

Solvent, Substituent, and Temperature Effects on the Absolute Rate Constants for Addition of Methoxytrimethylsilane to 1,1-Diarylsilenes

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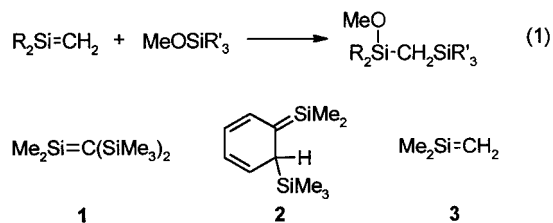
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Absolute rate constants have been measured for the reaction of methoxytrimethylsilane with a series of transient, para-substituted 1,1-diphenylsilenes ($\text{H}_2\text{C}=\text{Si}(\text{C}_6\text{H}_4\text{X})_2$, where $\text{X} = \text{H}, \text{Me}, \text{F}, \text{Cl},$ and CF_3) in hexane solution at room temperature. The data correlate with Hammett substituent constants, affording the reaction constant $\rho = +0.9 \pm 0.2$. For the parent compound and the 4,4'-bis(trifluoromethyl) derivative, rate constants have been determined over the 0–60 °C temperature range in hexane, 1,2-dichloroethane, and acetonitrile solution. The rate constants for reaction of the parent compound increase in the order hexane \approx 1,2-dichloroethane $<$ MeCN, but are relatively insensitive to solvent in the other case. However, differences are revealed in the Arrhenius activation energies for reaction, which are negative for both compounds in all three solvents. Those for the 4,4'-bis(trifluoromethyl) compound in particular change to more positive values with increasing solvent polarity. The data are consistent with a two-step mechanism involving reversible preassociation of the silene and the alkoxy silane to form a Lewis acid–base complex, which collapses to product by intramolecular transfer of trimethylsilyl from oxygen to the silenic carbon.

Introduction

The addition of alkoxy silanes is one of the commonly used trapping reactions to demonstrate the formation of reactive silenes from thermolysis or photolysis of appropriate precursors in solution or the gas phase (eq 1).^{1–4} The reaction is known to proceed with *syn*-stereospecificity,^{5–7} and early studies by Wiberg of the relative rates of reaction of the transient silene **1** with a wide variety of silene trapping reagents demonstrated that the reaction with methoxytrimethylsilane (MeOTMS) is several orders of magnitude slower than that of addition of simple alcohols such as methanol.^{8–10} This has been verified by our own absolute rate studies of the reactivity of aryldisilane-derived 1,3,5-(1-sila)-hexatrienes (e.g., **2**) in solution¹¹ and those of Davidson and Wood on 1,1-dimethylsilene (**3**) in the gas phase.¹²



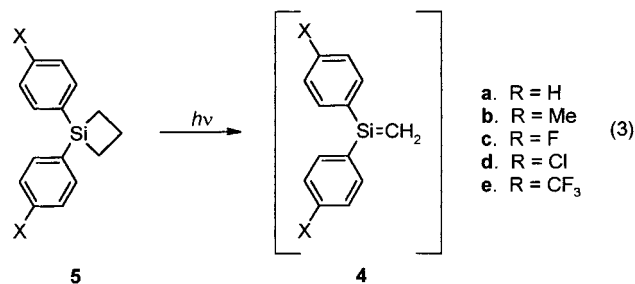
The stereochemistry of the reaction is consistent with either a concerted mechanism or a stepwise one involving the initial formation of a Lewis acid–base complex in which a high degree of double-bond character persists in the silenic Si=C bond, which proceeds to product by 1,3-migration of the trialkylsilyl group from oxygen to carbon (eq 2). A similar mechanism was first proposed by Wiberg for the addition of alcohols and other polar reagents to silene **1** on the basis of relative reactivities,^{9,13,14} and detailed product and/or kinetic studies have since provided compelling evidence that stepwise mechanisms involving initial nucleophilic attack are common to many of the polar addition reactions that silenes undergo, including addition of alcohols,^{15–20}

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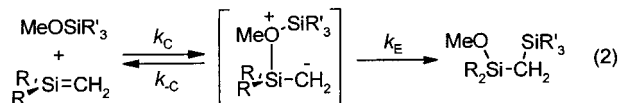
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carboxylic acids,^{18–20} ketones,^{11,21,22} and amines.^{23,24} Clearly, there is good reason to suspect that the addition of alkoxy-silanes should proceed by this mechanism as well.

