ELSEVIER

Journal of Organometallic Chemistry 561 (1998) 19–27

Journal of Organometallic Chemistry

A transient spectroscopic study of the photochemistry of vinyldisilanes

William J. Leigh [a],*, Christine J. Bradaric [a], Gregory W. Sluggett [1,a], Paul Venneri [a], Robert T. Conlin [b], M.S.K. Dhurjati [b], M.B. Ezhova [b]

[a] *Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, ON L8S 4M1, Canada*

[b] *Center for Organometallic Research and Education, Department of Chemistry, University of North Texas, Denton, TX 76203, USA*

Received 4 September 1997; received in revised form 4 February 1998

Abstract

The chemistry of the reactive intermediates produced by direct irradiation of pentamethylvinyldisilane (**1**), 1,1,2,2-tetramethyl-1,2-divinyldisilane (**2**), and 1,1,1,2-tetramethyl-2,2-divinyldisilane (**3**) in hydrocarbon solution have been studied by steady state and laser flash photolysis techniques. All three disilanes yield silenes derived from photochemical [1,3]-trimethylsilyl migration as the major product, as has been shown by the products of steady state trapping experiments. Direct irradiation of the three disilanes in 3-methylpentane matrices at 77 K leads to the formation of products with absorption maxima at 270, 270 and 325 nm, respectively, which disappear upon warming and are hence assigned to the silenes. Nanosecond laser flash photolysis of the disilanes in deoxygenated hexane solution at ambient temperatures gives rise to transient species with the same absorption maxima as found in the matrix experiments, and which decay over several tens of microseconds with mixed pseudo-first and second order kinetics. The assignment of these transients to the corresponding silenes is supported by their absolute rate constants for reaction with methanol, *t*-butanol, acetic acid, acetone, 2,3-dimethyl-1,3-butadiene (DMB), cyclohexene and oxygen, which vary over the range 10^5–10^8 M^{-1} s^{-1}, depending on the reagent and the silene. The transient spectrum and reactivity of one of the silenes have also been examined in acetonitrile solution. The variation in spectroscopic properties and reactivity as a function of structure is discussed, and compared to previously reported data for closely related reactive silenes. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Photochemistry; Vinyldisilanes; Reactive intermediates; Silene

---

1. Introduction

Silenes have been of intense fundamental interest over the past 30 years [1–3]. They are quite commonly involved as reactive intermediates in thermal and photochemical reactions of organosilicon compounds, both in the gas phase and solution [1–5], and following the pioneering efforts of Brook et al. [6], a large number of stable silenes have been synthesized and characterized. Until recently, our knowledge of the reactivity of silenes was based primarily on chemical trapping studies, and the more quantitative aspects of this were derived from competition experiments [7]. Spectroscopic data on reactive silenes were numerous even ten years ago, but virtually all of the known data in condensed phases were obtained using matrix isolation techniques at low temperatures [1].

Using the technique of nanosecond laser flash photolysis, it has been possible to generate reactive silenes in solution at ambient temperatures, under conditions where their UV absorption spectra and absolute rate constants for reaction with various silene trapping agents can be measured directly [8–25]. Such studies have afforded detailed information on the mechanisms of the addition of alcohols and carboxylic acids [11,15,18,19,21,25], the ene- and [2 + 2]-cycloaddition of ketones [14,16,20], and silene dimerization [12] and on the effects of substituents and solvent on silene reactivity.

---

* Corresponding author. Tel.: + 1 905 5259140; fax: + 1 905 5222509; e-mail: leigh@mcmaster.ca

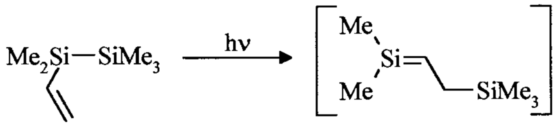
[1] Present address: Merck Research Laboratories, WP78-110, PO Box 4, West Point, PA 19486, USA.

PII S0022-328X(98)00510-5

Most of the work reported so far has involved phenyl-substituted or highly conjugated silenes, and we have been interested in extending these studies to simpler silene derivatives bearing only alkyl substituents at silicon. The generation of simple alkyl-substituted silenes in solution by photolysis of silacyclobutanes [24] (which has proven to be extremely convenient for the study of aryl-substituted silenes by time-resolved spectroscopic methods [14,18,19,25]) requires the use of short wavelength excitation. This technique, though viable [22,24], suffers from the fact that only reactions with relatively simple substrates such as aliphatic alcohols and water can be studied, due to the necessity that the transient quencher not be absorbing at the wavelength employed to excite the transient precursor. The study of a more extensive list of silene reactions, such as those with ketones, carboxylic acids, alkenes and dienes, necessitates the use of silene precursors which absorb at 248 nm and above.

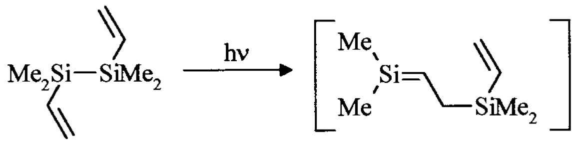
It is well-known that aryldisilanes undergo photochemical [1,3]-silyl migration (into the *ortho*-position of an aromatic ring) to yield silene intermediates [26], and indeed, this methodology has allowed the study of a number of silene trapping reactions by laser flash photolysis techniques [11,15,16,20]. The process is also known to occur in vinyldisilanes, where migration of a silyl group occurs from the vinyl silicon atom to the terminal sp^2 carbon of the vinyl substituent, to yield a silene intermediate [5,26–32]. The UV absorption spectra of simple vinyl-substituted peralkyldisilanes extends far enough into the mid-UV that these compounds should, in principle, be convenient precursors for the direct detection and study of simple alkyl-substituted silenes using 248 nm laser excitation.

