Steady state and time-resolved spectroscopic studies of the photochemistry of 1-arylsilacyclobutanes and the chemistry of 1-arylsilenes

William J. Leigh, Rabah Boukherroub, Christine J. Bradaric, Christine C. Cserti, and Jennifer M. Schmeisser

Abstract: Direct photolysis of 1-phenylsilacyclobutane and 1-phenyl-, 1-(2-phenylethynyl)-, and 1-(4′-biphenylyl)-1-methylsilacyclobutane in hexane solution leads to the formation of ethylene and the corresponding 1-arylsilenes, which have been trapped by photolysis in the presence of methanol. Quantum yields for photolysis of the three methyl-substituted compounds have been determined to be 0.04, 0.26, and 0.29, respectively, using the photolysis of 1,1-diphenylsilacyclobutane ($\Phi_{silene} = 0.21$) as the actinometer. The corresponding silenes have been detected by laser flash photolysis; they have lifetimes of several microseconds, exhibit UV absorption maxima ranging from 315 to 330 nm, and react with methanol with rate constants on the order of $(2–5) \times 10^9 \, M^{-1} \, s^{-1}$ in hexane. Absolute rate constants for reaction of 1-phenylsilene and 1-methyl-1-phenylsilene with water, methanol, *tert*-butanol, and acetic acid in acetonitrile solution have been determined, and are compared to those of 1,1-diphenylsilene under the same conditions. With the phenylethynyl- and biphenyl-substituted methylsilacyclobutanes, the triplet states can also be detected by laser flash photolysis, and are shown to not be involved in silene formation on the basis of triplet sensitization and (or) quenching experiments. Fluorescence emission spectra and singlet lifetimes have been determined for the three 1-aryl-1-methylsilacyclobutanes, 1,1-diphenylsilacyclobutane, and a series of acyclic arylmethylsilane model compounds. These data, along with the reaction quantum yields, allow estimates to be made of the rate constants for the excited singlet state reaction responsible for silene formation. 1-Methyl-1-phenylsilacyclobutane undergoes reaction from its lowest excited singlet state with a rate constant 10–80 times lower than those of the other three derivatives. The results are consistent with a stepwise mechanism for silene formation, involving a 1,4-biradicaloid intermediate that partitions between product and starting material.

Key words: silene, silacyclobutane, photochemistry, biradical.

Résumé : La photolyse directe du 1-phénylsilacyclobutane et des 1-phényl-, 1-(2-phényléthynyl)- et 1-(4′-biphénylyl)-1-méthylsilacyclobutane, en solution dans l'hexane, conduit à la formation d'éthylène et des 1-arylsilènes correspondants que l'on a piégés par photolyse en présence de méthanol. On a déterminé les rendements quantiques pour les photolyses des trois composés portant un groupe méthyle; si l'on utilise la photolyse du 1,1-diphénylcyclobutane ($\Phi_{silène} = 0,21$) comme actinomètre, les valeurs sont respectivement 0,04, 0,26 et 0,29. On a détecté les silènes correspondants à l'aide de la photolyse éclair au laser; leurs temps de vie sont de plusieurs microsecondes, ils présentent des maxima d'absorption UV à des valeurs allant de 315 à 330 nm et ils réagissent avec le méthanol avec des constantes de vitesse de l'ordre de $(2–5) \times 10^9 \, M^{-1} \, s^{-1}$, dans l'hexane. On a déterminé les constantes de vitesse absolue pour la réaction du 1-phénylsilène et du 1-méthyl-1-phénylsilène avec l'eau, le méthanol, l'alcool *tert*-butylique et l'acide acétique, en solution dans l'acétonitrile, et on les a comparées à celles du 1,1-diphénylsilène dans les mêmes conditions. Avec les méthylsilacyclobutanes substitués par des groupes phényléthynyle et biphényle, la photolyse éclair au laser permet aussi de détecter les états triplets et, en se basant sur des expériences de sensibilisation de triplets et/ou de désactivation, on a démontré qu'ils ne sont pas impliqués dans la formation du silène. On a déterminé les spectres d'émission de fluorescence et les temps de vie des singulets des trois 1-aryl-1-méthylsilacyclobutanes, du 1,1-diphénylsilacyclobutane et d'une série de composés arylméthylsilanes acycliques modèles. Ces données utilisées avec les rendements quantiques des réactions ont permis d'évaluer les constantes de vitesse de réaction de l'état singulet excité responsable de la formation du silène. La vitesse de réaction du 1-méthyl-1-phénylsilacyclobutane à partir de son

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état singulet excité le plus bas est de 10 à 80 fois plus rapide que les vitesses des trois autres dérivés. Ces résultats sont en accord avec un mécanisme par lequel la formation du silène se ferait par étapes impliquant un intermédiaire 1,4-biradicaloïde qui se répartirait entre le produit de la réaction et le produit de départ.

Mots clés : silène, silacyclobutane, photochimie, biradical.
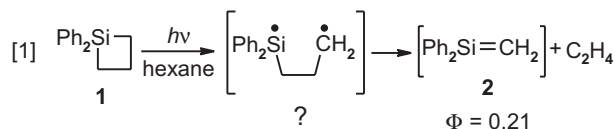
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Introduction

Silacyclobutanes are well known to yield products consistent with the formation of silene-reactive intermediates upon photolysis in solution or the gas phase, or upon pyrolysis at high temperatures (1–8). These compounds have proven to be tremendously useful as photochemical precursors for transient silenes, in experiments aimed at detecting the silenes directly and studying the kinetics and mechanisms of their reactions with alcohols and other "silenophiles" (9–17). Photochemical silene formation proceeds with useful efficiencies from silacyclobutanes that bear alkyl, vinyl, ethynyl, silyl, and phenyl substituents at silicon, and possess UV absorption maxima between 190 and 250 nm (2, 4, 12, 13, 17–20). In contrast, alkoxy substitution either directly at silicon or on the aromatic rings of phenylated derivatives renders the silacyclobutane moiety inert to photocycloreversion (13, 17).

Several details of the mechanism for the photochemical cycloreversion of silacyclobutanes are known, at least for 1,1-dialkyl-substituted derivatives that absorb below ~230 nm. The reaction is initiated from the lowest (σ,σ^*) excited singlet state, by cleavage of one of the ring Si—C bonds to form a biradicaloid intermediate that cleaves to silene and alkene, recloses to starting material, and undergoes intramolecular disproportionation if an alkyl substituent is present at C2 (20). The presence of substituents at C2 of the silacyclobutane ring directs the regiochemistry of the initial cleavage toward the Si—C2 bond, leading to an intermediate whose lifetime is long enough to allow bond rotations that lead to partial scrambling of the stereochemistry at this carbon (20). This mechanism contrasts that of the thermal cleavage of silacyclobutanes, which has been shown to proceed by a stepwise mechanism involving initial C2—C3 bond cleavage (21–24).

The situation is less clear with 1-phenyl-substituted derivatives, in which the phenyl substituent is the primary chromophore. 1,1-Diphenylsilacyclobutane (**1**) affords 1,1-diphenylsilene (**2**; eq. [1]) with reasonable efficiency $(\Phi_2 = 0.21)$, and time-resolved experiments have shown that silene formation occurs on the nanosecond time scale and cannot be quenched by saturation of the solution with oxygen or other triplet quenchers (11). The reactive excited state is thus most likely the lowest excited singlet state, which in these cases is predominantly of benzenoid π,π^* character. For efficient cleavage to occur, however, the ring Si—C bonds in the reactive excited state must obviously be weakened compared to the situation in the ground state, so the lowest benzenoid excited singlet state is presumably mixed with σ,σ^*, σ,π^* or π,σ^* configurations that activate the ring toward cleavage. Whether the reaction occurs by a concerted or stepwise mechanism has not been conclusively established, although the question has in fact been addressed in
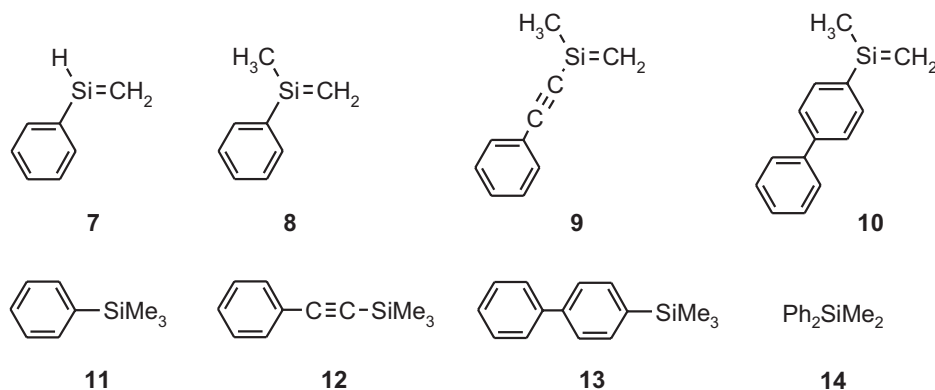
two early papers on the photochemistry of 2-phenyl-substituted silacyclobutanes (4, 25).