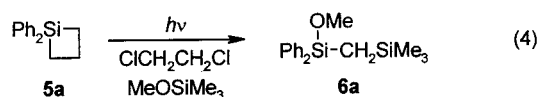


In this paper, we report the results of a study of the effects of solvent, substituent, and temperature on the absolute rate constants for addition of methoxytrimethylsilane to 1,1-diphenylsilene (**4a**) in solution. Silene **4a** and four ring-substituted derivatives (**4b–e**) have been generated by laser flash photolysis of the corresponding 1,1-diarylsilacyclobutanes **5a–e**, as reported previously by our group (eq 3),^{20,22} and absolute rate constants have been measured for their bimolecular reaction with MeOTMS in hexane solution at room temperature. In addition, kinetic data for two of the derivatives (**4a** and **4e**) have been obtained in hexane, 1,2-dichloroethane (DCE), and acetonitrile (MeCN) solution over the 0–60 °C temperature range. The results allow a definitive characterization to be made of the mechanism for the addition of alkoxy-silanes to the Si=C bond of transient silenes in solution.



Results and Discussion

Steady-state photolysis (254 nm) of a 0.05 M solution of 1,1-diphenylsilacyclobutane (**5a**) in dry, deoxygenated 1,2-dichloroethane solution in the presence of 0.075 M methoxytrimethylsilane (MeOTMS) at 25 °C afforded a single product in quantitative yield. The compound was isolated by column chromatography and identified as **6a** by comparison of its mass and ¹H and ¹³C NMR spectra to published data (see eq 4).²⁵



Nanosecond laser flash photolysis of air-saturated solutions of **5a–e** (~0.003 M) in dry hexane allows the direct detection of the corresponding arylsilenes **4a–e**

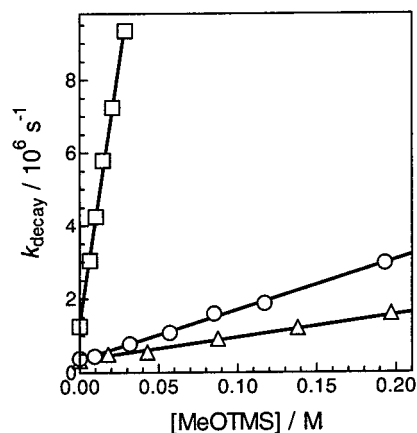


Figure 1. Plots of k_{decay} vs $[\text{MeOTMS}]$ for the 1,1-diarylsilenes **4a** (○), **4b** (△), and **4e** (□) in hexane solution at 24 °C.

Table 1. Absolute Rate Constants (in units of $10^7 \text{ M}^{-1} \text{ s}^{-1}$) for Reaction of MeOTMS with the Para-Substituted 1,1-Diphenylsilenes **4a–e in Hexane Solution at 24 °C^a**

4a (X = H)	4b (X = CH ₃)	4c (X = F)	4d (X = Cl)	4e (X = CF ₃)
1.9 ± 0.2	0.60 ± 0.05	2.4 ± 0.2	3.0 ± 0.2	12.0 ± 0.9

^a From the slopes of plots of k_{decay} vs $[\text{MeOTMS}]$ (see eq 5 and Figure 1). Errors are quoted as ±2σ.

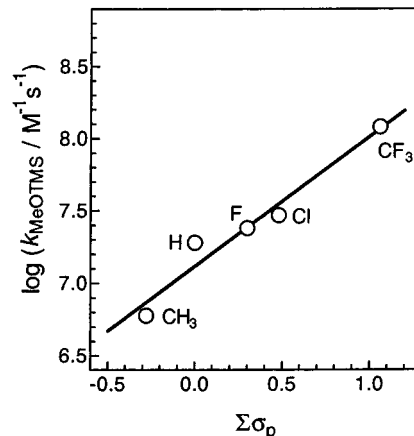


Figure 2. Hammett plot for the reaction of 1,1-diarylsilenes **4a–e** with MeOTMS in hexane solution at 24 °C.