In this paper, we report the results of a study of the photochemistry of pentamethylvinyldisilane (**1**), 1,1,2,2-tetramethyl-1,2-divinyldisilane (**2**), and 1,1,1,3-tetramethyl-2,2-divinyldisilane (**3**) in hydrocarbon solution, by a combination of steady-state irradiation techniques and static and time-resolved UV absorption spectroscopy, in low temperature glasses and in solution at room temperature (r.t.). The photochemistry of disilanes **1** and **2** in the presence of methanol, methoxytrimethylsilane, and/or 1,3-butadiene has been reported previously; the products of photolysis are consistent with the formation of silenes **4** and **5** as the major initial reactive intermediates (see Eqs. 1 and 2) [28,30]. In the present work, we supplement these data with the results of direct photolysis of (**1**) in the absence of silene traps, and of (**3**) in the presence of methanol and 1,3-butadiene. The latter results are consistent with the intermediacy of the 1,3-(2-sila)butadiene derivative **6** (Eq. 3). The UV absorption spectra of the three silenes in low temperature glasses and in solution at r.t. are reported, and absolute rate constants for their reactions with alcohols, acetic acid, acetone, 2,3-dimethyl-1,3-butadiene (DMB), cyclohexene and oxygen have been determined.



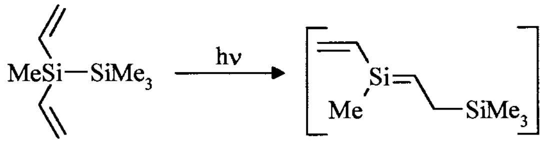
[1]

1 **4**



[2]

2 **5**

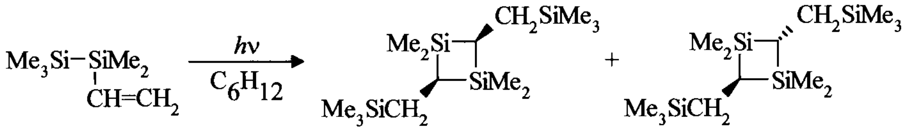


[3]

3 **6**

2. Results and discussion

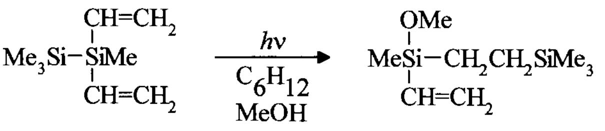
Direct irradiation of a deoxygenated cyclohexane solution of pentamethylvinyldisilane (**1**; 1.2 M) led to the formation of two products, in roughly equal yield, which could barely be separated by capillary gas chromatography/mass spectrometry (GC/MS). The two compounds were isolated as a mixture by semi-preparative GC, and identified as the isomeric 1,3-disilacyclobutane derivatives *cis*- and *trans*-**7** on the basis of ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectroscopy and mass spectrometry (see Eq. 4). These are the expected products of dimerization of silene **4**. As Ishikawa and coworkers reported for a related compound [28], the reaction proceeds with a high degree of (the expected) head-to-tail regioselectivity, but with little stereoselectivity. No other products could be detected in the photolysate after ca. 30% conversion of **1**.



[4]

1 *cis*-**7** *trans*-**7**

Direct irradiation of a deoxygenated solution of (**3**) (0.02 M) in cyclohexane containing methanol (0.13 M) led to the formation of a single product in nearly quantitative yield. The product was identified as the methanol adduct of silene **6**, methyl(vinyl)(2-(trimethylsilyl)ethyl)methoxysilane (**8**; Eq. 5), on the basis of spectroscopic data after isolation of the compound from the photolysis mixture by semi-preparative GC.



$$\mathrm{Me_3Si{-}SiMe(CH{=}CH_2)_2} \xrightarrow[\mathrm{C_6H_{12}}\ \mathrm{MeOH}]{h\nu} \mathrm{MeSi(OMe)(CH{=}CH_2){-}CH_2CH_2SiMe_3} \quad [5]$$

3 **8**

Irradiation of **3** in deoxygenated cyclohexane containing 1,3-butadiene under similar conditions afforded a complex mixture of at least seven major products which were not completely characterized. Four of these were tentatively identified as the isomeric silacyclobutanes resulting from [2 + 2]-addition of the diene to silene **6**, on the basis of GC/MS and the NMR spectrum of a mixture of the four products, which was isolated by semi-preparative GC. These were formed in a combined yield of ca. 60%. Two of the others (combined yield ca. 15%) were similarly identified tentatively as the isomeric silacyclohexenes resulting from [4 + 2]-cycloaddition of the diene to the silene.

Nanosecond laser flash photolysis (248 nm, ~16 ns, 70–100 mJ) [33] of deoxygenated *n*-hexane or isooctane solutions of **1**–**3** leads to weak, but readily detectable transient absorptions in the 270–350 nm range. The transient from photolysis of **2** decays with clean second-order kinetics, while those from **1** and **3** decay with mixed first- and second-order kinetics; all three exhibit lifetimes in excess of 15 μs at ambient temperatures (23–25°C). Fig. 1 shows transient UV absorption spectra for the three compounds, recorded in point-by-point fashion within a few microseconds after the laser pulse. Typical decay traces, recorded at monitoring wavelengths corresponding to the absorption maxima, are shown as inserts in Fig. 1. Flash photolysis of deoxygenated solutions of **1** in acetonitrile afforded similar results to those obtained for this compound in hexane solution.

The lifetimes of the transients obtained from photolysis of **1** and **2** are mildly sensitive to the presence of oxygen, such that in air-saturated solution, they decay with predominant pseudo-first order kinetics and lifetimes of about 10 μs. A bimolecular rate constant for quenching by oxygen was determined to be (k_{O_2} = (2.6 ± 0.3) × 10^7 M^{-1} s^{-1}) for the transient from **1** in hexane solution at 23°C. The lifetime of the transient from photolysis of **3** was about five times less sensitive