[1] $$Ph_2Si\rceil \xrightarrow[\text{hexane}]{h\nu} \left[Ph_2\overset{\bullet}{Si} \quad \overset{\bullet}{C}H_2 \right] \longrightarrow \left[Ph_2Si=CH_2 \right] + C_2H_4$$
1 ? **2** $\Phi = 0.21$

In this paper, we report the photochemistry of 1-phenyl-silacyclobutane (**3**) and the series of 1-methyl-1-arylsilacyclobutane derivatives **4–6**, in which the aryl substituent is varied between phenyl, phenylethynyl, and biphenyl. The main goal of this work was to determine how the photophysical properties of the chromophore affect the rates and efficiencies of silene formation in arylsilacyclobutane photolysis, and hence to better define the scope and limitations of silacyclobutane photolysis as a source of reactive silenes. It seemed likely to us that the phenylacetylene and biphenyl chromophores in **5** and **6** would allow study of the photochemistry and photophysics of arylsilacyclobutanes in
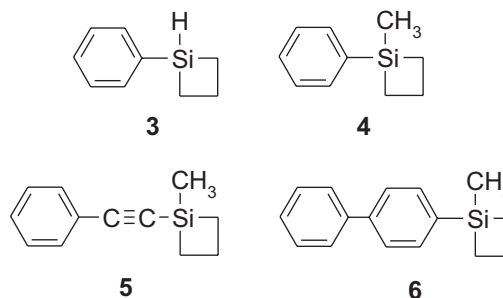
much greater detail than is convenient with simple phenyl derivatives, since these chromophores generally fluoresce strongly and promote efficient intersystem crossing to the lowest triplet states, which are usually detectable by laser flash photolysis. Thus, we have studied the photochemistry of the three 1-aryl-1-methylsilacyclobutanes (**4–6**) in detail, using steady state photolysis and time-resolved UV absorption and fluorescence emission spectroscopic techniques. Photolysis of all four compounds in hydrocarbon solvents yields the corresponding silenes (**7–10**), which have been detected directly by laser flash photolysis methods and characterized on the basis of their reactivity toward methanol and *tert*-butanol. Absolute rate constants for the reactions of **7** and **8** with the two alcohols, water, and acetic acid have been determined in acetonitrile solution, and are compared to those for 1,1-diphenylsilene (**2**) under similar conditions. Fluorescence spectra and lifetimes have also been determined for **1** and the acyclic arylsilanes **11–14**, to provide a more complete framework with which to understand the
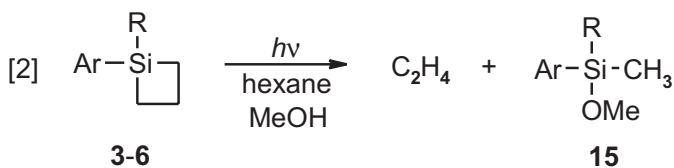
$$\underset{\mathbf{7}}{\overset{H}{\underset{}{Si=CH_2}}} \qquad \underset{\mathbf{8}}{\overset{H_3C}{\underset{}{Si=CH_2}}} \qquad \underset{\mathbf{9}}{\overset{H_3C}{\underset{}{Si=CH_2}}} \qquad \underset{\mathbf{10}}{\overset{H_3C}{\underset{}{Si=CH_2}}}$$

7   **8**   **9**   **10**

$Ph\text{-}SiMe_3$ (**11**) $Ph\text{-}C\equiv C\text{-}SiMe_3$ (**12**)   biphenyl-$SiMe_3$ (**13**) Ph_2SiMe_2 (**14**)

11   **12**   **13**   **14**

variations in photochemistry and photophysics of these arylsilacyclobutanes as a function of substituent.

Results

Silacyclobutanes **5** and **6** were prepared by reaction of 1-chloro-1-methylsilacyclobutane with phenylethynyllithium and 4-biphenylmagnesium bromide, respectively, using a procedure similar to those reported previously for the synthesis of **3** (26) and **4** (3). All four compounds were purified to >99% (GC) purity by vacuum distillation (**3–5**) or repeated recrystallization (**6**).

Photolysis (254 nm) of the four compounds as deoxygenated 0.04 M solutions in hexane containing methanol (0.05 M) led to the formation of ethylene and the methoxysilane **15** (eq. [2]). The methoxysilanes **15a–15c** were identified by GC–MS and GC coinjection with independently prepared authentic samples, while **15d** was isolated and identified on the basis of its ^{1}H NMR and mass spectra. No other products could be detected in the crude photolysates by GC analysis, up to ~20% conversion of the silacyclobutane, within the detection limits of our GC method.

$$[2] \quad \underset{\mathbf{3\text{-}6}}{Ar-\underset{\underset{\square}{\overset{R}{|}}}{Si}} \quad \xrightarrow[\substack{hexane \\ MeOH}]{h\nu} \quad C_2H_4 \quad + \quad \underset{\mathbf{15}}{Ar-\underset{\overset{|}{OMe}}{\overset{\overset{R}{|}}{Si}}-CH_3}$$

a. R = H; Ar = Ph
b. R = Me; Ar = Ph
c. R = Me; Ar = C≡C-Ph
d. R = Me; Ar = 4-C_6H_4-C_6H_5

Photolysis (350 nm) of a deoxygenated 0.05 M solution of benzophenone in hexane containing 0.01 M **6** and 0.1 M MeOH led to the slow formation of benzhydrol (identified by MS), but no destruction of the silacyclobutane. Methoxysilane **15d** could not be detected in the mixture, within the limits of our GC method.

Nanosecond laser flash photolysis (λ_{ex} = 248 nm) of continuously flowing, air-saturated solutions of **3** and **4** (~0.014 M) in hexane or acetonitrile leads to weak, but readily detectable, transient absorptions in the spectral region below

≈350 nm. The absorptions decay on the microsecond time scale with mixed first- and second-order kinetics to within 10% of the prepulse level, and exhibit lifetimes in the 2–3 μs range in scrupulously dried solvent. Time-resolved UV absorption spectra were recorded for air-saturated solutions of the two compounds, 0.1–0.4 μs after the laser pulse. The spectra recorded in hexane solution are shown in Fig. 1a, b along with typical decay traces, recorded at a monitoring wavelength of 315 nm. The lifetimes and intensities of the signals are unaffected by saturation of the solutions with either nitrogen or oxygen.

