Direct Detection and Characterization of a Transient 1-Silaallene Derivative in Solution

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Abstract: Direct irradiation of ((trimethylsilyl)ethynyl)pentamethyldisilane in hydrocarbon solution affords a mixture of reactive intermediates which have been detected and identified using laser flash photolysis techniques and trapped as the methanol adducts in steady state irradiation experiments. Flash photolysis of air-saturated hexane solutions of the disilane allows detection of transient species assigned to 1,1-dimethyl-3,3-bis(trimethylsilyl)-1-silaallene and dimethylsilylene, along with a non-decaying species assigned to 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacyclopropene. These were identified on the basis of their UV absorption spectra and reactivity toward various reagents. The 1-silaallene is a minor photoproduct, but it is readily observable in transient absorption experiments because it is relatively long-lived ($\tau = 2.4$ μs in air-saturated solution) and absorbs strongly, with absorption maxima considerably to the red of those of the 1-silacyclopropene. The 1-silaallene exhibits characteristic silene reactivity; it reacts with methanol, acetic acid, acetone ($k = 10^6$–10^8 M^{-1} s^{-1}) and oxygen ($k \sim 10^8$ M^{-1} s^{-1}), exhibits low reactivity toward aliphatic dienes and *tert*-butyl alcohol, and decays with second-order kinetics in the absence of quenchers. With methanol and acetic acid, it has been shown that reaction in hexane occurs with the monomeric ROH species *only*. Steady state irradiations in the presence of methanol afford methanol-addition products consistent with the formation of the silaallene, silacyclopropene, and silylene, along with bis(trimethylsilyl)acetylene as the major product.

Introduction

1-Silaallenes are a class of silenes (compounds containing a Si=C bond) that are of fundamental interest in organosilicon chemistry,[1] but which have received scant attention in the literature. West and co-workers have recently reported the first example of an isolable 1-silaallene derivative,[2] and a ruthenium complex of a more reactive 1-silaallene has also been reported.[3] However, no reactive 1-silaallene derivatives have yet been characterized spectroscopically, either in solution or solid matrices. In this paper, we report the first example of a transient 1-silaallene to be detected and characterized in solution at room temperature.

The direct irradiation of alkynyldisilanes in solution is known to lead to the formation of products ([2 + 2]-dimers or in the presence of alcohols, alkoxysilanes) consistent with the formation of 1-silaallene derivatives in low to moderate yields.[4–6] In most of these cases, the major product is the isomeric 1-sila-cyclopropene derivative (eq 1), which is generally isolable in

[1]
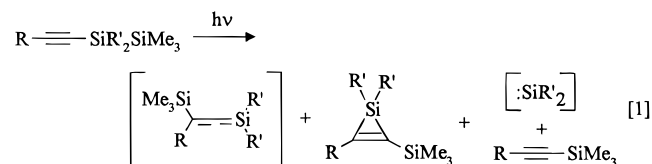
spite of possessing considerable reactivity toward oxygen, alcohols, and carbonyl compounds.[5–8] Ishikawa and co-workers

have demonstrated that the yields of 1-silaallene- and silylene- (:SiR′$_2$)-derived products are both significantly higher from ((trialkylsilyl)ethynyl)disilanes than from arylethynyl-derivatives.[4,5] This suggests that compounds of this type might prove to be convenient precursors to reactive 1-silaallene derivatives for study by transient spectroscopic methods, particularly if silylene extrusion might be suppressed through appropriate substitution. Thus, we have identified ((trimethylsilyl)ethynyl)-pentamethyldisilane (**1**) as a particularly promising candidate for study, and have examined its photorearrangement to the isomeric silacyclopropene (**2**) and 1-silaallene (**3**) derivatives in hydrocarbon solution.
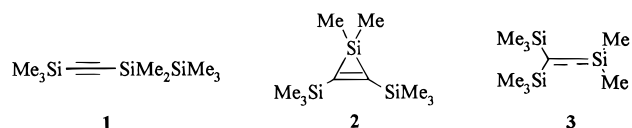
Results and Discussion

Compound **1** was prepared using a similar method to that reported by Ishikawa and co-workers for the synthesis of related alkynyldisilanes[4,5] and was obtained in >99% purity after chromatographic purification. This compound has been reported previously,[9] but no spectroscopic or analytical data were reported; those determined here are consistent with its proposed structure.