as moderately strong transient absorptions centered at $\lambda_{\text{max}} = 325 \text{ nm}$, as reported previously.^{20,22} The lifetimes of the silenes are shortened upon addition of MeOTMS to the solutions, and plots of the pseudo-first-order rate constant for silene decay (k_{decay}) versus MeOTMS concentration according to eq 5 (where k_0 is the pseudo-first-order rate constant for silene decay in the absence of the quencher) were linear in every case; Figure 1 shows representative plots for **4a**, **4b**, and **4e**. The slopes afford the second-order rate constants for reaction of the silene with MeOTMS (k_{MeOTMS}), which are collected in Table 1 for the five compounds. The data are plotted against Hammett substituent parameters²⁶ according to eq 6 in Figure 2. Linear least-squares analysis ($r^2 = 0.953$) affords the Hammett reaction constant $\rho = +0.9 \pm 0.2$, where the error is expressed as ±2σ.

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$$k_{\text{decay}} = k_0 + k_{\text{MeOTMS}}[\text{MeOTMS}] \quad (5)$$

$$\log k_{\text{MeOTMS}}^X = \log k_{\text{MeOTMS}}^H + \rho \Sigma \sigma_p^X \quad (6)$$

The absolute rate constants for addition of MeOTMS to **4a–e** in hexane solution are roughly 10–20 times lower than those for the ene-addition of acetone²² and roughly 100 times lower than those for addition of methanol or acetic acid.²⁰ The Hammett ρ -value indicates that the reaction is facilitated by (inductive) electron-withdrawing substituents at silicon, a result that can be most simply explained in terms of an effect on the degree of positive charge character at silicon. This would be expected to enhance reactivity if nucleophilic attack at the Si=C bond is the initial step in the reaction, as proposed in eq 2. The ρ -value for MeOTMS addition can be compared to those observed for reaction of the same compounds with methanol ($\rho = +0.31 \pm 0.06$), *tert*-butanol ($\rho = +0.55 \pm 0.08$), acetic acid ($\rho = +0.17 \pm 0.03$), and acetone ($\rho = +1.5 \pm 0.2$),^{20,22} all of which have been shown to proceed via stepwise mechanisms analogous to this one. The ρ -values for alcohol addition are particularly relevant in that the proton-transfer step involves a 1,3-transfer (as does the trimethylsilyl transfer shown in eq 2), rather than the 1,5-transfer that is involved in acetone and acetic acid additions. The effect is also analogous to that observed in Michael additions to β -nitrostyrene derivatives, which exhibit Hammett ρ -values in the range +0.2–1 depending on the nucleophile and the solvent.²⁷ The 100-fold reduction in rate compared to MeOH addition to **4a–e** can most reasonably be attributed to a slower rate of transfer of the electrophilic group ($-\text{SiMe}_3$, relative to $-\text{H}$) within the initially formed complex, since this involves cleavage of a relatively strong Si–O bond.

Further support for the stepwise reaction pathway is provided by the temperature dependences of the rates of MeOTMS addition to **4a** and **4e**. Absolute rate constants for reaction of the two silenes with MeOTMS were determined in hexane, 1,2-dichloroethane (DCE), and acetonitrile (MeCN) solution over the 0–60 °C temperature range; Figure 3 shows Arrhenius plots for the two compounds in the three solvents, while Table 2 lists the corresponding Arrhenius parameters and absolute rate constants recorded at a temperature of 24.0 \pm 0.5 °C. Solvent polarity has only modest effects on the rate constants for reaction of MeOTMS with **4a** and **4e** at 24 °C, and the effects are somewhat different in the two cases. Both silenes react slightly faster in the more polar solvent DCE than in hexane, but respond differently to the change in solvent to MeCN. The decrease in rate constant in MeCN compared to hexane that is observed for **4e** is the expected change, considering the results for other nucleophiles that have been studied in these two solvents.^{20,22} This has been attributed previously to weak complexation between the silene and solvent. As can be seen from the Arrhenius data, the reactions of both silenes exhibit negative activation energies in all three solvents. The two silenes exhibit similar E_a 's in both hexane and DCE, with those in the more polar DCE being somewhat more positive than in hexane solution. Slightly different behavior is

observed in MeCN solution, where **4e** (the more reactive of the two silenes) exhibits a significantly less negative activation energy than **4a**.