Addition of water, methanol, *tert*-butanol, or acetic acid $((0.5–5) \times 10^{-3}$ M) results in a reduction in the lifetimes of both transients and a change in decay kinetics to pseudo first order. Plots of the rate constant for decay (k_{decay}) versus concentration of added quencher according to eq. [3] (where k_0 is the first-order rate constant for the decay of the transient in the absence of added quencher and k_{ROH} is the second-order quenching rate constant) were linear in all cases. Bimolecular rate constants for reaction of **3** and **4** with the four reagents in acetonitrile solution are listed in Table 1, while those for reaction with MeOH and *t*-BuOH in hexane are listed in Table 2. Similar experiments were carried out using MeOD, *t*-BuOD, and acetic acid-*d* in MeCN solution; the k_H/k_D values calculated from these rate constants and those for reaction of the corresponding protiated reagents are included in Table 1. Previously reported rate constants for reaction of **2** with these reagents in acetonitrile are included for comparison.

$$[3] \quad k_{decay} = k_0 + k_{ROH}[Q]$$

Laser flash photolysis of deoxygenated hexane solutions of the phenylethynyl derivative **5** (2×10^{-5} M) led to complex behavior that could be shown to result from competing formation of the silacyclobutane triplet state and silene **9**, whose absorption spectra overlap almost exactly but differ considerably in intensity. Absorptions due to the triplet dominate the transient behavior in deoxygenated hexane solution. For example, flash photolysis of a deoxygenated solution of **5** gave rise to a long-lived ($\tau \sim 5$ μs), strongly absorbing, transient with λ_{max} = 315 nm. The lifetime of the transient was reduced substantially upon addition of oxygen or 1,3-octadiene, but was apparently unaffected upon addition of 0.005 M methanol. Monitoring at 260 nm, within the long-wavelength absorption band of the silacyclobutane, gave rise to a bleaching signal that recovered almost to the prepulse level with the same lifetime as that of the transient

Fig. 1. Time-resolved UV absorption spectra of silenes **7** (*a*), **8** (*b*), **9** (*c*), and **10** (*d*) in hexane solution at 23°C. The spectra of **9** and **10** were recorded in the presence of ~0.008 M 1,3-octadiene to shorten the lifetime of the corresponding silacyclobutane triplet to τ_T <20 ns.
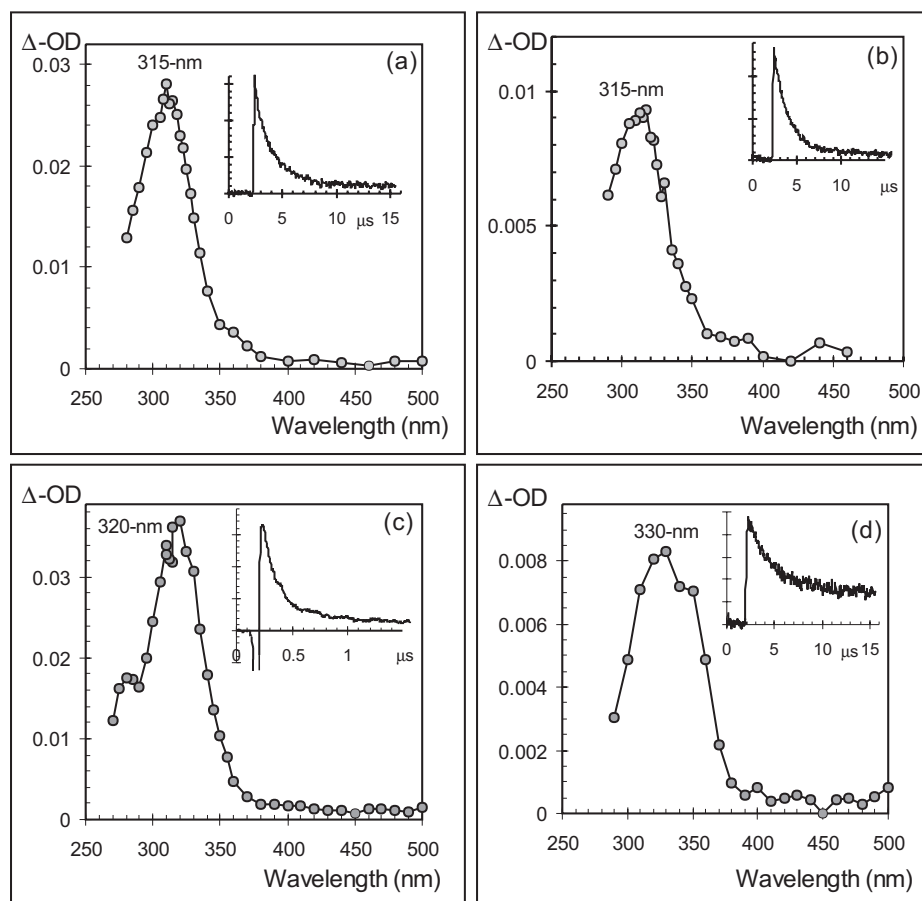

Table 1. Bimolecular rate constants for reaction of substituted 1-phenylsilenes **7**, **8**, and **2** with H_2O, MeOH(D), *t*-BuOH(D), and AcOH(D) in air-saturated acetonitrile solution at 23°C.[a]

$\begin{array}{c}Ph\\ \diagdown\\ Si{=}CH_2\\ \diagup\\ R\end{array}$	H_2O	MeOH		*t*-BuOH		HOAc	
R	k_q / 10^9 M^{-1} s^{-1}	k_q / 10^9 M^{-1} s^{-1}	k_H/k_D	k_q / 10^9 M^{-1} s^{-1}	k_H/k_D	k_q / 10^9 M^{-1} s^{-1}	k_H/k_D
H (**7**)	0.72 ± 0.01	1.63 ± 0.08	1.3 ± 0.1	0.67 ± 0.04	1.5 ± 0.1	1.85 ± 0.08	1.1 ± 0.1
Me (**8**)	0.56 ± 0.01	1.16 ± 0.02	1.6 ± 0.1	0.20 ± 0.09	1.4 ± 0.1	1.55 ± 0.04	1.0 ± 0.1
Ph (**2**)[b]	0.76 ± 0.09	1.2 ± 0.1	1.5 ± 0.2	0.22 ± 0.02	1.6 ± 0.1	1.23 ± 0.07	1.1 ± 0.1

[a]Errors are listed as twice the standard deviation from least-squares analysis of k_{decay} vs. concentration data according to eq. [3].

[b]Data from ref. 11.

Table 2. Time-resolved UV absorption spectra and bimolecular rate constants for reaction of substituted 1-phenylsilenes **7–10** and **2** with methanol and *tert*-butanol in hexane solution at 23°C.[a]

$\begin{array}{c}R\\ \diagdown\\ Si{=}CH_2\\ \diagup\\ Ar\end{array}$	Ar	R	λ_{max} (nm)	k_{MeOH} / 10^9 M^{-1} s^{-1}	$k_{t\text{-BuOH}}$ / 10^9 M^{-1} s^{-1}
7	Ph	H	315	3.1 ± 0.1	1.2 ± 0.1
8	Ph	Me	315	3.2 ± 0.2	1.2 ± 0.1
2[b]	Ph	Ph	325	1.9 ± 0.2	0.40 ± 0.07
9	PhC≡C	Me	320	5 ± 2	—
10	4-PhC$_6$H$_4$	Me	330	2.9 ± 0.3	—

[a]Measured by laser flash photolysis. Errors in the rate constants are listed as twice the standard deviation from least-squares analysis of k_{decay} vs. concentration data according to eq. [3].

[b]Data from ref. 11.

Fig. 2. Triplet–triplet absorption spectra for silacyclobutanes **5** (*a*) and **6** (*b*) in deoxygenated hexane solution containing 0.03 M methanol at 23°C.
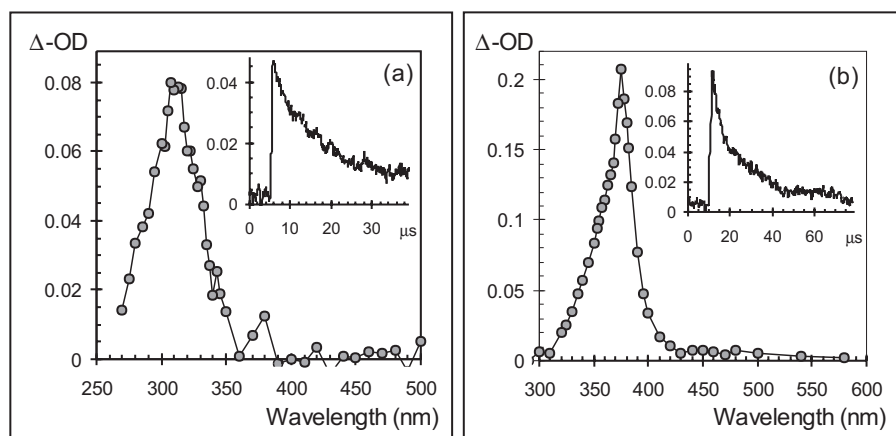
absorption at 315 nm. The lifetimes of the absorption and bleaching signals were also identical ($\tau \sim 500$ ns) in the presence of air, but differed in oxygen-saturated solution, where the 315 nm transient decay exhibited an average lifetime of $\tau \sim 240$ ns and the bleaching signal at 260 nm recovered with a clean pseudo-first-order lifetime $\tau \sim 100$ ns. Different behavior was noted upon addition of 0.0027 M 1,3-octadiene, where the bleaching signal was unresolvable from the laser pulse and the 315 nm transient decayed with a lifetime of $\tau \sim 600$ ns, was much weaker in intensity, and was superimposed on a strong fluorescence signal.

