

# Far-UV laser flash photolysis in solution. A time-resolved spectroscopic study of the chemistry of 1,1-dimethyl-1,3-(1-sila)-butadiene

Corinna Kerst, Martin Byloos, and William J. Leigh

**Abstract:** Laser flash photolysis (193 nm) of 1,1-dimethyl-(1-sila)cyclobut-2-ene in hexane solution leads to the formation of a transient species ( $\tau \sim 1.5 \mu\text{s}$  at 23°C) assigned to 1,1-dimethyl-1,3-(1-sila)butadiene on the basis of its UV absorption spectrum ( $\lambda_{\text{max}} = 312 \text{ nm}$ ), and reactivity toward methanol ( $k_{\text{MeOH}} = (3.6 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_{\text{H}}/k_{\text{D}} = 1.3 \pm 0.1$ ), ethanol ( $k_{\text{EtOH}} = (2.41 \pm 0.06) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), *tert*-butanol ( $k_{\text{BuOH}} = (1.8 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_{\text{H}}/k_{\text{D}} = 1.5 \pm 0.1$ ), and oxygen ( $k_{\text{O}_2} = (3.0 \pm 0.9) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ). Experiments using isooctane and acetonitrile as solvent are also described. In acetonitrile, the lifetime of the silene is shortened considerably compared to hydrocarbon solvents, presumably due to quenching by adventitious water. In isooctane, under conditions of low excitation intensity, the siladiene decays with clean pseudo-first-order kinetics and a maximum lifetime of  $\sim 5 \mu\text{s}$  at 23°C. The decay rate constant varies only slightly with temperature over the 20–60°C range, leading to Arrhenius activation parameters of  $E_a = 0.5 \pm 0.2 \text{ kcal/mol}$  and  $\log A = 5.7 \pm 0.2$ . While steady state irradiation experiments suggest that in the absence of silene traps the predominant fate of the silabutadiene is thermal ring closure to regenerate the precursor, it is concluded that the rate constants and activation parameters for decay of the siladiene measured by flash photolysis represent a composite of those due to thermal electrocyclic ring closure (with  $E_a > \sim 3 \text{ kcal/mol}$ ) and reaction with adventitious quenchers (probably water, with  $E_a < 0$ ). The measured Arrhenius parameters for reaction of the siladiene with methanol in isooctane ( $E_a = -2.6 \pm 0.3 \text{ kcal/mol}$  and  $\log A = 7.6 \pm 0.3$ ) are consistent with this proposal. The potential and limitations of the use of 193-nm laser excitation for flash photolysis studies in solution are discussed.

*Key words:* far-UV, silene, flash photolysis, kinetics, electrocyclic.

**Résumé :** Une photolyse éclair à 193 nm du 1,1-diméthyl-(1-sila)cyclobut-2-ène en solution dans l'hexane conduit à la formation d'une espèce transitoire ( $\tau \sim 1,5 \mu\text{s}$ , à 23°C) qui serait du 1,1-diméthyl-1,3-(1-sila)butadiène si l'on se base sur son spectre d'absorption UV ( $\lambda_{\text{max}} = 312 \text{ nm}$ ) et sa réactivité vis-à-vis du méthanol ( $k_{\text{MeOH}} = (3,6 \pm 0,1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_{\text{H}}/k_{\text{D}} = 1,3 \pm 0,1$ ), de l'éthanol ( $k_{\text{EtOH}} = (2,41 \pm 0,06) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), du *tert*-butanol ( $k_{\text{BuOH}} = (1,8 \pm 0,1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_{\text{H}}/k_{\text{D}} = 1,5 \pm 0,1$ ) et de l'oxygène ( $k_{\text{O}_2} = (3,0 \pm 0,9) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ). On décrit aussi des expériences impliquant de l'isooctane et de l'acétonitrile comme solvants. Dans l'acétonitrile, le temps de vie du silène est beaucoup plus court que dans les solvants hydrocarbonés, probablement à cause d'une désactivation par de l'eau qui s'y trouve par inadvertance. Dans l'isooctane, dans des conditions de faible intensité d'excitation, le siladiène se désagrège selon une cinétique propre de pseudo-premier ordre et un temps de vie maximal d'environ 5  $\mu\text{s}$ , à 23°C. Dans la plage de température allant de 20 à 60°C, la constante de la vitesse de désactivation ne varie que faiblement avec la température; ce qui conduit aux paramètres d'activation d'Arrhenius  $E_a = 0,5 \pm 0,2 \text{ kcal/mol}$  et  $\log A = 5,7 \pm 0,2$ . Même si des expériences d'irradiation en état stationnaire suggèrent que, en l'absence de pièges pour les silènes, le silabutadiène conduit principalement à une cyclisation thermique régénérant le précurseur, on conclut que les constantes de vitesse et les paramètres d'activation pour la décroissance du siladiène mesurés par la photolyse éclair correspondent à une situation mixte entre la cyclisation électrocyclique thermique (avec une  $E_a$  supérieure à environ 3 kcal/mol) et la réaction avec des molécules désactivantes présentes par inadvertance (probablement de l'eau, avec une  $E_a < 0$ ). Les paramètres d'Arrhenius mesurés pour la réaction du siladiène avec le méthanol dans l'isooctane ( $E_a = -2,6 \pm 0,3 \text{ kcal/mol}$  et  $\log A = 7,6 \pm 0,3$ ) sont en accord avec cette hypothèse. On discute des possibilités et des limites de l'utilisation de l'excitation laser à 293 nm pour les études de photolyse éclair en solution.