Irradiation of a deoxygenated hexane solution containing **1** (0.02 M) and MeOH (0.5 M) with the light from a 16-W Cd resonance lamp (228 nm) was carried to ca. 50% conversion of

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the alkynyldisilane. This resulted in the formation of four major products, according to GC analysis of the photolysate; these were isolated by radial chromatography and identified as **4**−**7** on the basis of spectroscopic data (see eq 2). Product yields
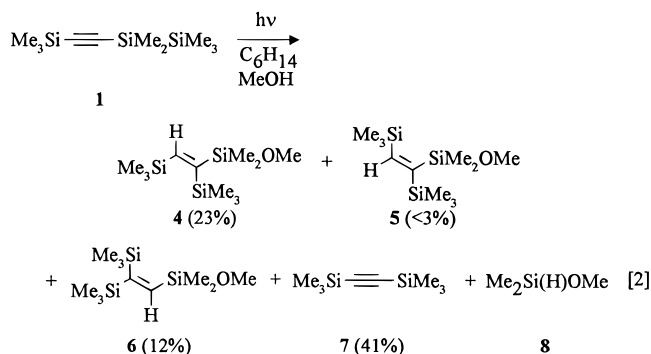
were determined by GC analysis as a function of irradiation time. Monitoring of the photolysate between 5 and 60% conversion indicated compound **5** to be a secondary product, and also revealed the presence of dimethylmethoxysilane (**8**) in the reaction mixture.

The methanol-adducts **4**−**6** were identified on the basis of one- and two-dimensional ^1H, ^{13}C, and ^{29}Si NMR experiments. ^1H−^{29}Si heteronuclear multiple bond correlation (HMBC) experiments allowed determination of ^1H−^{29}Si coupling constants between the vinylic hydrogen and the three silicon atoms in the three compounds; those involving the alkoxysilyl silicon atom (J_{H-SiO}) were the most useful for structural assignments, assuming the normal ordering $J_{trans} > J_{cis} \gg J_{geminal}$. The three compounds exhibited J_{H-SiO} values of 17.6, 21.6, and 6.8 Hz, and were thus assigned as **4**, **5**, and **6**, respectively.

Compound **4** has been reported previously, as the product of addition of MeOH to silacyclopropene **2**,[7,8] and is most likely responsible for the formation of **5** by secondary photoisomerization at higher conversions.[7,8] Compound **6** can be attributed to reaction of MeOH with 1,1-dimethyl-3,3-bis(trimethylsilyl)-1-silaallene (**3**).[4−6]

Corroboration of the structural assignments for **4**−**6** and the proposed pathways by which they arise was derived from an experiment in which an argon-saturated hexane solution of **1** was irradiated to ca. 20% conversion in the *absence* of methanol. The photolysate in this case contained only two major products, **7** (ca. 40%) and a compound identifiable as **2** on the basis of its GC retention time and mass spectrum.[8] The photolysate also contained at least ten minor products of relatively high molecular weight which were not present in the reaction mixture from photolysis in the presence of methanol. Addition of MeOH to the photolysate resulted in the rapid disappearance of the compound identified as **2** and the formation of **4**, but had no effect on the yields of the other products of photolysis. Most significantly, compound **6** was *not* produced in this experiment. This verifies that the product arises from reaction of methanol with a relatively short-lived reactive intermediate, as silaallene **3** is expected to be. Presumably, the numerous minor products formed in this experiment can be assigned as due to reaction of silaallene **3** with itself and/or **1**.

Laser flash photolysis of continuously flowing, deoxygenated 0.028 M hexane solutions of **1** ($\epsilon_{248} = 85$ M^{-1} cm^{-1}) with the 248-nm pulses from a Kr/F$_2$ excimer laser produced readily detectable, long-lived absorptions throughout the 250−350 nm spectral range. The appearance of the traces varied markedly depending on the monitoring wavelength (λ_{mon}). Those recorded over the $\lambda_{mon} = 300$−350 nm range decayed with complex kinetics over several tens of microseconds to nearly the pre-

pulse level, while those recorded over the $\lambda_{mon} = 250$−270 nm range showed an initial decay (of identical temporal behavior to those recorded at higher wavelengths) to a residual absorption level that was stable over the full 5-ms time scale of our system. Saturation of the solution with air led to a reduction in the lifetime of the transient absorption and a change to pseudo-first-order decay kinetics ($\tau \sim 2.4$ μs) but had no effect on the lifetime or yield of the non-decaying residual absorption. Experiments carried out with a nitrogen-saturated solution using a shorter time scale revealed the presence of an additional transient species which absorbs in the 400−600 nm range and decays with a ∼50 ns lifetime. This component could not be detected in experiments with air-saturated solutions. Thus, three primary products are detectable from photolysis of **1**: an extremely short-lived one which absorbs in the visible and is very reactive toward oxygen ($k > 10^9$ M^{-1} s^{-1}), a moderately short-lived one which absorbs in the UV and is moderately reactive toward oxygen ($k \sim 10^8$ M^{-1} s^{-1}), and an apparently stable one ($\tau > 50$ ms) which absorbs in the deep UV and is not detectably reactive toward oxygen within the time resolution of our system ($k < 10^3$ M^{-1} s^{-1}).