The kinetic behavior of the bleaching signal is consistent with the formation of a transient whose decay mainly regenerates the precursor, as would be expected for a triplet state. We thus assign the transient absorption spectrum recorded under deoxygenated conditions as consisting largely of the triplet–triplet absorption spectrum of silacyclobutane **5**, superimposed on a second, more weakly absorbing, transient (assigned to the silene **9**, vide infra) that is resolvable only under conditions where the triplet is strongly quenched. The spectrum of the triplet, recorded in deoxygenated hexane solution containing 0.03 M methanol to remove contributions from the silene (Fig. 2*a*), exhibits $\lambda_{max} = 315$ nm, in the range expected for a phenylacetylene triplet (27, 28). The rate constant for quenching of the triplet by 1,3-octadiene in hexane was found to be $(9.9 \pm 0.6) \times 10^9$ M^{-1} s^{-1}, which is also consistent with its assignment. A rate constant for triplet quenching by oxygen was estimated as $k_q \sim 6 \times 10^8$ M^{-1} s^{-1} from the rates of recovery of the precursor bleaching signal in air- and oxygen-saturated solution.

In hexane solution containing 0.001 M 1,3-octadiene or saturated with oxygen, the lifetime of the residual transient absorption at 315 nm is reduced upon addition of methanol. The spectrum of the transient observed under these conditions exhibits $\lambda_{max} = 320 \pm 2$ nm (Fig. 1*c*), and can thus be most reasonably assigned to 1-methyl-1-phenylethynylsilene (**9**). The transient is quenched efficiently by MeOH, though unfortunately we were able to obtain only a qualitative estimate of the rate constant ($k_{MeOH} = (5 \pm 2) \times 10^9$ M^{-1} s^{-1}), because of interference from the triplet absorptions and sample fluorescence at higher alcohol concentrations. Experiments with solutions containing higher concentrations of

diene (e.g., 0.003 M) led to no improvement in accuracy because the silene signal was weaker due to screening of the excitation light by the diene. The fact that the silene is observable under conditions where the triplet lifetime is reduced to <25 ns indicates that the silene is formed from the lowest excited singlet state of the silacyclobutane, and not from the triplet.

Similar results were obtained in laser flash photolysis experiments with the 4′-biphenyl-substituted derivative **6**. Accordingly, flash photolysis of deoxygenated 6×10^{-5} M solutions of **6** in hexane containing 0.03 M MeOH gave rise to a long-lived ($\tau = 12.5$ μs) transient that decayed with pseudo-first-order kinetics at very low laser intensities, and exhibited $\lambda_{max} = 375$ nm (Fig. 2*b*). This transient is assigned to the triplet state of **6** on the basis of the similarity of its spectrum to that of the 4-trimethylsilyl-4′-biphenyl (**13**) triplet ($\lambda_{max} = 375$ nm under similar conditions) and the fact that it is quenched by 1,3-octadiene with a rate constant $k_q = (4.9 \pm 0.5) \times 10^9$ M^{-1} s^{-1}. Alternatively, flash photolysis of air-saturated solutions of **6** in hexane containing 0.008 M 1,3-octadiene gave rise to a transient that decayed with clean pseudo-first-order kinetics ($\tau = 2.1$ μs) and exhibited $\lambda_{max} = 330$ nm. The species proved to be sensitive to the presence of methanol; a plot of k_{decay} vs. [MeOH] according to eq. [2] was linear, and afforded a slope $k_{MeOH} = (2.9 \pm 0.3) \times 10^9$ M^{-1} s^{-1}. On the basis of these data, this transient is assigned to silene **10**.

The time-resolved UV absorption spectra of silenes **9** and **10** in air-saturated hexane solution containing 0.008 M 1,3-octadiene are shown in Figs. 2*c*,*d*. The bimolecular rate constants for their reaction with MeOH under the same conditions are summarized in Table 2, along with the corresponding data for **7**, **8** and 1,1-diphenylsilene (**2**) (11). Quenching by *t*-BuOH was not investigated in these two cases.

Quantum yields for disappearance of **4**–**6** were determined by 254 nm merry-go-round photolysis of deoxygenated 0.03–0.04 M solutions in hexane containing methanol (0.05 M), using 1,1-diphenylsilacyclobutane (**1**) as actinometer. Photolysis of **1** in methanolic hexane solution affords ethylene and diphenylmethoxymethylsilane (**16**) as the only detectable products (2, 4, 11) — the latter due to trapping of

Table 3. Reaction quantum yields (Φ_{sil}),[a] fluorescence emission maxima, and singlet lifetimes for 1-aryl-1-methylsilacyclobutanes **4–6**, 1,1-diphenylsilacyclobutane (**1**), and the corresponding model compounds **11–14**, determined in deoxygenated isooctane solution at 23°C. Estimates of excited state reaction rate constants and state efficiencies for formation and reaction of biradicaloid intermediates are also included.

Compound	Φ_{sil}	λ_F (nm)[b]	τ_S (ns)[b,c]	$k_{sil}/10^7$ s^{-1} [d]	$k_{BIR}/10^7$ s^{-1} [e]	ϕ_{BIR} [e]	ϕ_{sil} [f]
4	0.04 ± 0.02	284	30 ± 2	0.13 ± 0.07	0.7 ± 0.4	0.21	0.19
11 (PhSiMe$_3$)	—	284	38 ± 3	—	—		
5	0.26 ± 0.04	300	6.6 ± 0.2	3.9 ± 0.9	10.2 ± 0.8	0.67	0.38
12 (PhCCSiMe$_3$)	—	300	20.0 ± 0.1	—	—		
6	0.29 ± 0.03	310	7.0 ± 0.3	4.1 ± 0.5	6.7 ± 0.5	0.47	0.61
13 (4′-BiphSiMe$_3$)	—	310	13.2 ± 0.4	—	—		
1	0.21 ± 0.03	285	2.6 ± 0.1	8.1 ± 0.9	9.0 ± 0.9	0.23	0.90
14 (Ph$_2$SiMe$_2$)	—	285	3.4 ± 0.2	—	—		

[a]For disappearance of substrate, from photolysis of deoxygenated 0.03–0.04 M solutions of silacyclobutane in hexane containing 0.05 M MeOH, using **1** as actinometer. Errors are listed as the standard deviation from the mean of duplicate determinations.

[b]Recorded in deoxygenated isooctane solution, at concentrations of 10^{-5}–10^{-4} M.

[c]Determined by time-correlated single photon counting. Errors are listed as $\pm 2\sigma$.

[d]Calculated from Φ_{sil} and τ_S^{SCB} (see eq. [5]).

[e]Estimated from the fluorescence lifetimes of silacyclobutane and corresponding model compounds according to eqs. [8] and [9].

[f]Calculated from Φ_{sil} and ϕ_{BIR} according to eq. [7].