The origin of a negative activation energy can be understood by consideration of the expression for the observed second-order rate constant for reaction that is predicted by the mechanism of eq 2. The expression is given in eq 7, where the fundamental rate constants k_C , k_{-C} , and k_E are defined in eq 2 and the steady-state approximation has been applied to the intermediate Lewis acid–base complex between the silene and the alkoxy silane. A negative activation energy results when the complex partitioning ratio $k_E/(k_E + k_{-C})$ decreases with increasing temperature, either because k_E and k_{-C} vary with temperature in opposing fashion or because k_E increases less steeply than k_{-C} with increasing temperature. Either situation will result when entropic factors dominate the rate constant for the product-forming step, k_E . Over a very wide range in temperature, the superposition of the negative temperature dependence of the ratio $k_E/(k_E + k_{-C})$ on the positive temperature dependence of k_C will result in a bell-shaped Arrhenius plot, with a positive slope (negative E_a) over the range where $k_{-C} > k_E$ and a negative slope (positive E_a) over the range where $k_{-C} < k_E$.

$$k_{\text{MeOTMS}} = k_C [k_E / (k_E + k_{-C})] \quad (7)$$

The activation energies for reaction of **4a** and **4e** with MeOTMS in hexane are much more negative than those exhibited by other nucleophilic additions to these compounds, suggesting that $k_{-C} \gg k_E$ for both compounds over the 0–60 °C temperature range; that is, the silene–alkoxy silane complex is likely to be in rapid equilibrium with the free reactants, and product formation is comparatively slow. The less negative E_a values observed in DCE and MeCN suggest that this reversibility is reduced in the more polar solvents, possibly due to stabilization of the polar, zwitterionic complex relative to the free reactants. We exercise caution in this interpretation, however, since only one of the two compounds (**4e**) exhibits the predicted further decrease in $-E_a$ in MeCN compared to that in DCE. The difference in the activation energies for reaction of **4a** and **4e** in MeCN solution is also common to the reaction of these two silenes with other nucleophiles in this solvent and is consistent with the complex partitioning ratio being somewhat larger for **4e** than for **4a** at any particular temperature.^{18–20,22} However, the behavior might also originate from solvent complexation effects, which are expected to be relatively weak in acetonitrile, but still clearly stronger than would be expected in the other solvents. More detailed study of these effects are the subject of ongoing work in our laboratory.

The positive Hammett ρ -value observed for the reaction of **4a–e** with MeOTMS is the composite of cooperative effects on k_C , the rate constant for complexation, and $k_E/(k_E + k_{-C})$, the ratio defining the partitioning of the complex between product and starting materials. The individual effects are difficult to unravel, although both k_C and $k_E/(k_E + k_{-C})$ are expected to increase in magnitude with increased electron-withdrawing power of substituents at silicon. Only in MeCN, where a difference in activation energy is observed for reaction of **4a** and **4e**, can a distinct effect on the complex

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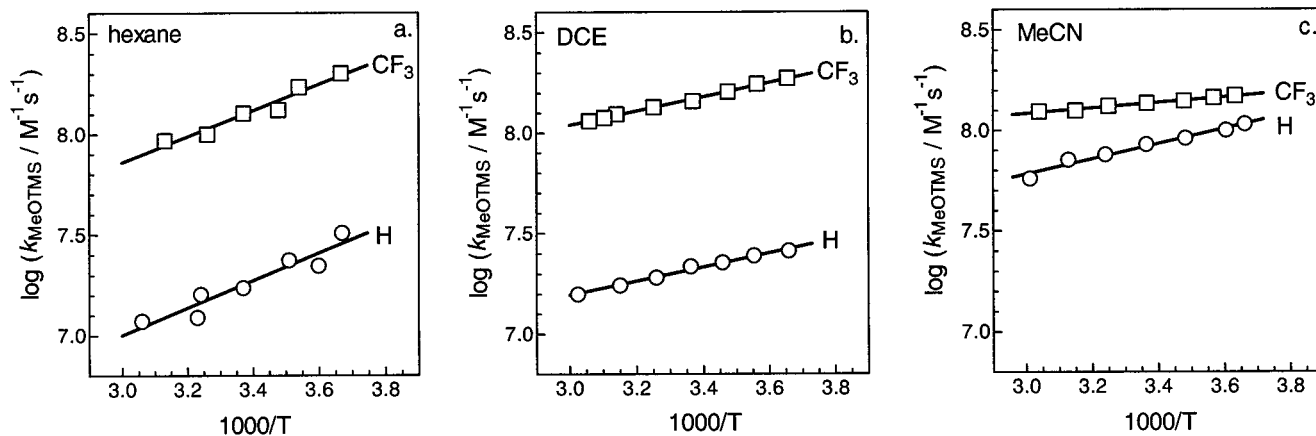


