silyl group shift to generate a silene. It should be noted however that hexa-*tert*-butylcyclotrisilane is an exception—it is saturated, and its photolysis cannot produce a silene. An unsaturated silicon compound, tetra-*tert*-butyldisilene, is formed and absorbs in the same spectral region as the observed transient, but its lifetime is on the order of minutes, not the 12 ms observed. Thus, the 440-nm transient from cyclo-(*t*-Bu)₂Si₃ can be identified with confidence as di-*tert*-butylsilylene.



The transient generated from compound C of Table III is also unlikely to be a silene, since methyl groups in the ortho position are known to hinder the 1,3-silyl shift, or its equivalent, necessary to form it.³⁷

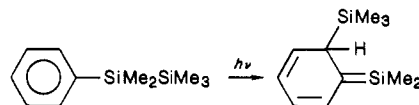
The similarity of the absorption maxima and the uniform trend of increasing transient lifetime with increasing steric bulk at the divalent silicon make it plausible that all these transients are silylenes. The similarity in the reactivity pattern for all these transients and the effect of steric hindrance on reactivity, as revealed by the rate constants given in Table III for second-order reactions of the transients with same set of trapping agents—oxygen, methanol, 2,3-dimethylbutadiene, and triethylsilane—also suggest that all the transients are of the same structural type. If so, they must all be silylenes. All seven transients react with oxygen and methanol, but their second-order rate constants decrease by 6 orders of magnitude from the precursor of dimethylsilylene to the precursor of an exceedingly hindered bis(tetrakis(trimethylsilyl)cyclohexenyl)silylene. All seven transients react more rapidly with oxygen than with methanol, and for six of the

(37) Ishikawa, M.; Katayama, S.; Kumada, M. *J. Organomet. Chem.* 1983, 248, 251–60.

seven 2,3-dimethylbutadiene also reacts, but more slowly than methanol, and trimethylsilane reacts yet more slowly. The two most hindered transients reacted too slowly for their rate constants to be measured, and the bis(cyclohexenyl) species also was too sluggish in its reaction with 2,3-dimethylbutadiene for a rate measurement.

Photolysis of a Silene Precursor and Comparison with Silylene Precursors

Finally, let us look more closely at the most likely alternative structure for the observed transients, that of a silene. Shizuka et al. have extensively studied the photophysics and photochemistry of phenylpentamethylidisilane^{38–42} which has been reported by Kumada and co-workers to yield a silene as the major photoproduct.^{43,44}



Shizuka et al. reported growth of a transient believed to be the silene with a buildup time of 30 ps, equal to the decay time of the emission from a singlet (2p π 3d π) excited charge-transfer state of the disilane.⁴² Thus, it was suggested that the silene is formed directly from the excited state. First-order decay of the transient

(38) Shizuka, H.; Obuchi, H.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* 1981, 405–6.

(39) Shizuka, H.; Sato, Y.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* 1982, 439–41.

(40) Shizuka, H.; Sato, Y.; Ueki, Y.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* 1984, 80, 341–57.

(41) Shizuka, H.; Obuchi, H.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* 1984, 80, 383–401.

(42) Shizuka, H.; Okazaki, K.; Tanaka, M.; Ishikawa, M.; Sumitani, M.; Yoshihara, K. *Chem. Phys. Lett.* 1985, 113, 89–92.

(43) Ishikawa, M.; Fuchikami, T.; Sugaya, T.; Kumada, M. *J. Am. Chem. Soc.* 1975, 97, 5923–4.

(44) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* 1978, 162, 223–38.

identified as a silene was reported to occur with a lifetime of 4.8 μs in cyclohexene, with no added trapping agents.

We have compared the reactivity of this transient with that of the transients we believe to be Me_2Si : and MePhSi :. The data are presented in Table I. Since the precursor is a disilane, extrusion of a silylene is difficult, and we have *not* trapped dimethylsilylene when the irradiation is carried out in the presence of 5 M HSiMe_2Et , with a detection limit of ca. 5% yield of Si-H- insertion product.³⁵

We see that for three substrates—oxygen, ethanol, and 2,3-dimethylbutadiene—the transients identified as a silene and dimethylsilylene show high and nearly identical reactivity, while the transient believed to be methylphenylsilylene reacts 1 to nearly 3 orders of magnitude less rapidly. Toward Et_3SiH , however, the reported silene is unreactive, while the silylenes react with the Si-H bond, as demonstrated above by isotope effect measurements. The short lifetime of the transient attributed to the silene, $t_{1/2} = 4.1 \mu\text{s}$ in our experiments, would however make a reaction with a rate constant below $10^5 \text{ M}^{-1} \text{ s}^{-1}$ difficult to detect. The decay of the silene transient absorption in the absence of added trapping agent differs from that of dimethylsilylene and methylphenylsilylene in its kinetic order as well as its rate. The silylene transient absorption decay in second-order processes while the silene disappears in a first-order manner.

Conclusion

In conclusion, a program to study the rates of silylene reactions is under way but has been slowed by the necessity to carefully examine the evidence for the identification of the transients observed upon photolysis of silylene precursors. The evidence is preponderantly on the side of silylene structures for the carriers of the transients observed on the microsecond time scale upon

the irradiation of substituted trisilanes. The jury is still out, however,⁴² and until the dust has settled it would be well to remember Kamen's dictum: "Until solid results take over, the more powerful the method, the more catastrophic the errors."⁴⁵

Thus far, the clearest trend in silylene reactivity revealed by the kinetic studies is the strong influence of steric hindrance. This has been previously noted for that rare case of a substituted carbene that does *not* rearrange rapidly, dimesitylmethylene.⁴⁶ The rate constants we have measured thus far are very encouraging for the prospects of characterizing the transition states of silylene reactions via activation parameters derived from the temperature dependence of the rate constants, and these will be the next experiments to be carried out.

Silenes too are of great interest, and from the results reported here on the single silene thus far examined, it is clear that they are highly reactive. Kinetic studies are likely to elucidate their reaction mechanisms. For both silenes and silylenes, however, the immediate future requires development of new efficient and specific photochemical generators, and we are engaged in this task also.

This work has received encouragement and financial support from the National Science Foundation under Grant CHE-8414358. Preliminary experiments were carried out at the regional laser facility in the Department of Chemistry, University of Pennsylvania, and in the research laboratories of the McDonnell Douglas Corporation in St. Louis. For helpful discussions, advice, encouragement, and good cheer, more than thanks are due to T. J. Barton, R. T. Conlin, E. Corey, I. M. T. Davidson, D. Griller, M. Jones, Jr., P. R. Jones, J. Michl, R. Walsh, W. P. Weber, R. West, and Carole Gaspar.

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(46) Zimmerman, H. E.; Paskovich, D. H. *J. Am. Chem. Soc.* 1964, 86, 2149-60.