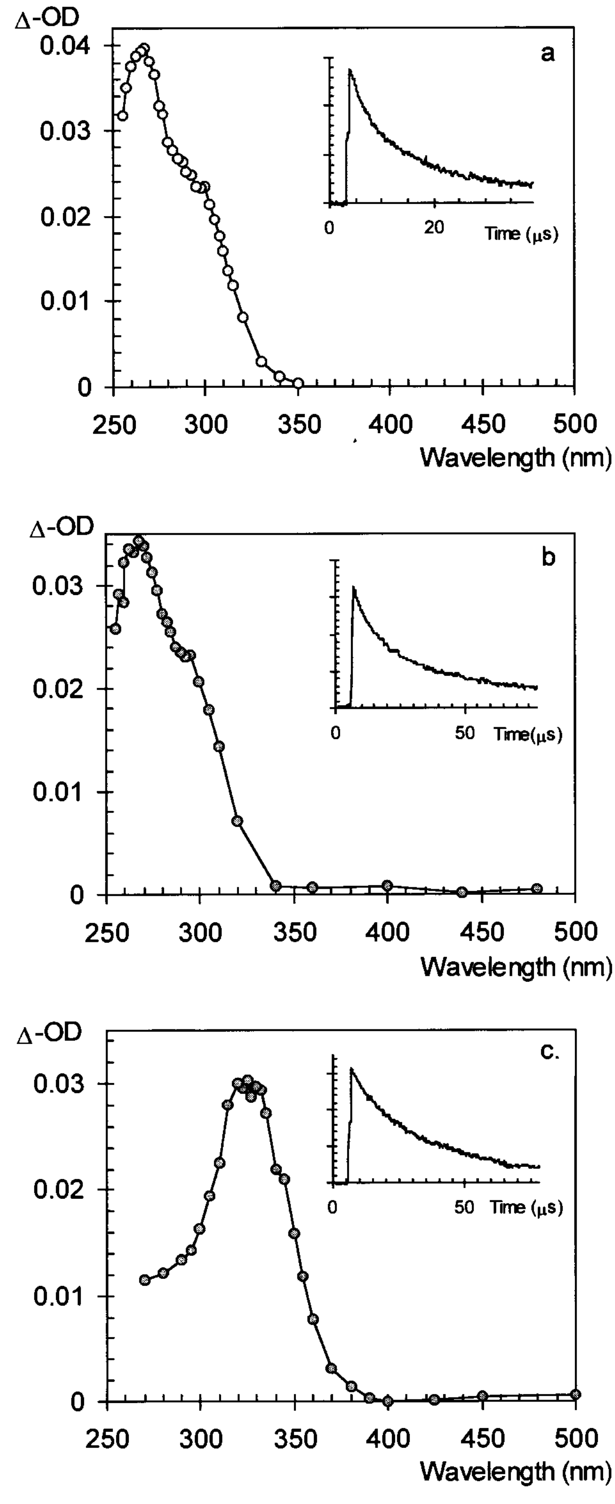


Fig. 1. Transient UV absorption spectra recorded at 23 ± 1°C by nanosecond laser flash photolysis of deoxygenated *n*-hexane solutions of (a) pentamethylvinyldisilane (**1**; 0.01 M), (b) 1,1,2,2-tetramethyl-1,2-divinyldisilane (**2**; 0.0018 M) and (c) 1,1,1,2-tetramethyl-2,2-divinyldisilane (**3**; 0.0041 M). Spectra were recorded 0.1–1 μs (**1**) and 1–10 μs (**2** and **3**) after the laser pulse. The inserts show typical decay traces, recorded at 270 nm for **1** and **2**, and 325 nm for **3**.

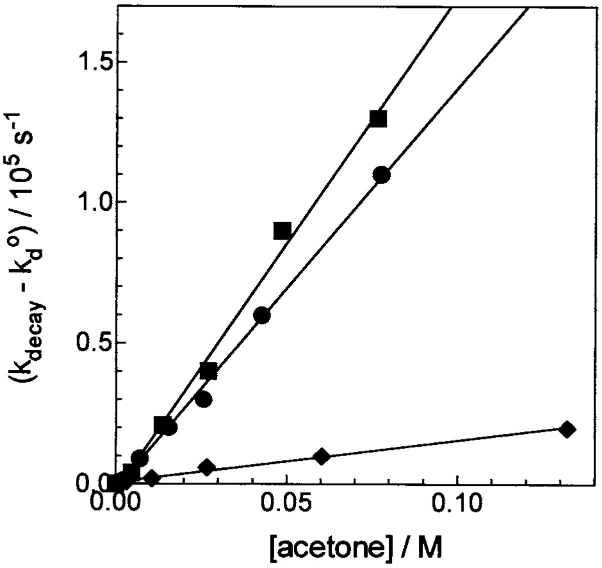


Fig. 2. Plots of ($k_{\mathrm{decay}} - k_{\mathrm{d}}^0$) versus acetone concentration (see Eq. 4) from nanosecond laser flash photolysis of deoxygenated *n*-hexane solutions of **1** (■), **2** (●) and **3** (◆), containing acetone at 23 ± 1°C.

to oxygen than those from **1** and **2**, requiring that the solution be saturated with oxygen in order to reduce its lifetime to ~ 10 μs. This allows an estimate of $k_{O_2} \sim 5 \times 10^6\ M^{-1}\ s^{-1}$ for the rate constant for quenching of the transient from photolysis of **3** by oxygen.

Addition of methanol, *t*-butanol, or acetone to hexane solutions of **1–3** resulted in shortening of the lifetime of the transients and a change in the decay kinetics to pseudo-first order, but elicited no reduction in the initial transient yields or the production of new transient absorptions elsewhere in the spectra. Similar behavior was found for solutions of disilane **1** in acetonitrile. Plots of the rate constants for transient decay (k_{decay}) versus concentration of added quencher (Q) according to Eq. 6 (where k_q is the bimolecular rate constant for transient quenching by Q, and k_d^0 is the pseudo-first order decay rate constant in the absence of Q) were linear in the case of acetone. Typical plots for quenching of the three transients by this reagent at 23°C are shown in Fig. 2. The corresponding plots for quenching by the alcohols were also linear, but were typically quite scattered and sometimes showed a hint of positive curvature. For example, Fig. 3 shows plots of k_{decay} versus [ROH] for quenching of the transients from **1** in acetonitrile (Fig. 3a) and **3** in hexane (Fig. 3b) by methanol and *t*-butanol. Bimolecular quenching rate constants were obtained by linear least squares analyses of the data according to Eq. 6. Several measurements of the rate constants for quenching by methanol and *t*-butanol were made for each of the three silenes, and the values obtained varied within ~ 30%. This is primarily due to the signal strengths, which were quite weak at times.

$$k_{\mathrm{decay}} = k_d^0 + k_q[Q] \tag{6}$$

On the basis of the UV absorption spectra of the three transients, their reactivity toward these known silene traps, and the identity of the products isolated from direct photolysis of the three disilanes under various conditions, (vide supra and refs. [28,30]) they can be assigned with reasonable certainty to the silenes **4–6**. In the absence of quenchers, the silenes decay with predominant second-order kinetics, consistent with dimerization being the major mechanism for silene decay in the absence of traps. This has been verified directly for silene **4** from (**1**), which yields the corresponding [2 + 2]- head-to-tail dimers upon direct photolysis in hexane (Eq. 4). We have not determined the