Time-resolved UV absorption spectra, recorded for air-saturated solutions 0.2−1 and 22−33 μs after the laser pulse, are shown in Figure 1a, along with a spectrum recorded for a nitrogen-saturated solution 15−55 ns after the pulse. The Inserts in Figure 1a show decay traces recorded at 270 nm (air-saturated), where both the long-lived transient and "stable" product can be detected, and at 450 nm over the shorter time scale. Figure 1b shows the isolated spectrum of the long-lived transient species, calculated by simple subtraction of the two air-saturated spectra in Figure 1a. The short-lived transient with $\lambda_{max} = 460$ nm can be assigned to dimethylsilylene, on the basis of its characteristic absorption spectrum and sensitivity to oxygen and alcohols.[10,11]

Addition of O$_2$, MeOH, MeOD, acetic acid (HOAc), or acetone to the hexane solutions of **1** resulted in shortening of the lifetime of the 325-nm transient absorption, but had no effect on its initial "yield" (*i.e.* the initial Δ-OD of the transient) or on the yield or stability of the residual absorption over a 5-ms time scale. This indicates that these reagents all react with the transient but not with the non-decaying species, and furthermore, that they do not react efficiently with the photochemical precursor(s) to these species. A plot of the transient decay rate constant (k_{decay}) versus quencher (Q) concentration according to eq 3 was linear for acetone, affording a value of $k_q = (1.78 \pm 0.05) \times 10^6$ M^{-1} s^{-1}. The rate constant for quenching by O$_2$ was estimated to be $k_q = (1.1 \pm 0.2) \times 10^8$ M^{-1} s^{-1} from the lifetimes of the transient in air- ($\tau = 2.4$ μs) and O$_2$-saturated ($\tau = 640$ ns) hexane solution. 1,3-Octadiene and *tert*-butyl alcohol were ineffective transient quenchers; lifetimes measured in the absence and presence of relatively high concentrations of added reagent afforded upper limits of $k_q \leq 4 \times 10^4$ M^{-1} s^{-1} for the quenching rate constants in these cases.

$$k_{decay} = (1/\tau_o) + k_q[Q] \qquad (3)$$

On the basis of these trends in reactivity, the transient giving rise to the absorption spectrum shown in Figure 1b ($\lambda_{max} = 275, 325$ nm) is assigned to 1-silaallene **3**. The spectrum of the stable residual component, with its weak band at $\lambda_{max} = 345$ nm and prominent absorption below 250 nm, is assigned

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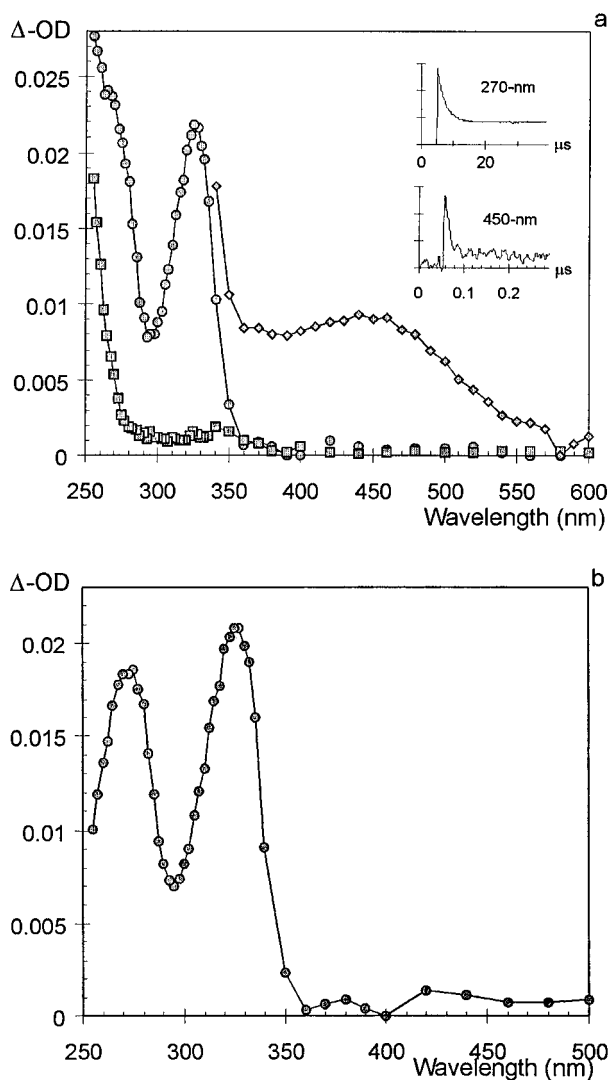
Figure 1. (a) Transient UV absorption spectra recorded by nanosecond laser flash photolysis of 0.028 M solutions of **1** in hexane at 23 °C: 0.2–1.0 (●) and 22–33 μs (■) after excitation of an air-saturated solution and 15–55 ns (♦) after excitation of a nitrogen-saturated solution. (b) Difference spectrum calculated from the two air-saturated spectra of part a. Typical decay traces, recorded at monitoring wavelengths of 270 and 450 nm, are shown as Inserts in part a.

to 1-silacyclopropene **2** on the basis of comparison to the published UV absorption spectrum.[7,8] As might be expected, its known reactivity toward oxygen and alcohols[7,8] is not high enough to be detected under the conditions of our experiments ($k_{O_2} < 10^3$ M^{-1} s^{-1}; $k_{MeOH} < 10$ M^{-1} s^{-1}).