Fig. 3. Concentration vs. time plots for merry-go-round photolysis of deoxygenated 0.03–0.04 M solutions of silacyclobutanes **4** (□), **5** (◆), **6** (△), and **1** (●) in hexane containing methanol (0.05 M) at 25°C.
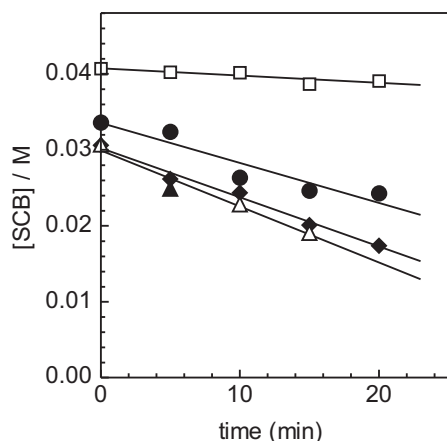
1,1-diphenylsilene (**2**) — and is characterized by a quantum yield of $\Phi_2 = 0.21 \pm 0.03$ (11). Quantum yields were calculated from the relative slopes of plots of concentration vs. photolysis time, which are shown in Fig. 3. The results of these experiments are collected in Table 3. Qualitative observations indicated the quantum yield for photolysis of **3** to be similar to that of **4** under similar conditions.

Steady state fluorescence emission spectra of **4–6** and **1** were recorded in deoxygenated isooctane solutions at concentrations in the 10^{-5}–10^{-4} M range. The fluorescence spectra of **4–6** were slightly weaker but otherwise indistinguishable from those of the corresponding model compounds **11–13** in each case. The fluorescence spectrum of dimethyldiphenylsilane (**14**) consisted of a prominent band centered at 285 nm along with a weaker shoulder centered at ~335 nm that is tentatively attributed to intramolecular excimer formation. A similar spectrum was observed for **1**, except the long-wavelength shoulder was much weaker than in the spectrum of **14**. The fluorescence excitation spectra of
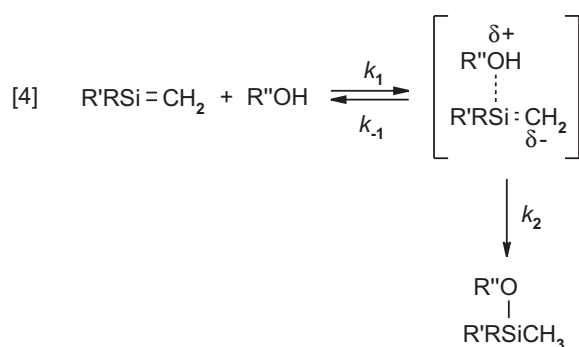
the eight compounds matched the static absorption spectra (in the region above ~240 nm) in each case. Fluorescence lifetimes were determined for all eight compounds at the emission maxima by time-correlated single photon counting, under the same conditions as those employed for the determination of the steady state fluorescence spectra. In all eight cases, the fluorescence decay profiles analysed either to single exponential kinetics or to two exponentials, which consisted of a prominent (>98%) short-lived decay superimposed on a very weak (<2%) long-lived decay whose origin was not investigated. Identical fluorescence lifetimes were obtained from solutions of ca. 2-fold higher concentration in substrate, within experimental error, indicating that, at these concentrations, self-quenching of fluorescence (due to *inter*molecular excimer formation, for example) is insignificant. The fluorescence emission maxima and singlet lifetimes obtained from these experiments are listed in Table 1, along with various kinetic parameters calculated from the reaction quantum yields and singlet lifetimes (vide infra).

Discussion

The steady state photochemistry and time-resolved spectroscopic behavior of all four of the silacyclobutanes **3–6** are consistent with the formation of ethylene and the corresponding arylsilenes **7–10** as the exclusive products of photolysis, within the limits of our (GC and ^{1}H NMR) detection limits. The four silenes exhibit the expected trends in lifetime ($\tau = 2$–5 µs), λ_{max} (315–330 nm), and reactivity toward alcohols ($k_{MeOH} = (2$–5$) \times 10^9$ M^{-1} s^{-1} in hexane at 23°C), considering our previously reported data for 1,1-diphenylsilene (**2**) (9, 11). The steady state results reported here for photolysis of **3** in the presence of methanol are analogous to those reported previously for the photolysis of this compound in the presence of other alcohols (26).

As we reported previously for **2** (11), the reactivities of silenes **7** and **8** are significantly lower in acetonitrile solution than in hexane, probably due to weak complexation by the nitrile solvent, and in all cases the rate constants follow

the trend $k_{HOAc} \sim k_{MeOH} > k_{H_2O} > k_{t\text{-}BuOH}$. The reactivities of the three phenylsilene derivatives with each reagent are remarkably similar to one another in this solvent, probably because the small differences in rate that are expected, based on the electronic effects of the substituents (17), are offset by opposing steric and solvation effects. The three compounds show a slightly greater spread in reactivity toward methanol in hexane solution than in acetonitrile, which might reflect differences in solvation throughout the series by the nitrile solvent. As we found previously for **2** (11), the rate constants for reaction with water and the alcohols are subject to small, but clearly primary, deuterium kinetic isotope effects. This is consistent with a reaction mechanism involving initial, reversible complexation followed by rate-controlling proton transfer from oxygen to carbon (eq. [4]) (10, 11, 13, 17, 29–33).

$$[4] \quad R'RSi\!=\!CH_2 + R''OH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[\begin{array}{c} \delta+ \\ R''OH \\ \vdots \\ R'RSi \vdots CH_2 \\ \delta- \end{array} \right]$$

$$\Big\downarrow k_2$$

$$\begin{array}{c} R''O \\ | \\ R'RSiCH_3 \end{array}$$

Laser flash photolysis studies of 1,1-diphenylsilacyclobutane (**1**) in nitrogen-saturated hexane solution have shown that 1,1-diphenylsilene (**2**) is formed within the duration of the excitation pulse from a KrF excimer laser (~15 ns) (11). This establishes an upper limit (of the same value) for the lifetime of the excited state responsible for the formation of the reactive intermediate. In this case, the identification of the reactive excited state (i.e., singlet or triplet) by conventional triplet sensitization or quenching experiments is not a trivial task, and we can rule out the triplet state as the precursor only providing that its lifetime is in excess of about 10 ns. We have been unsuccessful in our attempts to detect the triplet state of **1** directly by laser flash photolysis, but this is not unexpected for a benzene derivative bearing nonconjugative substituents (27).

The results reported here for **5** and **6** provide strong evidence that the lowest triplet states of 1-arylsilacyclobutanes are not involved in silene formation. In these two cases, the triplet states are easily detectable by laser flash photolysis because intersystem crossing is more efficient in phenylalkynes and biphenyls than in simple benzene derivatives, and the triplets absorb considerably more strongly (27, 28, 34). The triplet lifetimes of these two molecules were determined to be ~14 and 12 μs, respectively, in deoxygenated hexane solution at room temperature, which should be considered to be lower limits. Quenching of the triplets by oxygen or 1,3-octadiene proceeds rapidly in both cases, but has no discernible effect on the yield of silene (as measured by the initial ΔOD of the silene absorption in the presence of
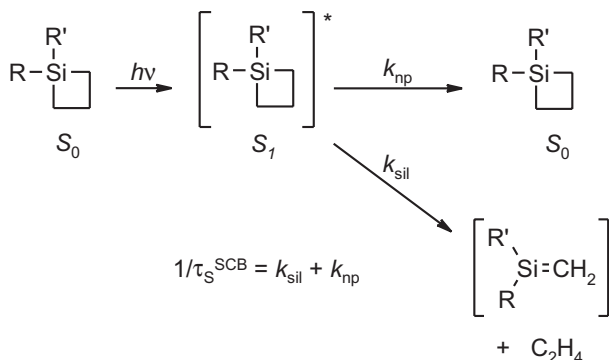
oxygen or diene). In fact, the presence of diene is necessary in order to detect the corresponding silenes (**9** and **10**) cleanly by laser flash photolysis, because their spectra overlap severely with those of the triplet states of the precursors. Similarly, benzophenone-sensitization experiments with **6**, at a concentration corresponding roughly to 90% efficient triplet sensitization, failed to produce detectable amounts of the methanol trapping product of silene **10**. These experiments conclusively demonstrate that the reactive excited state of arylsilacyclobutanes, with respect to [2 + 2] photocycloreversion to the corresponding silenes, is the lowest excited singlet state.