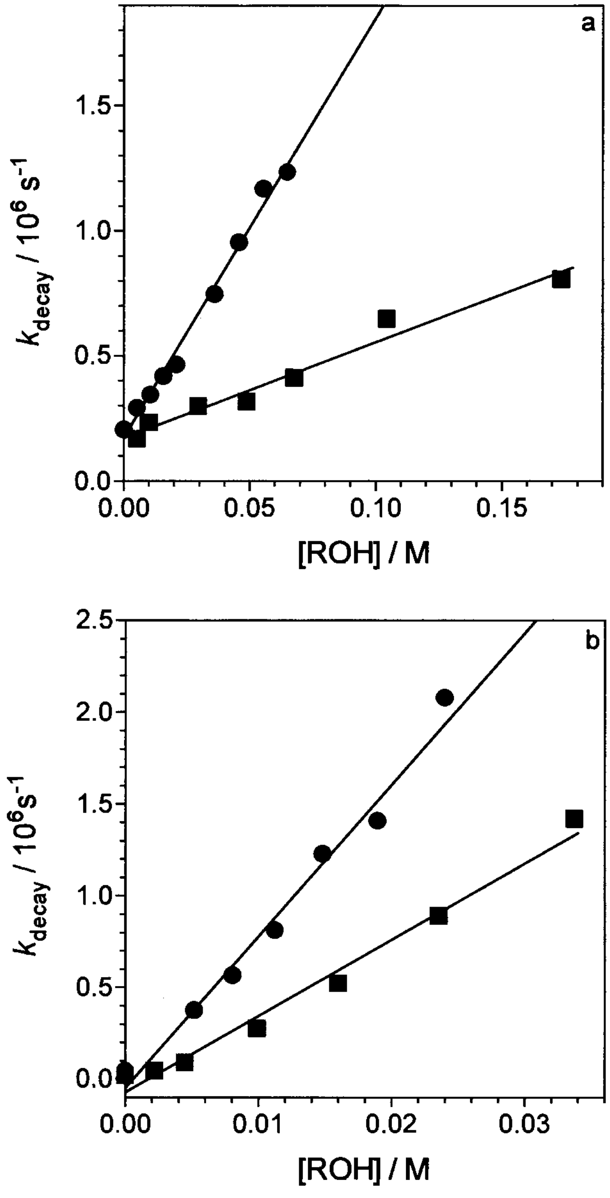
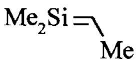


Fig. 3. Plots of k_{decay} versus [ROH] concentration for the quenching of silene **4** in acetonitrile (a) and silene **6** in hexane (b) by methanol (●) and *t*-butanol (■) at 23°C.

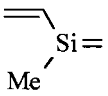
absolute second order rate constants for dimerization of the silenes, since extraction of these numbers from the flash photolysis data requires knowledge of extinction coefficients for the silene absorption spectra.

Similar UV absorption spectra were obtained upon irradiation (254 nm) of deoxygenated solutions of **1–3** in 3-methylpentane glasses at 77 K. Thus, irradiation of **1** and **2** resulted in the appearance of new absorption bands with absorption maxima at $\lambda_{max} = 270$ nm in both cases, while similar experiments with **3** yielded a product absorbing with $\lambda_{max} = 325$ nm. In each case, warming the matrix resulted in the disappearance of the new absorption band, and it did not reappear upon re-cooling unless irradiation was continued. These properties are consistent with the absorptions being due to silenes **4–6**.

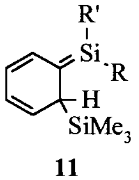
As would be expected, the UV spectra of **4** and **5** are similar, showing a prominent band with $\lambda_{max} \sim 270$ nm and a shoulder at ~ 300 nm. By way of comparison, the spectrum of 1,1,2-trimethylsilene (**9**) is similarly featured [$\lambda_{max} = 255$, 285 nm(sh)] but blue-shifted by ~ 15 nm compared to those of **4** and **5** [34]. We attribute the bathochromic shift to a hyperconjugative effect of the trialkylsilyl substituent at the 3-position of the 1,1-dimethyl-(1-sila)propene structure in **4** and **5**. The analogous effect on the UV absorption spectra of alkenes [35,36] and other reactive silenes [23] is well documented. This hyperconjugative effect may also affect the UV spectrum of the 1,3-(2-sila)butadiene derivative **6** ($\lambda_{max} \sim 325$ nm), although the closest model compound available for comparison is 2-methyl-1,3-(2-sila)butadiene (**10**). The spectrum of this reactive silene exhibits $\lambda_{max} = 305$ nm in hydrocarbon solution at ambient temperatures [37].



9

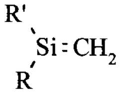


10



11

a. R = R' = Me
b. R = Me; R' = Ph
c. R = R' = Ph



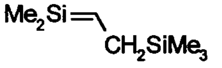
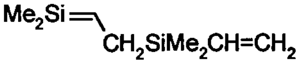
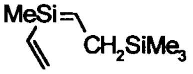
12

A few additional quenching experiments were carried out with other reagents, although as in the cases of acetone and *t*-butanol, these have not been followed up with product studies. Quenching of the silenes by DMB is relatively slow, and is difficult to determine quantitatively owing to screening of the disilane precursors at the high diene concentrations necessary for substantial reductions in the transient lifetimes. Thus, it was possible to obtain only very rough values for the rate constants for quenching of the three silenes by DMB; these are on the order of $\sim 10^6$ M^{-1} s^{-1}. Quenching by cyclohexene proved to be even slower, requiring the use of solutions containing 1–2 M concentrations of chromatographically-purified alkene in order to reduce screening of the precursor absorption at 248 nm by impurities. The rate constants obtained, which are on the order of 10^4–10^5 M^{-1} s^{-1}, should be considered to be very crude upper limits. A rate constant for quenching of silene **4** by acetic acid in dried, deoxygenated acetonitrile solution was also determined, along with the values for quenching by methanol, methanol-O*d*, *t*-butanol, and acetone. Rate constants for quenching of silenes **5** and **6** by methanol-O*d* were determined in hexane solution. The results of these experiments are collected with the others in Table 1.