Figure 3. Arrhenius plots for the reaction of MeOTMS with 1,1-diphenylsilene (**4a**) and 1,1-bis(4-trifluoromethylphenyl)silene (**4e**) in (a) hexane, (b) DCE, and (c) MeCN solution.

Table 2. Arrhenius Parameters and Absolute Rate Constants (25 °C) for Reaction of MeOTMS with 1,1-Diphenylsilene (**4a**) and 1,1-Bis(4-trifluoromethylphenyl)silene (**4e**) in Hexane, 1,2-Dichloroethane (DCE), and Acetonitrile (MeCN) Solution^a

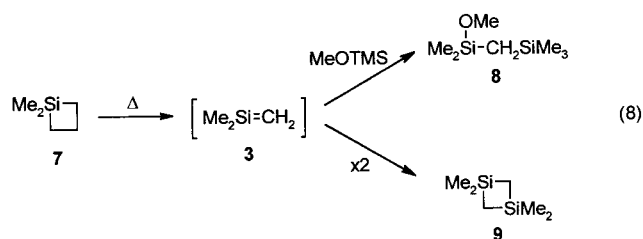
compound		hexane	DCE	MeCN
4a	$k^{24C}/10^7 \text{ M}^{-1} \text{ s}^{-1}$	2.1 ± 0.1	2.2 ± 0.1	8.6 ± 0.3
	E_a (kcal/mol)	-3.1 ± 0.4	-1.6 ± 0.1	-1.7 ± 0.1
	$\log(A/\text{M}^{-1} \text{ s}^{-1})$	5.0 ± 0.3	6.2 ± 0.1	6.6 ± 0.1
4e	$k^{24C}/10^7 \text{ M}^{-1} \text{ s}^{-1}$	12.0 ± 0.9	14.4 ± 0.8	13.7 ± 1.1
	E_a (kcal/mol)	-3.0 ± 0.3	-1.6 ± 0.1	-0.6 ± 0.1
	$\log(A/\text{M}^{-1} \text{ s}^{-1})$	5.9 ± 0.3	7.0 ± 0.1	7.7 ± 0.1

^a Errors are quoted as $\pm 2\sigma$.

partitioning ratio be ascertained; as discussed above, the less negative E_a observed for **4e** compared to **4a** is consistent with a larger value of the partitioning ratio for the more reactive of the two compounds. The same trend in E_a is observed for the addition of alcohols, acetic acid, and acetone to **4a** and **4e**.^{20,22} In contrast, no difference in E_a is detectable for reaction of the two compounds with MeOTMS in hexane and DCE. This may indicate that the partitioning ratio is insensitive to substituents in the less polar solvents, but it should be noted that the activation energy will be relatively insensitive to variations in the partitioning ratio when its magnitude is relatively small; i.e., when k_C is considerably larger than k_E .