The UV absorption spectrum of **3** can be compared to that of the simple silenic model compound **9** ($\lambda_{max} = 275$, 300 nm (sh)) in the same solvent.[12] The ~30 nm bathochromic shift of the spectral maximum for **9** relative to that of 1,1-dimethylsilene ($\lambda_{max} = 244$-nm[13]) can be ascribed to the effects of hyperconjugative interactions between the β-trimethylsilyl group and the Si=C bond,[12] based on analogies in alkene spectroscopy.[14,15] More substantial spectroscopic effects are anticipated for **3**, since it contains two trimethylsilyl groups in the required orientation for hyperconjugation with the Si=C bond.

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As is the case for acetone, the reaction of **3** with MeOH, MeOD, and HOAc proved to be significantly slower than those reported previously for other silenes.[16-20] Plots of k_{decay} *vs* [Q] for these three reagents in hexane solution (see Figure 2) exhibit negative curvature, which is barely detectable for MeOH and MeOD, but distinct in the case of acetic acid. Treatment of the data for MeOH(D) according to the simple expression given in eq 3 (*i.e.*, ignoring the slight curvature) affords apparent quenching rate constants of $k_q = (1.7 \pm 0.1) \times 10^6$ M^{-1} s^{-1} for MeOH and $k_q = (7.4 \pm 0.8) \times 10^5$ M^{-1} s^{-1} for MeOD, and the indication of a sizable primary deuterium kinetic isotope effect ($k_H/k_D = 2.3 \pm 0.2$) on the addition of MeOH to **3**.

A rigorous analysis of the data for MeOH and HOAc must take into account the fact that both reagents undergo significant oligomerization in hexane at bulk concentrations greater than ca. 0.01 M.[21,22] Oligomerization will have significant effects on the kinetics of reaction, since it will cause the actual concentration of potentially reactive species to be lower than the nominal bulk ROH concentration. These effects will be even greater if the reactivity of ROH oligomers differs from that of the monomer owing to differences in nucleophilicity and/or acidity. Such effects have been reported previously for singlet carbene insertion reactions with alcohols, where the rate determining step is protonation of the carbene and is faster for oligomeric than monomeric alcohol.[23] In contrast to the situation with carbenes, the negative curvature in the quenching plots for **3** (Figure 2) suggests that oligomerization reduces the overall reactivity of MeOH and HOAc toward addition to the Si=C bond in **3**.

Addition of alcohols and acetic acid to silenes is thought to occur by a two-step mechanism involving initial formation of a zwitterionic silene–alcohol complex, which collapses to product by proton transfer from oxygen to the silenic carbon (see Scheme 1).[16,18,20,24-26] With methanol, the proton-transfer step is the slow one in the sequence, and occurs by two competing pathways: one which predominates at low alcohol concentrations, involving unimolecular transfer within the complex, and a higher order pathway involving a second molecule of alcohol.[16,18,20,25] The latter has been identified as general base catalysis (*i.e.*, deprotonation at oxygen followed by protonation at carbon) on the basis of kinetic results.[18] The overall rate of reaction in this case depends on alcohol nucleophilicity, since the equilibrium constant for complex formation is contained in the expression for the overall rate constant. Reaction of silenes with HOAc differs in that

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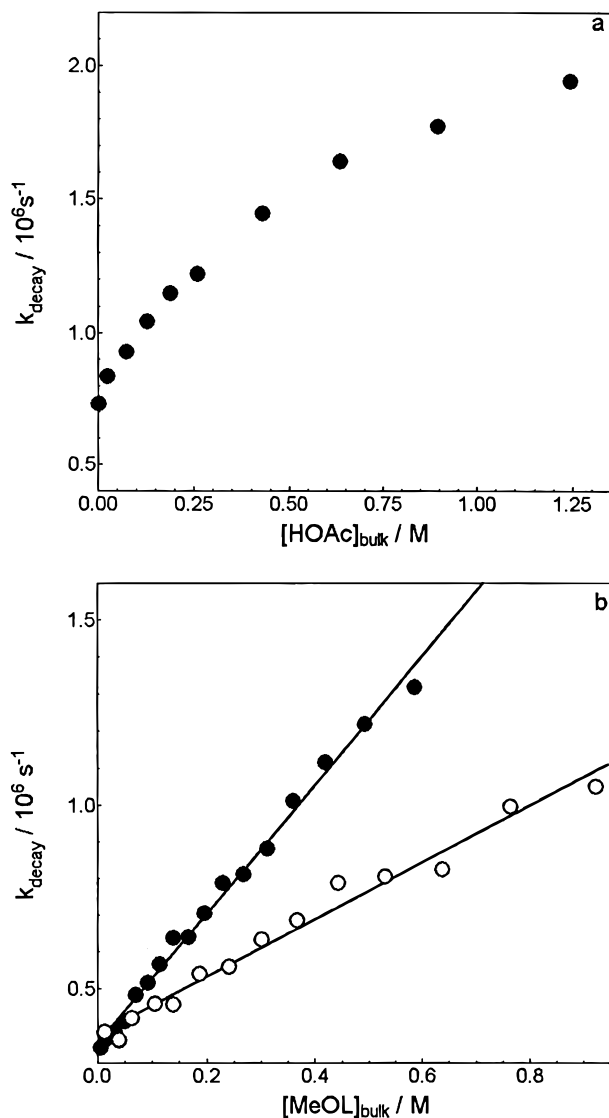(21) Landeck, H.; Wolff, H.; Gotz, R. *J. Phys. Chem.* **1977**, *81*, 718.