The relative reactivities of each of the silenes **4–6** towards methanol, *t*-butanol, acetone, 2,3-dimethylbutadiene and cyclohexene are similar to those reported for other transient silenes, such as aryldisilane-derived 1-(sila)hexatrienes (e.g. **11**) [11,15,16] and 1,1-diphenylsilene (**12c**) [14,19], and follow the same relative ordering ($k_{MeOH} > k_{BuOH} > k_{acetone} > > k_{diene} > k_{alkene}$). As usual, the rate constants are three to ten times lower in acetonitrile than in hexane, and acetic acid is substantially more reactive as a silene trap than methanol. Acetone reacts with silenes such as **12** by formal ene-addition to yield the silyl enol ether [14], while reaction with acetic acid yields the corresponding acyloxysilane [19]. The products of these reactions have not been determined in the present cases, however.

There is considerable evidence which is consistent with a mechanism for addition of alcohols to simple silenes involving initial, reversible formation of a silene–alcohol complex, which collapses to alkoxysilane product by rate-limiting proton transfer from oxygen to carbon (Scheme 1) [11,15,18,19,22,24,25,32,38,39]. This process proceeds with *syn*-stereochemistry [32,40] and results in a simple first order dependence of the rate constant for silene consumption on alcohol concentration [18,19,22,24,25]. Small primary deuterium kinetic isotope effects (consistent with proton transfer being rate-limiting) and negative Arrhenius activation energies (consistent with the involvement of a reversibly-formed complex) have been observed in a number of cases [18,19,22,24,25]. The absolute rate constants for reaction of **4–6** with methanol are all reduced significantly for the O-deuteriated alcohol, and while the differences are small, they are similar to those observed for other reactive silenes. Our results are thus consistent with the general mechanism shown in Scheme 1 for the addition of methanol and *t*-butanol to silenes **4–6**. Kinetic studies of the addition of acetic acid to substi-

Table 1
Bimolecular rate constants (in M^{-1} s^{-1}) for quenching of silenes **4–6**, from laser flash photolysis of deoxygenated *n*-hexane or acetonitrile solutions of **1–3** at 23 ± 1°C[a]

Disilane	1		2	3
Silene				
Quencher	k_q / 10^7 $M^{-1}s^{-1}$		k_q / 10^7 $M^{-1}s^{-1}$	k_q / 10^7 $M^{-1}s^{-1}$
	hexane	acetonitrile	hexane	hexane
MeOH	15 ± 2	1.7 ± 0.2	13 ± 2	8.3 ± 1.0
MeOD	*n.d.*	1.2 ± 0.1	10 ± 2	5.4 ± 0.6
t-BuOH	10 ± 2	0.38 ± 0.06	5 ± 2	4.2 ± 0.5
HOAc	*n.d.*	73 ± 7	*n.d.*	*n.d.*
acetone	1.9 ± 0.2	0.60 ± 0.08	1.6 ± 0.2	0.20 ± 0.02
DMB	0.32 ± 0.06	*n.d.*	< 0.01	~ 0.5
cyclohexene	0.0040 ± .0015	*n.d.*	0.009 ± 0.005 [b]	0.006 ± 0.003 [b]
oxygen	2.6 ± 0.3	*n.d.*	*n.d.*	~ 0.5

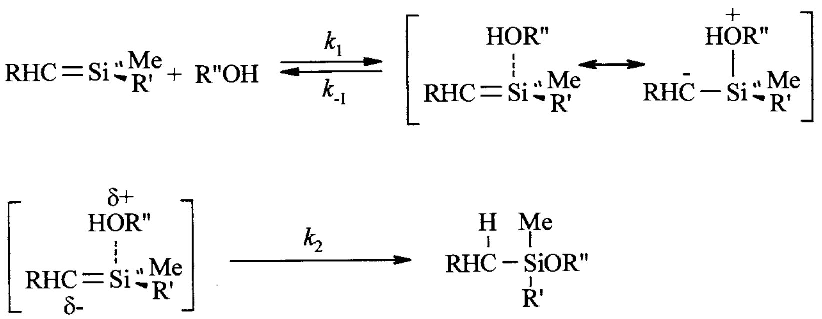
[a] Errors are quoted as twice the standard deviation from linear least squares analysis of k_{decay} versus [Q], according to Eq. 6.

[b] Upper limits calculated from the silene lifetimes in the absence and presence of 2.0 M cyclohexene.

tuted 1,1-diphenylsilenes suggest that it adds by a similar mechanism, but with complex formation being rate-determining [25].

When the rate constant for proton transfer within the complex is relatively slow and/or the concentration of alcohol is high, the collapse of the complex to product can proceed by a pathway involving a second molecule of alcohol. This extracomplex proton transfer process competes with the intracomplex pathway and can manifest itself in a number of ways, such as concentration dependent product distributions [15,19,32,39] or a quadratic dependence of the pseudo-first order rate constant for silene consumption on alcohol concentration [11,15]. This second pathway does not appear to be important at the alcohol concentrations employed here for our kinetic studies of **4–6**. Furthermore, quenching studies with methanol and *t*-butanol in hexane solution were all confined to solutions of concentration below that where oligomerization of the alcohols starts to become significant (≤ 0.03 M for MeOH; ≤ 0.1 M for *t*-BuOH [41,42]), so as to avoid potential complexities in the kinetics [21,23]. Thus, the rate constants reported in Table 1 for methanol and *t*-butanol in hexane refer to those for reaction of **4–6** with the monomeric forms of both alcohols.