The only other kinetic study of alkoxy silane addition to reactive silenes that has been reported is that of Davidson and Wood, who employed high-temperature pyrolysis techniques to study the addition of MeOTMS to 1,1-dimethylsilene (**3**) in the gas phase over the 450–550 °C temperature range, using 1,1-dimethylsilylcyclobutane (**7**) as the silene precursor.¹² Rate constants were determined from the yields of the addition product (**8**) relative to that of the silene dimer **9** (eq 8) and using the kinetic data reported earlier by Nametkin and co-workers for the dimerization of **3** over the 25–300 °C temperature range ($k = 6.6 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$; $E_a = 0$).²⁸ This afforded activation parameters of $E_a = +1.5 \pm 0.5 \text{ kcal/mol}$ and $\log(A/\text{M}^{-1} \text{ s}^{-1}) = 5.3 \pm 0.2$ for the reaction of **3** with MeOTMS under these conditions. While the

value of the dimerization rate constant for **3** in the gas phase at 25 °C was later revised upward by Potzinger and co-workers (to $k_{\text{dim}} = (3.3 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$),²⁹ indirect evidence from other experiments appears to corroborate the value of $E_a \approx 0$.³⁰ Thus, only the preexponential factor reported by Davidson and Wood for the addition of MeOTMS to **3** need be considered inaccurate, and the small positive value of E_a should be meaningful. Given the fact that **4a** and **3** exhibit similar overall reactivity toward MeOH addition, a similarity that extends to the sign and magnitude of the Arrhenius activation energies for reaction of the two silenes,^{18,31} the apparent differences in their activation energies for reaction with MeOTMS are extremely interesting, despite the pronounced differences in reaction conditions. Further studies of the kinetics of the addition of alkoxy silanes to reactive silenes in solution are in progress.



Experimental Section

NMR spectra were recorded in deuteriochloroform on a Bruker AC200 spectrometer and were referenced to tetramethylsilane. Ultraviolet absorption spectra were recorded on Hewlett-Packard HP8451 or Cary 50 UV spectrometers. Low-resolution mass spectra were determined by GC/MS, using a Hewlett-Packard 5890II gas chromatograph equipped with a HP-5971A mass selective detector and DB-5 fused silica capillary column (30m \times 0.25 mm; Chromatographic Specialties, Inc).

Analytical gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with conventional heated splitless injector, a flame ionization

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detector, a Hewlett-Packard 3396A integrator, and a DB1701 megabore capillary column (15m × 0.53 mm; Chromatographic Specialties, Inc.).

Acetonitrile (Caledon Reagent) was refluxed over calcium hydride (Fisher) for several days, distilled under dry nitrogen, and then cycled three times through a 1 in. × 6 in. column of neutral alumina (Aldrich) which had been activated by heating under vacuum (ca. 0.05 Torr) at 320 °C for 10 h with periodic shaking. Hexane (Caledon HPLC) was used as received from the supplier. 1,2-Dichloroethane (DCE) was shaken with basic alumina, stored for 24 h over sodium hydroxide to remove acid impurities, and distilled from phosphorus pentoxide. Methoxytrimethylsilane was synthesized by reaction of methanol with excess hexamethyldisilazane and purified by distillation (bp 56–58 °C). The 1,1-diarylsilacyclobutanes (**5a–e**) were prepared according to the published methods.²⁰

Steady-state photolysis of a solution of **5a** (1 mmol) and MeOTMS (2.3 mmol) in dry 1,2-dichloroethane (25 mL) was carried out in quartz tubes using a Rayonet reactor containing eight RPR2537 lamps. The photolysis was taken to ca. 90% conversion (ca. 24 h), with periodic shaking and monitoring by GC. The solvent was removed on the rotary evaporator to leave a yellow oil. Chromatography on a silica gel column with hexane as eluant afforded a single product in 52% yield; it was identified as methoxydiphenyl(trimethylsilylmethyl)silane (**6a**)

by comparison of its mass and ¹H/¹³C NMR spectra to published data.²⁵

Nanosecond laser flash photolysis experiments employed the pulses (248 nm; 15–20 ns; 70–120 mJ) from Lumonics 510 or Lambda Physik Compex 100 excimer lasers, filled with F₂/Kr/He mixtures, and the microcomputer-controlled detection system described previously.^{20,22} Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7 (0.003–0.004 M) and were flowed continuously through a 3 × 7 Suprasil flow cell connected to a calibrated 100 mL reservoir. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple that was inserted directly into the flow cell. MeOTMS was added directly to the reservoir by microliter syringe as aliquots of standard solutions. Rate constants were calculated by linear least-squares analysis of decay rate-concentration data (6–10 points) that spanned at least a factor of 5 (usually more than 1 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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