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(26) The structures of the intermediates in Scheme 1 are those thought to be involved in alcohol additions to silenes. Addition of HOAc probably involves (rate-determining) attack by the carbonyl oxygen, followed by or in concert with proton transfer. See: Bradaric, C. J.; Leigh, W. J. *J. Am. Chem. Soc.* **1996**, *118*, 8971.
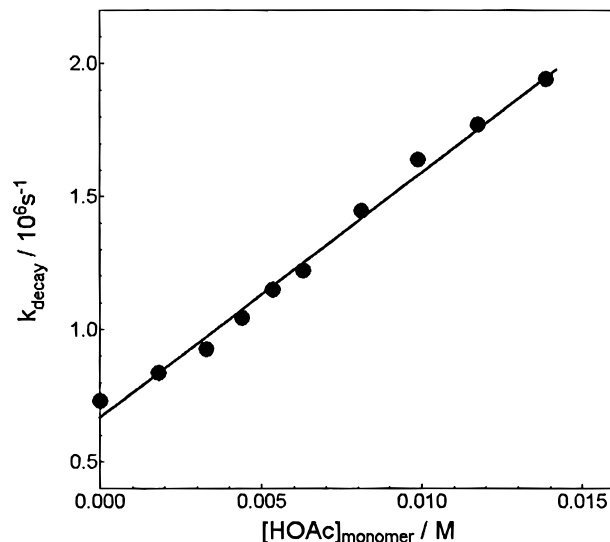
Figure 3. Plots of k_{decay} versus monomeric HOAc concentration for quenching of 1-silaallene **3** in air-saturated hexane solution at 23 °C.

Scheme 1

HOAc: $k_2 > k_1$; $k_2 \gg k_{-1}$, k_3

MeOH: $k_1, k_{-1} > k_2$; k_3[MeOH] ~ k_2

Figure 2. Plots of k_{decay} versus bulk ROH concentration for quenching of 1-silaallene **3** in air-saturated hexane solution at 23 °C by (a) HOAc and (b) MeOH (●) and MeOD (○).

nucleophilic attack is rate determining, followed by fast proton transfer.[16,18,20] In both cases, it would be predicted that ROH oligomers should be substantially less reactive than the monomers, because of the dependence of the rate on nucleophilicity.
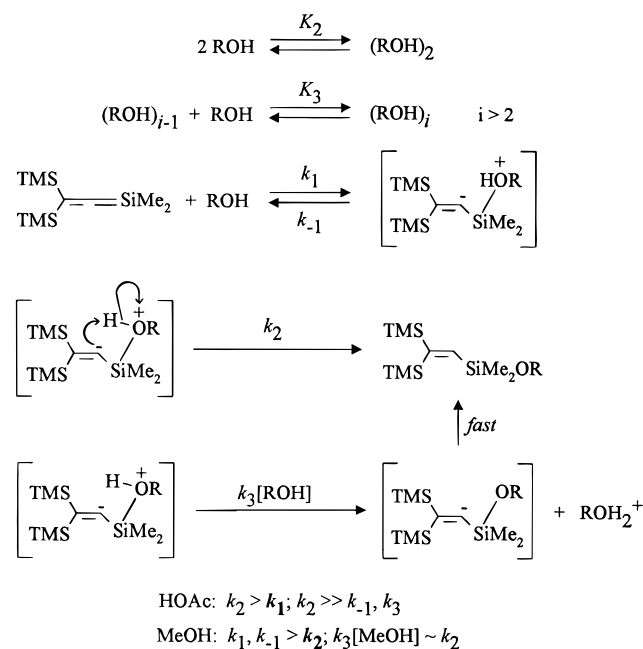
The data for acetic acid are the simplest to treat quantitatively, since the mechanism is kinetically simpler (see Scheme 1[26]), and it is known that oligomers higher than the dimer are not formed to a significant extent.[22] The data of Figure 2a are replotted *versus* monomeric HOAc concentration in Figure 3, using the reported equilibrium constant for dimeric HOAc formation in hexane ($K_2 = 3200 \pm 500$ M^{-1} at 25 °C)[22] to calculate the monomer concentrations as a function of the bulk concentration. The linearity in the plot is excellent, and the slope affords a value of $k_q = (9.8 \pm 0.6) \times 10^7$ M^{-1} s^{-1} for the bimolecular rate constant for quenching of **3** by monomeric acetic acid in hexane solution.