While the precision in the bimolecular rate constants for reaction of **4–6** is lower than usual due to low signal intensities, it is sufficient to allow a few general comparisons to be made within the series of compounds. As might be expected, silenes **4** and **5** exhibit very similar reactivity toward most of the reagents examined. In contrast, comparison of the rate constants for reaction of **6** with alcohols and acetone to those for **4** and **5** indicates that the reactivity of the Si=C bond in the 1,3-(2-sila)butadiene moiety in **6** is significantly lower than that of the isolated Si=C bonds in **4** and **5**, ranging from a factor of two to three for methanol to almost a factor of ten for acetone. The effect of vinylic substitution at silicon on the reactivity of these compounds with methanol is similar in magnitude to that



$$k_{ROH} = \frac{k_1 k_2}{k_{-1} + k_2}$$

Scheme 1. Mechanism for the addition of methanol and *t*-butanol to silenes **4**–**6**.

observed for 1,1-dimethylsilene (**12a**) and 2-methyl-1,3-(2-sila)butadiene (**10**) [24,37], even though the latter two compounds are significantly more reactive than their counterparts here. It is interesting to note that this is exactly opposite to what has been predicted on the basis of ab initio theoretical calculations on 1,3-(1-sila)butadiene, 1,3-(2-sila)butadiene and silene ($H_2Si=CH_2$) [43]. These calculations suggest there to be substantially greater polarization of the Si=C bond in (2-sila)butadiene than in either the (1-sila) isomer or silene, leading to the expectation of greater reactivity toward nucleophiles. (2-Sila)butadiene **6** ($k_{MeOH} \sim 8.3 \times 10^7$ M^{-1} s^{-1}) is roughly 20 times less reactive toward alcohols than the less-substituted analog **10** ($k_{MeOH} \sim 1.8 \times 10^9$ M^{-1} s^{-1} [37]), a difference which can only be due to the presence of the CH_2SiMe_3 substituent on the silenic carbon. The same trend is observed for silene **4** ($k_{MeOH} \sim 1.5 \times 10^8$ M^{-1} s^{-1}) and 1,1-dimethylsilene (**12c**; $k_{MeOH} \sim 4.9 \times 10^9$ M^{-1} s^{-1} [24]).

We tentatively ascribe these trends in reactivity to the effects of hyperconjugative electron donation by the trimethylsilylmethyl substituent, which would be expected to reduce the amount of positive π-charge density at the silenic silicon atom and hence reduce the rate constants for reactions in which nucleophilic attack occurs in or precedes the rate-determining step [44]. The trimethylsilylmethyl group is a moderately strong π-electron donor, as indicated by the magnitude of its σ^0_R value (-0.20 [45]). Kinetic isotope effect and Arrhenius studies of the addition of alcohols to **10** [24] and **12c** [37] in hexane solution suggest that in both cases, nucleophilic attack occurs reversibly and precedes rate-limiting proton transfer within the initially formed silene–alcohol complex. Similar isotope effects are observed here for **4** and **6**. Hence, the lower reactivities of **4** and **6** toward methanol and *t*-butanol under the same conditions suggests that complex formation is significantly slowed due to the electron-donating substituent at the silenic carbon. We cannot, at the present time, fully evaluate the extent to which steric effects contribute to the decreased reactivity of these compounds, and this is the subject of current work in our laboratory. It is certainly well known that sterically-bulky substituents at the 2-position in silenes contribute significantly to their kinetic stabilities [1,7,46,47].

3. Summary and conclusions

In this work, the silene intermediates (**4**–**6**) formed in the direct photolysis of pentamethylvinyldisilane (**1**), 1,1,2,2-tetramethyl-1,2-vinyldisilane (**2**), and 1,1,1,2-tetramethyl-2,2-divinyldisilane (**3**) have been characterized. Silenes **4** and **5** have been previously proposed to be the major initial products of photolysis of **1** and **2** in solution [27–29]; the photolysis of disilane **3** is reported here for the first time. Irradiation in hydrocarbon solution in the presence of methanol or 1,3-butadiene affords the expected trapping products of silene **6**. The silenes have been detected directly by UV absorption spectroscopy in 3-methylpentane matrices at 77 K and by laser flash photolysis in solution at r.t. Using the latter technique, absolute rate constants for reaction of the three silenes with methanol, *t*-butanol, acetone, DMB, cyclohexene and oxygen have been determined.

Comparison of the rate constants for alcohol addition to **4** and **5** with the corresponding values for other silenes which have been studied previously indicate that the trimethylsilylmethyl substituent present in both compounds exerts significant kinetic stabilization on the Si=C bond. This is consistent with a reduction in positive π-charge density at the silenic silicon atom due to the moderately strong resonance electron-donor characteristics of this substituent. Hyperconjugative electron-donation by the β-trimethylsilyl group also exerts an effect on the frontier molecular energies, causing a red-shift of the lowest energy (π,π*) absorption bands in the UV spectra of these compounds.

More detailed studies of the effects of substituents on the reactivity of transient silenes are in progress.

4. Experimental

^{1}H-, ^{13}C- and ^{29}Si-NMR spectra were recorded on Varian Gemini 200 or Varian VXR300 spectrometers in deuteriochloroform or benzene-d$_6$ solution, and are referenced to TMS. IR spectra were recorded on a Perkin-Elmer 1330 spectrometer and are referenced to the 1601.9 cm^{-1} polystyrene absorption. Static UV absorption spectra were recorded on a Hewlett-Packard HP8451A diode array spectrometer. MS were recorded on a GC/MS system consisting of a Hewlett Packard HP5790A gas chromatograph equipped with an HP-5970A mass selective detector and a silicon oil column (50 m × 0.25 mm; Supelco). Analytical GC analyses were carried out using a Hewlett-Packard HP 5840A gas chromatograph equipped with a conventional heated injector, a flame ionization detector, a Hewlett-Packard 3396A integrator, and a SP-2100 fused silica column (3 m × 0.53 mm; Supelco). Semi-preparative GC separations were performed on a Varian 90A gas chromatograph equipped with a thermal conductivity detector and a 15% OV-17 on 40–60 Chromosorb W column ($\frac{1}{4}$" × 15'; Supelco). Steady state photolyses were carried out in a Rayonet Photochemical Reactor containing 12–16 RPR-2537 lamps (Southern New England Ultraviolet).

2,2,4-Trimethylpentane (isooctane; Baker HPLC), *n*-hexane (BDH Omnisolv), methanol (Caledon), acetone (Baker Reagent), chloroform (BDH Omnisolv), DMB (Aldrich), and 1,3-octadiene (Columbia) were all used as received from the suppliers. Acetonitrile (BDH Omnisolv) was distilled after refluxing for several days over calcium hydride. Cyclohexene (Aldrich) was purified by conventional column chromatography on a 10% silver nitrate/silica gel column (eluting with pentane), followed by distillation; the absorbance of the purified, neat material was > 0.1 at 248 nm.