Comparison of the singlet lifetimes of the silacyclobutanes **1** and **4–6** with those of the corresponding model compounds (**11–14**), in which the silacyclobutane ring carbons are replaced by two methyl groups, provides additional evidence for the direct involvement of the lowest excited singlet state in silene formation. Compared to the corresponding silacyclobutanes, the latter four compounds are all essentially non-photoreactive, allowing the conclusion that their singlet lifetimes are controlled mainly by *nonproductive* decay processes such as fluorescence, intersystem crossing, and internal conversion. In fact, the singlet lifetimes of the three trimethylsilyl-substituted compounds **11–13** are similar to those of the corresponding methylarenes under similar conditions (toluene, 34 ns (35); 1-phenylpropyne, 15 ns;[3] 4′-methylbiphenyl, 15.2 ns (35)), indicating that trialkylsilyl substitution has little intrinsic effect on the photophysics of the arene chromophore in each of these compounds. In contrast, the singlet lifetime of dimethyldiphenylsilane (**14**; τ_S = 3.4 ns) is substantially shorter than that of diphenylmethane (τ_S = 25.3 ns (35)). We tentatively attribute this to intramolecular excimer formation on the basis of the long-wavelength shoulder in the static fluorescence emission spectrum of the diarylsilane. This weak emission band occurs at a position characteristic of inter- and intramolecular excimer emissions in substituted benzene derivatives (36). A similar band appears in the emission spectrum of **1**, though it is weaker than in that of **14**. Diphenylmethane does not form an intramolecular excimer (35, 36), and consequently its singlet lifetime is similar to that of toluene. In any event, the singlet lifetimes of the silacyclobutane derivatives are in each case significantly shorter than those of the corresponding model compounds, which is consistent with the presence of an additional mode of excited singlet state decay due to reaction involving the four-membered ring. The alternate possibility that the shorter singlet lifetimes of the cyclics are due to an enhancement in one or more of the nonproductive decay modes cannot, however, be rigorously ruled out. Fluorescence and intersystem crossing could be quantitatively evaluated through quantum yield measurements but, even then, possible differences in the rates of nonproductive internal conversion cannot be easily evaluated.

We were surprised to discover that the quantum yield for silene formation from 1-methyl-1-phenylsilacyclobutane (**4**) is ~5 times lower than that for 1,1-diphenylsilacyclobutane (**1**), and up to ~8 times lower than those for **5** and **6**, which have lower excited singlet state energies. This must be due to a substituent effect on the rate constants for reac-

Scheme 1.

$$1/\tau_S^{SCB} = k_{sil} + k_{np}$$

Scheme 2.

$$1/\tau_S^{SCB} = k_{BIR} + k_{np}$$

$$\Phi_{sil} = k_{BIR}\phi_{sil}\tau_S^{SCB}$$

$$(\phi_{sil} = k_{cleave}/(k_{cleave}+k_{couple}))$$

tive excited state decay and (or) (if silene formation is non-concerted) the partitioning of the biradicaloid intermediate between silene and starting material. Scheme 1 depicts the simplest possible mechanism to account for excited state decay in these compounds, where silene formation occurs directly from the excited singlet state by concerted cycloreversion with rate constant k_{sil}, and k_{np} is the sum of the rate constants for all nonproductive pathways for excited state decay. The reaction rate constants can be calculated from the quantum yields and singlet lifetimes according to eq. [5], and are listed in Table 3. It should be noted that these are true elementary rate constants only if silene formation occurs directly from the lowest excited singlet state by a concerted mechanism.

[5] $\Phi_{sil} = k_{sil} \tau_S^{SCB}$

If silene formation occurs by a stepwise mechanism, then the k_{sil} values calculated above are a more complex function of the primary rate constant for excited state bond cleavage to form the biradicaloid intermediate (k_{BIR}) and an efficiency factor (ϕ_{sil}) that describes its partitioning between silene and the ground state of the silacyclobutane (Scheme 2 and eq. [6]). In other words, the overall quantum yield for reaction is given by the product of the state efficiencies for biradicaloid formation ($\phi_{BIR} = k_{BIR} \tau_S^{SCB}$) and for silene formation from the biradicaloid ($\phi_{sil} = k_{cleave} \tau_{BIR}$), as shown in eq. [7]. The rigorous determination of these parameters requires additional information, which could be obtained if the intermediate could be detected either directly or indirectly via chemical trapping. Unfortunately, no additional transient absorptions that might be assigned to such species have been observed on the nanosecond time scale, in these or any of the other arylsilacyclobutanes that we have studied.

[6] $k_{sil}=k_{BIR}\cdot\phi_{sil}$

[7] $\Phi_{sil}=\phi_{BIR}\cdot\phi_{sil}$

The best we can do at present is to approximate k_{BIR} values from the singlet lifetimes of the silacyclobutanes and their model compounds, making the admittedly crude assumption that the sum of the rates of the nonproductive decay processes in each of the silacyclobutanes is equal to the inverse singlet lifetime of its model compound. To the extent that this assumption is reasonable, k_{BIR} and ϕ_{BIR} can be estimated using eqs. [8] and [9], and ϕ_{sil} then follows from eq. [7]. These parameters are collected in Table 1.
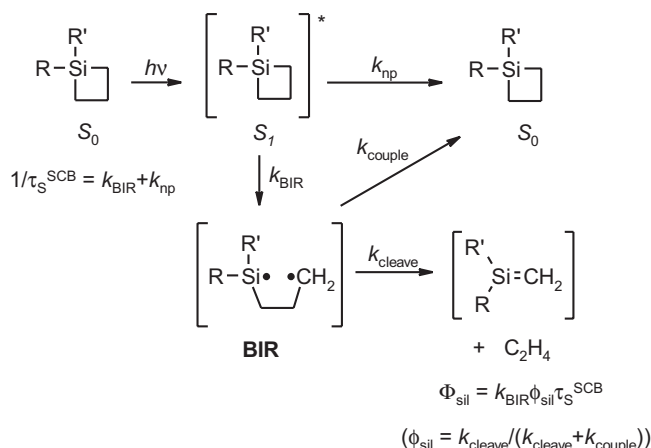
[8] $k_{BIR} \approx 1/\tau_S^{SCB} - 1/\tau_S^{mod}$

[9] $\phi_{BIR}=k_{BIR} \tau_S^{SCB} \approx 1 - (\tau_S^{SCB}/\tau_S^{mod})$

The k_{sil} and k_{BIR} values summarized in Table 1 both indicate that the excited singlet state of 1-methyl-1-phenylsilacyclobutane (**4**) is significantly less reactive toward bond cleavage than those of **1**, **5**, and **6**. The most reasonable explanation for this is that the mixing of benzenoid π and (or) π* MOs with Si—C σ and (or) σ* MOs in the lowest excited singlet state, which is required in order to activate the silacyclobutane ring toward bond cleavage, is much less efficient in **4** than in the other three derivatives. Presumably, the more extended π-systems in **1**, **5**, and **6** assist in this mixing by perturbing the symmetries of the relevant π-type molecular orbitals.

The calculated ϕ_{BIR} and ϕ_{sil} values for the four silacyclobutanes also show some interesting trends. The data for **1** and **4** suggest that the difference in overall reaction quantum yield for these two compounds is primarily due to differences in the behavior of the biradicaloid intermediates, not to differences in the efficiencies of excited state Si—C bond cleavage. The approximately equal ϕ_{BIR} values for the two compounds result from the fact that substituent-induced perturbations that affect k_{BIR} also tend to affect the rates of the nonproductive decay processes: in spite of the fact that **4** is ~10 times less reactive than **1**, the intrinsic lifetime of its excited singlet state (as measured by τ_S^{mod}) is also ~10 times longer. In fact, the data indicate that ϕ_{BIR} varies relatively little throughout the entire series of compounds. On the other hand, ϕ_{sil} varies smoothly throughout the series, suggesting that the biradicaloid from **1** mainly cleaves ($k_{cleave} \sim 9k_{couple}$) while that from **4** mainly couples to regenerate starting material ($k_{couple} \sim 4k_{cleave}$).