Treatment of the data for MeOH(D) quenching in analogous fashion, employing the oligomerization data of Wolff and co-workers for the alcohols in *n*-hexane,[21] leads to less satisfactory results because the data are of poorer quality than those for HOAc. Nevertheless, plots of k_{decay} *vs* monomeric MeOH(D) concentration exhibit strong positive curvature, suggesting a quadratic concentration dependence analogous to that reported

previously for the reaction of other reactive silenes with this alcohol.[16,20] This would be consistent with the addition mechanism shown in Scheme 1, with a particularly strong contribution from the pathway which is overall second order in methanol. It is interesting to note that the reported equilibrium constants for oligomerization of MeOD in *n*-hexane are somewhat higher than those for MeOH,[21] suggesting that the true isotope effect on the rate constant for methanol addition to **3** may be substantially smaller than that suggested by the data in Figure 2b.

The absolute rate constants for reaction of silaallene **1** with the reagents studied in this work are collected in Table 1. In all cases, these values were obtained by analysis of k_{decay} vs concentration data according to eq 3 (and for HOAc, using calculated values of the monomeric acid concentration).

The results of steady state photolysis of **1** suggest that silylene extrusion (yielding Me$_2$Si: and **7**) competes with trimethylsilyl migration (yielding **2** and **3**), to an extent comparable to that observed for 1-((trimethylsilyl)ethynyl)-1,1-diaryl-2,2,2-tri-methyldisilanes (**10**).[5,27] The predominance of this product has no effect on the spectra of the longer-lived species or the rate

Table 1. Absolute Rate Constants for Quenching of
1,1-Dimethyl-3,3-bis(trimethylsilyl)-1-silaallene (**3**) in Air-Saturated
Hexane Solution at 23.0 ± 0.2 °C[a]

quencher	$k_q/10^6$ M^{-1} s^{-1}
MeOH	1.7 ± 0.1
MeOD	0.74 ± 0.08
t-BuOH[b]	~0.02[b]
HOAc[c]	98 ± 6
acetone	1.78 ± 0.05
O$_2$	110 ± 20
1,3-octadiene[b]	≤0.04[b]

[a] From analysis of k_{decay} vs concentration data according to eq 3.
Errors are quoted as twice the standard deviation obtained from linear
least-squares analysis of these data. [b] Estimates obtained from k_{decay}
values obtained in the absence and presence of quencher at a single
(high) concentration. [c] For quenching by monomeric HOAc (the slope
of the plot shown in Figure 3).

constants for quenching of **3**, because it is over two orders of
magnitude shorter lived than **3** in air-saturated solutions (even
more so in the presence of additional quenchers). Quenching
of Me$_2$Si: by oxygen, alcohols, etc. is *not* accompanied by a
reduction in the initial Δ-OD of the absorption assigned to **3**,
allowing the conclusion that the silaallene is formed directly
by photorearrangement of **1**. The relative yield of **2** and **3** from
photolysis of **1** is also similar to that obtained from photolysis
of **10**. In spite of the fact that **3** is formed in only ~15%
chemical yield, it is readily detectable by flash photolysis
because its UV absorption spectrum is relatively intense and is
well-shifted from those of the precursor and the other products
formed.

Qualitatively, 1-silaallene **3** exhibits reactivity which is
characteristic of silicon–carbon double bonds. On a more
quantitative level, the absolute rate constants for reaction toward
the characteristic silene traps studied here (see Table 1) are
significantly slower than those determined for other transient
silenes which have been studied. It is premature to speculate
as to the origins of these differences; fortunately, the manipula-
tion of both the alkynyl and silyl substituents in **1** is synthetically
straightforward and affords convenient photochemical precursors
to a variety of transient 1-silaallene derivatives. The spectro-
scopic characterization and more detailed studies of the bimo-
lecular reactivity of these organosilicon reactive intermediates
are the subject of continued investigation in our laboratory.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX500
spectrometer in deuteriochloroform solution and are referenced to
tetramethylsilane. ^{29}Si NMR spectra were obtained from ^{1}H–^{29}Si
gradient heteronuclear multiple bond correlation (HMBC) experiments,
also in deuteriochloroform. High-resolution mass spectra and exact
masses were determined on a VGH ZABE mass spectrometer. Low-
resolution spectra were recorded on a Hewlett-Packard 5890II gas
chromatograph equipped with an HP-5971A mass selective detector
and a DB5 fused silica capillary column (30 m × 0.25 mm;
Chromatographic Specialties, Inc.). Ultraviolet absorption spectra were
recorded on a Perkin Elmer Lambda 9 spectrometer interfaced to an
IBM PS/2-286 microcomputer, or on a Hewlett-Packard HP8451 UV
spectrometer. Gas chromatographic (GC) analyses were carried out
using a Hewlett-Packard 5890II+ gas chromatograph equipped with a
conventional heated injector, a flame ionization detector, a Hewlett-
Packard 3396A integrator, and a DB1701 megabore capillary column
(15 m × 0.53 mm; Chromatographic Specialties, Inc). Radial chro-
matography was carried out using a Chromatotron (Harrison Research)
and 2- or 4-mm silica gel 60 thick layer plates.