Disilanes **1**–**3** were synthesized by reaction of vinyl magnesium bromide with the corresponding chloro- or dichlorodisilane, according to the published methods [30,48]. 1,1,1,2-Tetramethyl-2,2-divinyldisilane (**3**) was identified on the basis of the following spectroscopic data. ^{1}H-NMR (C$_6$D$_6$): δ 0.17 (s, 9H), 0.21 (s, 3H), 5.70 (dd, 2H, $J = 4.16$, 19.74 Hz), 5.96 (dd, 2H, $J = 4.16$, 14.42 Hz), 6.21 (dd, 2H, $J = 14.42$, 19.74 Hz). ^{13}C-NMR (C$_6$D$_6$): δ −6.44, −2.10, 132.43, 136.63. ^{29}Si-NMR (C$_6$D$_6$): δ −29.1, −19.81. IR (KBr, cm^{-1}): 3050 (m), 3003 (w), 2951 (s), 2896 (m), 1893 (w), 1588 (w), 1438 (w), 1401 (s), 1246 (s), 1007 (s), 946 (s), 859 (s), 837 (s), 786 (s), 785 (s), 721 (s), 690 (s), 670 (w). UV (3-MP): $\lambda_{max} = 234$ nm, ($\varepsilon = 5.4 \times 10^4$). MS: m/z (I) = 170 (0.2), 169 (0.1), 157 (6), 156 (12), 155 (77), 127 (14), 97 (16), 95 (20), 85 (39), 73 (100), 71 (42), 59 (65), 55 (28), 53 (15), 45 (83), 43 (65), 29 (18).

4.1. Direct photolysis of pentamethylvinyldisilane (1)

A solution of **1** (0.116 g, 0.73 mmol) in cyclohexane (0.6 ml) was placed in a quartz tube, deoxygenated with a stream of dry nitrogen, and photolyzed in a Rayonet reactor containing fourteen RPR2537 lamps, with periodic monitoring of the progress of the photolysis by GC. Photolysis for 30 hours resulted in ca. 30% conversion of **1** and the formation of two major products which could be detected by GC/MS. The two compounds were isolated as a mixture by semi-preparative GC, and tentatively identified as *cis*- and *trans*-1,3-tetramethyl-2,4-bis(trimethylsilylmethyl)-1,3-disilacyclobutane on the basis of the following spectroscopic data: ^{1}H-NMR (CDCl$_3$): δ −0.09 (d), −0.09 (d), −0.02 (s), 0.08 (s), 0.14 (s), 0.18 (s), 0.57 (s), 0.59 (s), 1.54 (s). ^{13}C-NMR (CDCl$_3$): δ −5.27, −1.67, −1.63, −1.26, 2.43, 8.53, 9.54, 10.75. ^{29}Si-NMR (CDCl$_3$): δ 1.66, 1.91, 9.88, 11.1. GC/MS, isomer no. 1: m/z (I) = 316 (12), 243 (4), 227 (10), 155 (24), 116 (14), 73 (100), 45 (19). GC/MS, isomer no. 2: m/z (I) = 316 (12), 243 (3), 227 (10), 155 (23), 116 (14), 73 (100), 45 (20).

4.2. Direct photolysis of 3 in the presence of methanol

A solution of **3** (0.10 g, 0.58 mmol) and methanol (0.187 g, 5.8 mmol) in cyclohexane (30 ml) was placed in a 25 mm o.d. quartz tube. After purging with argon, the solution was irradiated for 4.5 h, giving rise to the formation of a single product in nearly quantitative yield. The compound was isolated by semi-preparative GC ($\frac{1}{4}$" × 3' 20% OV-17 on Chromosorb W) as a colorless liquid, and identified as methyl(vinyl)(2-(trimethylsilyl)ethyl)methoxysilane on the basis of the following spectroscopic data:
^{1}H-NMR (CDCl$_3$): δ −0.006 (s, 9H), 0.17 (s, 3H), 0.56 (m, 4H), 1.04 (dd, 1H, $J = 5.5$ Hz, $J = 7.58$ Hz), 3.33 (s, 3H), 5.8 (dd, 1H, $J = 19.24$, 5.16 Hz), 5.98 (dd, 1H, $J = 5.16$, 14.9 Hz), 6.17 (dd, 1H, $J = 14.9$, 19.24 Hz). ^{13}C-NMR (CDCl$_3$): δ −4.95, −2.2, 7.12, 8.04, 50.35, 133.62, 136.56. ^{29}Si-NMR (CDCl$_3$), $\delta = 0.4$, 4.34. MS: m/z (I) = 202 (1), 187 (36), 159 (10), 102 (10), 101 (100), 88 (20), 75 (23), 73 (35), 71 (15), 59 (32), 45 (28), 43 (12).

Low temperature UV absorption spectra were measured on the HP8451A spectrometer using a Dewar flask with optical quartz windows and cooled with liquid nitrogen. Samples were contained in a 1 × 1 cm cryogenic quartz cell equipped with a Teflon stopcock, and were degassed with three freeze/pump/thaw cycles prior to irradiation. The samples were irradiated in the Dewar flask using the Rayonet reactor, and monitored periodically by UV spectroscopy.

Nanosecond laser flash photolysis experiments employed the pulses (248 nm, ~16 ns, 80–120 mJ) from a Lumonics 510 excimer laser filled with F_2/Kr/He mixtures, and a microcomputer-controlled detection system [11,33,49]. Disilane solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7 in a 3 mm cell. Solutions of **2** and **3** were contained in a calibrated 100 ml reservoir which supplies a flow cell constructed from 3×7 mm rectangular Suprasil quartz tubing (Vitro Dynamics). Quenchers were added to the reservoir as aliquots of the neat liquids or concentrated stock solutions in hexane. A few experiments with **1** were carried out using static 3×7 mm Suprasil cells, because of the higher concentrations employed for this disilane. Bimolecular quenching rate constants were determined from linear least-squares analysis of plots of transient decay rate versus quencher concentration; generally, a minimum of six points was used for the analyses, with the range in quencher concentration adjusted to span at least an order of magnitude in transient decay rate.

Acknowledgements

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada and the Robert A. Welch Foundation for financial support of this work.