Such a large variation in the relative rate constants for cleavage and coupling of the putative 1,4-biradicaloid intermediates is surprising. The two main factors that should affect the partitioning of such species between cleavage and coupling are the relative thermodynamic stabilities of the coupling and cleavage products and the conformational preferences of the 1,4-biradical as they are reflected in the relative transition state energies for cleavage and coupling (37–41). In the present cases, thermodynamics would clearly be expected to strongly favor coupling over cleavage in all

cases. Cleavage requires a colinear arrangement of the central C—C bond with the *p*-orbitals on the trivalent centers, but has little dependence on conformation about the central C—C bond. Coupling, on the other hand, can only occur from *gauche* conformers. While steric effects would clearly be predicted to lead to an increase in cleavage over coupling in the biradicaloid from **1** compared to that from **4**, it is difficult to rationalize the variation in ϕ_{sil} between **4**, **5**, and **6** on the basis of these simple arguments.

We stress again that our analysis of the data in terms of a stepwise reaction mechanism is based on the crude assumption that the singlet lifetimes of the model compounds **11–14** provide a reasonable estimate of the nonproductive contributions to the singlet lifetimes of the corresponding silacyclobutanes (i.e., $k_F + k_{IC} + k_{ISC}$). Further work will be required in order to address the validity of this assumption. To the extent that it is valid (and equally so in all cases), then the intermediacy of a 1,4-biradical en route to the corresponding silene is only really demanded for the monoaryl-substituted derivatives **4–6**, for which the k_{sil} and k_{BIR} values calculated from the lifetime data are significantly different. In the case of **1**, our data cannot rule out the possibility that silene formation occurs by a concerted $\sigma_{2s}+\sigma_{2s}$ cycloreversion mechanism.

Conclusions

The formation of 1-arylsilenes by formal $\sigma_{2s}+\sigma_{2s}$ photocycloreversion of 1-arylsilacyclobutanes is a reaction of the lowest excited singlet state, which is shown by the behavior of derivatives for which the arylsilacyclobutane triplet state can be detected directly by laser flash photolysis. Photocycloreversion proceeds with a quantum yield of only 0.04 in 1-methyl-1-phenylsilacyclobutane, which is 5 times lower than in 1,1-diphenylsilacyclobutane. The quantum yield is even higher in derivatives in which the phenyl group is replaced with 2-phenylethynyl or 4′-biphenyl substituents. The resulting silenes, 1-phenyl-, 1-methyl-1-phenyl-, 1-methyl-1-(2-phenylethynyl)-, and 1-(4′-biphenylyl)-1-methylsilene, react with aliphatic alcohols at rates on the order of $(2–5) \times 10^9$ M^{-1} s^{-1} in hydrocarbon or acetonitrile solution at ambient temperature. Deuterium isotope and solvent effects on the rate constants are consistent with a mechanism involving reversible complexation of the silene with the alcohol, followed by rate-determining proton transfer from silicon to carbon.

Comparison of the singlet lifetimes of the three 1-aryl-1-methylsilacyclobutanes and the corresponding aryltrimethylsilane suggests that cycloreversion proceeds by cleavage of one of the ring Si—C bonds to yield a 1,4-biradicaloid that partitions between silene and starting material. A similar analysis for 1,1-diphenylsilacyclobutane is consistent with either concerted or stepwise mechanisms for silene formation. The lifetime data allow calculation of rate constants for the primary excited state ring cleavage process and state efficiencies for formation of the intermediate and its collapse to silene, assuming that the singlet lifetimes of the model compounds approximate the rates of the nonproductive contributions to excited state decay in the corresponding silacyclobutane. Variations in the rate constant for excited state cleavage throughout the series are tentatively attributed to the effects of substituents on the degree of mixing of the benzenoid π-type molecular orbitals of the chromophore with σ-type molecular orbitals localized in the silacyclobutane ring. Modest variations in excited singlet state energy have no discernible effect on the rate constant, within this limited series of compounds. The relative rates of cleavage and coupling in the putative 1,4-biradicaloid intermediate are very sensitive to substitution at the silicon center; coupling predominates in the biradical from 1-methyl-1-phenylsilacyclobutane, while cleavage predominates in that from 1,1-diphenylsilacyclobutane.

Future work in this area will be directed at developing a better understanding of the various factors that contribute to the efficient formation of reactive silenes from photolysis of arylsilacyclobutanes, and exploiting this reaction for potentially useful applications.

Experimental

Ultraviolet absorption spectra were recorded on a Perkin Elmer Lambda 9 spectrometer interfaced to a Pentium microcomputer. Fluorescence emission spectra and lifetimes were determined using a Photon Technologies Inc. LS-100 spectrofluorimeter, which also enables lifetime determinations by the time-correlated single-photon counting technique. 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 DB1 megabore capillary column (15 m × 0.53 mm; Chromatographic Specialties, Inc.). Mass spectra and GC–MS analyses 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.). Semipreparative gas chromatographic separations were carried out using a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and a 3.8% UCW982 on 80/100 Supelcoport (24 ft × 0.25 in.; Supelco, Inc.) stainless steel column. Elemental analyses were performed by Guelph Chemical Laboratories, Inc.

2,2,4-Trimethylpentane (isooctane) and hexane were BDH Omnisolv grade and were used as received from the supplier. Acetonitrile (BDH Omnisolv) was distilled from calcium hydride and then further dried by several passages through activated alumina. Methanol, methanol-*O-d*, *tert*-butanol, *tert*-butanol-*O-d*, glacial acetic acid, acetic acid-*d*, trimethylphenylsilane (**11**), and phenyl(trimethylsilyl)acetylene (**12**) were of the highest purity available, and were used as received from Aldrich Chemical Co. 4′-Trimethylsilyl-biphenyl (**13**; mp 49–50°C) (42) and dimethyldiphenylsilane (**14**; bp 99°C (0.75 Torr; 1 Torr = 133.3 Pa) (43)) were prepared by the reported procedures, and purified by recrystallization or vacuum distillation to purities in excess of 99%, as estimated by capillary GC.

1-Phenylsilacyclobutane (**3**) was prepared by lithium aluminum hydride reduction of 1-phenyl-1-chloro-1-silacyclobutane as reported by Bertrand et al. (26). The compound was purified by vacuum distillation (bp 97–100°C/20 Torr (26)), and exhibited the following spectroscopic properties. IR: 2963.0 (m), 2924.0 (s), 2854.2 (s), 2122.6 (m), 1731.4

(m), 1625.5 (s) 1569.4 (s), 1510.1 (m), 1428.9 (m), 1119.5 (s), 699.4 (s), 499.2 (m); ^{1}H NMR, δ (ppm): 1.25 (m, 4H), 2.20 (m, 2H), 5.33–5.35 (m, 1H), 7.41 (m, 3H), 7.66 (m, 2H); ^{13}C NMR, δ (ppm): 12.7, 18.6, 19.7, 128.0, 128.2, 129.9, 134.4, 135.2, 135.8; MS, *m/z* (*I*): 148 (30), 120 (83), 105 (100), 79 (15), 67 (8), 53 (25), 43 (8).

1-Methyl-1-phenylsilacyclobutane (**4**) was prepared by the method of Auner and Grobe (3), and purified by column chromatography on silica gel using hexane as eluant. The compound was characterized on the basis of the following spectroscopic data. IR: 2963.8 (s), 2856.5 (m), 1428.2 (s), 1396.3 (s), 1249.9 (s), 1115.5 (s), 867.2 (s), 772.1 (s), 732.5 (s), 697.6 (s), 427.7 (s); ^{1}H NMR, δ (ppm): 0.55 (s, 3H), 1.26 (m, 4H), 2.19 (p, 2H), 7.40 (m, 3H), 7.64 (m, 2H); ^{13}C NMR, δ (ppm): –1.8, 14.3, 18.2, 127.9, 129.4, 133.5; MS, *m/z* (*I*): 162 (10), 134 (100), 119 (45), 105 (20), 93 (7), 79 (5), 53 (10), 43 (13).