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M.; Higuchi, T.; Miyamoto S. *J. Am. Chem. Soc.* **1981**, *103*, 2324. (b)
Ishikawa, M.; Matsuzawa, S.; Sugisawa, H.; Yano, F.; Kamitori, S.; Higuchi,
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Hexane (BDH Omnisolv) was used as received from the supplier.
Quenchers were of the highest purity available and were used as
received from Aldrich Chemical Co. Chloropentamethyldisilane was
prepared by the method of Ishikawa and co-workers.[28] It was used in
the synthesis of **1** as a ~80:20 mixture with hexamethyldisilane.

((Trimethylsilyl)ethynyl)pentamethyldisilane (1) was prepared by
a modification of the procedure reported by Ishikawa and co-workers
for related alkynyldisilanes.[6] An oven-dried, 2-neck, 250-mL, round-
bottom flask fitted with magnetic stirrer, rubber septum, and nitrogen
inlet was placed in a dry ice–2-propanol bath. Anhydrous ether (60
mL) and (trimethylsilyl)acetylene (13.0 g, 0.13 mol) were introduced
by syringe. After stirring for ~15-min, *n*-butyllithium (85 mL of a
1.6 M hexane solution; 0.14 mol) was added over several minutes. The
dry ice bath was removed, the mixture was allowed to warm for
20 min, and chloropentamethyldisilane (0.13 mol) was added over 1 h
via syringe after cooling the reaction mixture back down to −78 °C.
The resulting mixture was stirred at room temperature under nitrogen
for 12 h, quenched by slow addition of distilled water (100 mL), and
extracted with ether (5 × 50 mL). The combined ether extracts were
washed with water (2 × 50 mL), dried over anhydrous magnesium
sulfate, and filtered. Evaporation of the solvent on the rotary evaporator
yielded a yellow liquid (~50 mL), which was purified in 1-mL portions
by radial chromatography using a 4-mm silica plate and hexane as the
eluant. Fractions containing >99.8% of the major component of the
reaction mixture (as determined by GC analysis) were combined and
stripped of solvent, resulting in an isolated yield of 8.2 g (0.036 mol,
27%) of ((trimethylsilyl)ethynyl)pentamethyldisilane (**1**; bp 48 °C (0.3
mmHg)). The compound was identified on the basis of the following
data: ^{1}H NMR, δ 0.095 (s, 9H), 0.143 (s, 9H), 0.167 (s, 6H); ^{13}C NMR,
δ −3.12, −2.68, 0.03, 112.92, 116.5; ^{29}Si NMR, δ −37.55 (SiMe$_3$),
−19.41 (SiMe$_3$), −18.95 (SiMe$_2$); MS, *m/e* (I) 228 (49), 213 (70), 155
(100), 140 (55), 119 (71); exact mass, Calcd for C$_{10}$H$_{24}$Si$_3$, 228.1186,
found 228.1198; UV (hexane), λ_{max} (ϵ/M^{-1} cm^{-1}) = 195 (17750), 217
nm (7100).

Preparative scale irradiations of **1** were carried out using a cadmium
resonance lamp (228 nm; Philips 93107E) and a water-cooled Pyrex
immersion well with a Suprasil inner sleeve. A solution of **1** (0.32 g,
1.4 mmol), *n*-dodecane (0.027 g), and anhydrous methanol (1.12 g, 35
mmol) in anhydrous hexane (70 mL) was stirred vigorously and
continuously degassed with a stream of dry nitrogen throughout
photolysis to 48% conversion (1.5 h), with periodic monitoring of the
course of the photolysis by GC. Three major products were formed,
in approximate yields (determined from the slopes of concentration vs
time plots, with "concentrations" determined from the relative areas
of the GC peaks due to product and *n*-dodecane) of 42% (**7**), 12% (**6**),
and 23% (**4**) (listed in order of increasing GC retention time).
Compound **5** (elutes before **6**; ca. 4% after 48% conversion) increased
in yield throughout the course of the photolysis, allowing it to be
identified as a secondary photoproduct. Compound **7** was identified
by GC/MS and by coinjection of the photolysate with an authentic
sample of bis(trimethylsilyl)acetylene (Aldrich). The other three
products were isolated from the photolysate as colorless liquids by radial
chromatography (using a 2-mm silica gel plate and hexane as the eluant)
after evaporation of the solvent and volatiles. Coinjection of each of
the purified components with a portion of the original photolysate
verified that they survived purification intact. They were identified
on the basis of the following spectroscopic data ($J_{Si–H}$ refer to coupling
constants between silicon atoms and the single vinylic hydrogen in
each of the adducts):