References

[1] G. Raabe, J. Michl, Chem. Rev. 85 (1985) 419.
[2] A.G. Brook, K.M. Baines, Adv. Organomet. Chem. 25 (1986) 1.
[3] A.G. Brook, M.A. Brook, Adv. Organomet. Chem. 39 (1996) 71.
[4] A.G. Brook, The photochemistry of organosilicon compounds, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, New York, 1989, pp. 965–1005.
[5] M.G. Steinmetz, Chem. Rev. 95 (1995) 1527.
[6] A.G. Brook, J.W. Harris, J. Lennon, M. El Sheikh, J. Am. Chem. Soc. 101 (1979) 83.
[7] N. Wiberg, J. Organomet. Chem. 273 (1984) 141.
[8] H. Shizuka, K. Okazaki, M. Tanaka, M. Ishikawa, M. Sumitani, K. Yoshihara, Chem. Phys. Lett. 113 (1985) 89.
[9] P.P. Gaspar, D. Holten, S. Konieczny, J.Y. Corey, Acc. Chem. Res. 20 (1987) 329.
[10] R.T. Conlin, S. Zhang, M. Namavari, K.L. Bobbitt, M.J. Fink, Organometallics 8 (1989) 571.
[11] G.W. Sluggett, W.J. Leigh, J. Am. Chem. Soc. 114 (1992) 1195.
[12] S. Zhang, R.T. Conlin, P.F. McGarry, J.C. Scaiano, Organometallics 11 (1992) 2317.
[13] W.J. Leigh, G.W. Sluggett, J. Am. Chem. Soc. 115 (1993) 7531.
[14] W.J. Leigh, C.J. Bradaric, G.W. Sluggett, J. Am. Chem. Soc. 115 (1993) 5332.
[15] W.J. Leigh, G.W. Sluggett, J. Am. Chem. Soc. 116 (1994) 10468.
[16] W.J. Leigh, G.W. Sluggett, Organometallics 13 (1994) 269.
[17] G.W. Sluggett, W.J. Leigh, Organometallics 13 (1994) 1005.
[18] C.J. Bradaric, W.J. Leigh, J. Am. Chem. Soc. 118 (1996) 8971.
[19] W.J. Leigh, C.J. Bradaric, C. Kerst, J.H. Banisch, Organometallics 15 (1996) 2246.
[20] N.P. Toltl, W.J. Leigh, Organometallics 15 (1996) 2554.
[21] C. Kerst, C.W. Rogers, R. Ruffolo, W.J. Leigh, J. Am. Chem. Soc. 119 (1997) 466.
[22] C. Kerst, M. Byloos, W.J. Leigh, Can. J. Chem. 75 (1997) 975.
[23] C. Kerst, R. Ruffolo, W.J. Leigh, Organometallics 16 (1997) 5804.
[24] C. Kerst, R. Boukherroub, W.J. Leigh, J. Photochem. Photobiol. A: Chem. 110 (1997) 243.
[25] C.J. Bradaric, W.J. Leigh, Can. J. Chem. 75 (1997) 1393.
[26] M. Ishikawa, M. Kumada, Adv. Organomet. Chem. 19 (1981) 51.
[27] M. Ishikawa, T. Fuchikami, M. Kumada, J. Organomet. Chem. 117 (1976) C58.
[28] M. Ishikawa, T. Fuchikami, M. Kumada, J. Organomet. Chem. 149 (1978) 37.
[29] H. Sakurai, Y. Kamiyama, Y. Nakadaira, J. Am. Chem. Soc. 98 (1976) 7424.
[30] R.T. Conlin, K.L. Bobbitt, Organometallics 6 (1987) 1406.
[31] M. Ishikawa, Y. Nishimura, H. Sakamoto, Organometallics 10 (1991) 2701.
[32] M. Kira, T. Maruyama, H. Sakurai, J. Am. Chem. Soc. 113 (1991) 3986.
[33] W.J. Leigh, M.S. Workentin, D. Andrew, J. Photochem. Photobiol. A: Chem. 57 (1991) 97.
[34] C. Kerst, R. Boukherroub, S. Jenkins, W.J. Leigh, K. Sung, T.T. Tidwell, for publication.
[35] B.G. Ramsey, Electronic Transitions in Organometalloids, Academic Press, New York, 1969, pp. 65–134.
[36] R. Ponec, V. Chvalovsky, E.A. Cernysev, N.G. Komarenkova, S.A. Baskirova, Coll. Czech. Chem. Commun. 39 (1974) 1177.
[37] W.J. Leigh, R. Boukherroub, C. Kerst, J. Am. Chem. Soc., submitted.
[38] S. Nagase, T. Kudo, K. Ito, Structures, stability, and reactivity of doubly bonded compounds containing silicon or germanium, in: V.H.J. Smith, H.F. Schaefer, K. Morokuma (Eds.), Applied Quantum Chemistry, D. Reidel, Dordrecht, 1986, pp. 249–267.
[39] M.G. Steinmetz, B.S. Udayakumar, M.S. Gordon, Organometallics 8 (1989) 530.
[40] P.R. Jones, T.F. Bates, J. Am. Chem. Soc. 109 (1987) 913.
[41] H. Landeck, H. Wolff, R. Gotz, J. Phys. Chem. 81 (1977) 718.
[42] Y. Fujii, H. Yamada, M. Mizuta, J. Phys. Chem. 92 (1988) 6768.
[43] G. Trinquier, J.P. Malrieu, J. Am. Chem. Soc. 103 (1981) 6313.
[44] Y. Apeloig, M. Karni, J. Am. Chem. Soc. 106 (1984) 6676.
[45] D.D.M. Wayner, Free energy relationships, in: J.C. Scaiano (Ed.), CRC Handbook of Organic Photochemistry, CRC Press, Boca Raton, 1989, pp. 395–400.
[46] A.G. Brook, S.C. Nyburg, F. Abdesaken, et al., J. Am. Chem. Soc. 104 (1982) 5667.
[47] N. Wiberg, G. Wagner, Chem. Ber. 119 (1986) 1467.
[48] T.J. Barton, W.D. Wulff, J. Organomet. Chem. 168 (1979) 23.
[49] G.W. Sluggett, W.J. Leigh, Organometallics 11 (1992) 3731.