1-Methyl-1-phenylethynylsilacyclobutane (5)

To a cooled (–78°C) solution of phenylacetylene (0.55 mL, 5.0 mmol) in anhydrous ether (20 mL) was added a 1.6 M hexane solution of *n*-butyllithium (3.1 mL, 5.0 mmol). The solution was allowed to warm to room temperature and stirred for an additional 2 h. The solution was recooled to –78°C, and a solution of 1-chloro-1-methylsilacyclobutane (0.48 g, 4 mmol) in dry diethyl ether (10 mL) was added dropwise over ~10 min with stirring. The solution was allowed to warm to room temperature over 12 h, and then hydrolyzed with water (20 mL). The aqueous layer was extracted with ether (3 × 10 mL). The ether extracts were combined and dried over anhydrous magnesium sulfate, filtered, and stripped of solvent to yield a colorless liquid that was purified by silica gel column chromatography using hexane as eluant. The product (0.63 g, 3.4 mmol, 85%) was obtained as a colorless liquid and identified as 1-methyl-1-phenylethynylsilacyclobutane (**3**) on the basis of the following data: IR (neat): 3096 (w), 2970 (m), 2928 (m), 2156 (s), 1488 (s), 1251 (m), 1220 (m), 1121 (s), 879 (s); UV, λ_{max}: 247-nm, $\varepsilon_{248\ nm}$: 78 990 ± 1200 M^{-1} cm^{-1}; ^{1}H NMR, δ: 0.5 (s, 3H), 1.12 (m, 2H), 1.28 (m, 2H), 2.15 (m, 2H), 7.32 (m, 3H), 7.48 (m, 2H); ^{13}C NMR, δ: –0.1, 15.4, 18.4, 92.4, 107.1, 122.8, 128.3, 128.8, 132.0; MS, *m/z*: 186 (20), 158 (67), 143 (100), 129 (20), 117 (11), 103 (10), 77 (8), 53 (15), 43 (25); HRMS, calcd. for C$_{12}$H$_{14}$Si: 186.08647; found: 186.08633.

1-(4′-Biphenylyl)-1-methylsilacyclobutane (6)

Magnesium turnings (6.0 g, 0.25 g-at.) were placed in a 250 mL 2-necked round-bottom flask fitted with a condenser, addition funnel, magnetic stirrer, and gas inlet, and covered with anhydrous ether. A solution of 4-bromobiphenyl (6.38 g, 0.027 mol) in anhydrous ether (100 mL) was then added dropwise, at a rate sufficient to sustain reflux of the reaction mixture (~1 mL/min). To the resulting dark gray reaction mixture was added, dropwise with stirring over 15 min, a solution of 1-chloro-1-methylsilacyclobutane (3.0 g, 0.025 mol) in anhydrous ether (20 mL). The mixture was stirred for a further 16 h at room temperature, the stirrer was removed, and the resulting grey-brown solution was decanted from the suspended magnesium salts into a 500 mL Erlenmeyer flask. Water (200 mL) was added; the mixture

was stirred vigorously for 10 min and then placed in a separatory funnel to separate the aqueous and organic layers. The yellow ether solution was washed with water (3 × 25 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent on the rotary evaporator afforded an oily yellow solid (5.1 g), whose ^{1}H NMR spectrum was consistent with the desired product **6**. The solid was recrystallized twice from 95% ethanol to yield the product as slightly yellow plates (2.5 g, 0.0105 mol, 42%). A portion of the material (0.2 g) was further purified by column chromatography on silica gel using hexane as the eluant. Three more recrystallizations from 95% ethanol afforded the product as colourless plates (mp 41–41.5°C), which were identified as 1-(4-biphenylyl)-1-methylsilacyclobutane (**6**) on the basis of the following data: IR (neat): 3068.7 (w), 3021.8 (w), 2960.8 (m), 2926.0 (m), 1382.8 (m), 1249.7 (m), 1116.1 (s), 863.2 (s), 757.4 (s), 723.2 (s), 695.9 (s), 653.5 (s); UV, λ_{max}: 257 nm, $\varepsilon_{248\ nm}$: 24 000 ± 2000 M^{-1} cm^{-1}; ^{1}H NMR, δ: 0.58 (s, 3H), 1.22 (m, 2H), 1.29 (m, 2H), 2.17 (m, 2H), 7.53 (m, 3H), 7.65 (m, 6H); ^{13}C NMR, δ: –1.81, 14.37, 18.25, 92.4, 126.58, 127.08, 127.37, 128.71, 133.94, 137.24, 140.93, 142.08; MS, *m/z*: 238 (17), 211 (22), 210 (100), 195 (49), 167 (18), 165 (22), 152 (10), 53 (25), 43 (67). Anal. calcd. for C$_{16}$H$_{18}$Si: C 80.63, H 7.62; found: C 80.60, H 7.80.

Methoxymethylphenylsilane (**15a**) and methoxydimethylphenylsilane (**15b**) were prepared by reaction of methylphenylchlorosilane and dimethylphenylchlorosilane, respectively, with methanol in ether in the presence of trimethylamine (43, 44).

Methoxydimethyl(phenylethynyl)silane (**15c**) was prepared by the method of Corriu et al. (45), and exhibited analytical and spectroscopic data similar to those reported. 4-Methoxydimethylsilyl-4′-biphenyl (**15d**) was identified after isolation from a semipreparative scale photolysis of a deoxygenated solution of **6** (0.24 g, 1 mmol) and methanol (0.4 mL, 10 mmol) in hexane (10 mL), in a quartz photolysis tube with 8 RPR-2537 low-pressure mercury vapor lamps. The photolysis was carried out to ca. 70% conversion of **6** (ca. 5 h). The resulting bright yellow photolysate was stripped of solvent to yield a yellow oil, which was chromatographed on a Florisil column using hexane–dichloromethane mixtures. The product, which was isolated in modest purity (ca. 95% by GC) as a light yellow oil (0.05 g, 0.2 mmol, 20%), exhibited ^{1}H NMR and mass spectral data consistent with its proposed structure: ^{1}H NMR, δ: 0.06 (s, 6H), 3.48 (s, 3H), 7.34–7.53 (m, 9H); MS, *m/z*: 243 (5), 242 (27), 228 (21), 227 (100), 197 (31), 181 (8), 167 (9), 165 (11), 152 (10), 59 (21).

Analytical-scale photolyses were carried out using a Rayonet reactor fitted with 4–8 RPR-2537 lamps and a merry-go-round apparatus. Aliquots of hexane or cyclohexane-d_{12} solutions containing **3–6** (0.03–0.04 M) and methanol (0.05 M) were placed in Suprasil quartz cuvettes (3 mm × 10 mm), sealed with rubber septums, and saturated with dry argon. Hexadecane (0.01 M) was included as an internal GC standard for the runs carried out in hexane. The only products detected in these photolyses were ethylene, the corresponding methoxysilane (**15a–15d**), and small amounts of products identified as the corresponding hydroxysilanes on the basis of GC–MS analysis, presumably due to the presence of small amounts of water. The alkoxysilanes were

identified by GC–MS and GC coinjection with the authentic samples. Quantum yield experiments were carried out in similar fashion, simultaneously irradiating solutions of **1** and **4–6** in hexane containing 0.05 M methanol.

Fluorescence emission spectra and lifetimes were recorded on argon-saturated isooctane solutions, whose concentrations were adjusted to yield an absorbance of 0.1–0.2 at the excitation wavelength (245–260 nm). In each case, the fluorescence excitation spectrum matched the UV absorption spectrum in the region above ~240 nm.

Nanosecond laser flash photolysis experiments employed the pulses (248 nm; ca.15–25 ns; 70–150 mJ) from Lumonics 510 or Lambda Physik Compex 120 excimer lasers filled with F_2–Kr mixtures in helium or neon, and a microcomputer-controlled detection system (46). The intensity of the beam was reduced to <10 mJ at the cell using a series of stainless steel wire meshes as neutral density filters. Solutions were prepared at concentrations such that the absorbance at the excitation wavelength was ca. 0.7 (~8×10^{-4} M), and were flowed continuously through a 3×7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir. Nitrogen or oxygen was bubbled continuously through the reservoir throughout the experiments. Solution temperatures were controlled to within 0.1°C with a VWR 1166 constant temperature circulating bath plumbed to a brass sample holder, and 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 vs. concentration data (six or more points) that 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.

Acknowledgments

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