1-(Methoxydimethylsilyl)-(E)-1,2-bis(trimethylsilyl)ethene (4). ^{1}H
NMR, δ 0.159 (s, 9H), 0.166 (s, 6H), 0.169 (s, 9H), 3.364 (s, 3H),
7.426 (s, 1H); ^{13}C NMR, δ −1.344 (SiMe$_2$), 0.765 (SiMe$_3$), 1.629
(SiMe$_3$), 50.259 (OMe), 165.868 (=CH), 166.867 (=C); ^{29}Si NMR, δ
−10.85 (SiMe$_3$, $J_{Si–H}$ = 5.1 Hz), −9.04 (SiMe$_3$, $J_{Si–H}$ = 21.5 Hz),
10.29 (SiMe$_2$, $J_{Si–H}$ = 17.6 Hz); MS, *m/e* (I) 260 (0.5), 245 (20), 187
(33), 157 (27), 156 (28), 147 (11), 141 (32), 89 (62), 73 (100), 59
(49).

1-(Methoxydimethylsilyl)-(Z)-1,2-bis(trimethylsilyl)ethene (5). ^{1}H
NMR, δ 0.065 (s, 9H), 0.109 (s, 9H), 0.189 (s, 6H), 3.373 (s, 3H),

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7.335 (s, 1H); ^{13}C NMR, δ −0.169 (SiMe$_3$), −0.028 (SiMe$_2$), 0.529 (SiMe$_3$), 49.322 (OMe), 165.886 (=CH); ^{29}Si NMR, δ −11.01 (SiMe$_3$, J_{Si-H} = 6.2 Hz), −3.09 (SiMe$_3$, J_{Si-H} = 16.6 Hz), 6.19 (SiMe$_2$, J_{Si-H} = 21.6 Hz); MS, *m/e* (I) 260 (0.5), 246 (19), 187 (32), 157 (34), 156 (26), 147 (11), 141 (32), 89 (62), 83 (11), 73 (100), 59 (48).

1-(Methoxydimethylsilyl)-2,2-bis(trimethylsilyl)ethene (6). ^1H NMR, δ 0.088 (s, 9H), 0.161 (s, 9H), 0.224 (s, 6H), 3.404 (s, 3H), 7.160 (s, 1H); ^{13}C NMR, δ −0.591 (SiMe$_2$), 0.225 (SiMe$_3$), 1.601 (SiMe$_3$), 50.117 (OMe), 159.524 (=CH), 172.301 (=C); ^{29}Si NMR, δ −7.87 (SiMe$_3$, J_{Si-H} = 16.8 Hz), −0.79 (SiMe$_3$, J_{Si-H} = 21.3 Hz), 2.95 (SiMe$_2$, J_{Si-H} = 6.8 Hz); MS, *m/e* (I) 260 (0.7), 245 (19), 187 (30), 157 (35), 156 (24), 147 (11), 141 (28), 89 (57), 83 (11), 73 (100), 59 (55).

Analytical-scale photolyses were carried out using the same lamp, but using solutions contained in quartz tubes (50 mm × 5 mm) which were clamped ∼0.5 in. from the light source. Photolysis of **1** in the absence of methanol employed a 0.5-mL aliquot of a 0.02 M solution of **1** in anhydrous hexane solution, which was sealed in a 50 × 5 mm tube with a rubber septum and deoxygenated with a stream of dry argon. The contents were photolyzed with periodic monitoring by GC to check the course of the photolysis. Two major volatile products and ∼10 minor ones of considerably longer retention time than **1** could be detected in the photolysis mixture. One of the major products was identified as **7** (∼40%), while the other was identified as **1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacyclopropene (2,** ∼20%) by comparison of its mass spectrum (recorded by GC/MS) to literature data:[8] MS, *m/e* (I) 228 (25), 213 (34), 156 (11), 155 (61), 140 (32), 125 (16), 97 (18), 83 (17), 73 (100). Addition of an excess of anhydrous methanol to the photolysate resulted in the disappearance of **2** and concomitant formation of **4**.

Nanosecond laser flash photolysis experiments employed the pulses (248 nm; ca.16 ns; 70−120 mJ) from a Lumonics 510 excimer laser filled with F$_2$/Kr/He mixtures, and a microcomputer-controlled detection system.[29] The system incorporates a brass sample holder whose temperature is controlled to within 0.1 °C by a VWR 1166 constant temperature circulating bath. Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7 (0.028 M), and were flowed continuously through a 3 × 7 mm Suprasil flow cell connected to a calibrated 100-mL reservoir. Where required, nitrogen was bubbled continuously through the reservoir throughout the experiments. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple which was inserted directly into the flow cell. Quenchers were added directly to the reservoir by microlitre syringe as aliquots of standard solutions. Rate constants were calculated by linear least-squares analysis of decay rate−concentration data (6 or more points) which spanned at least one order of magnitude in the transient decay rate. Errors are quoted as twice the standard deviation obtained from the least squares analysis in each case.

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