*Mots clés :* UV lointain, silène, photolyse éclair, cinétique, électrocyclique.

[Traduit par la rédaction]

Received February 14, 1997.

This paper is dedicated to the memory of Sam Sugamori.

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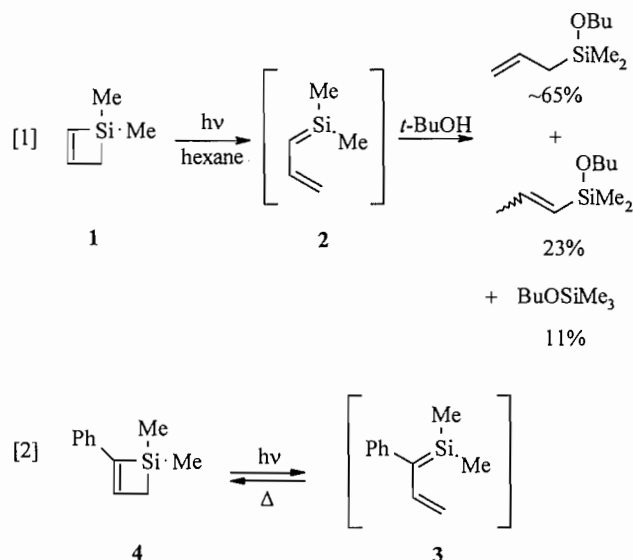
## Introduction

The chemistry of the silicon-carbon double bond has been an area of active interest over the past few decades. While a large number of stable (or at least, persistent) derivatives containing this functionality are known, *silenes* are more frequently encountered as reactive intermediates in various thermal and photochemical reactions of organosilicon compounds (1-4). Most commonly, their intermediacy is inferred from the results of trapping experiments, employing water, alcohols, or alkoxysilanes to trap the silene as the [1,2]-addition product. Numerous bimolecular pericyclic processes are also well known, such as ene-, [2+2]-, and [4+2]-cycloadditions with alkenes, dienes, and carbonyl compounds, and [2+2]-dimerization. Unimolecular pericyclic reactions have been much less extensively investigated.

Nanosecond laser flash photolysis techniques have proven to be extremely useful for the generation and direct detection of reactive silenes in solution (5-8) and, through determination of the effects of solvent, substituent, and temperature effects on absolute reaction rate constants, have allowed study of the mechanisms of several classic silene trapping reactions (9-15). To date, we have employed two general methodologies for the generation of transient silenes for these studies, photoinduced [1,3]-silyl migrations of aryl- (8, 11, 12, 15, 16), alkynyl- (17), and vinyldisilanes,<sup>2</sup> and photoinduced [2+2]-cycloreversion of arylsilylacyclobutanes (10, 13, 14). The UV absorption spectra of these silene precursors extend to at least 260 nm in every case, which allows study of a wide variety of transient silenes using conventional pulsed UV lasers (KrF excimer (248 nm) or Nd/YAG (266 nm)) as excitation sources.

Time-resolved studies of silenes that are most conveniently derived from photolysis of precursors absorbing below ~240 nm have been largely confined to the gas phase, where 193 nm (ArF excimer) laser excitation can be employed (18, 19). In fact, this is true of *all* chemical reaction intermediates derived from precursors absorbing only in the far-UV. The principal reason for this is obvious — most organic solvents absorb significantly at such short wavelengths, either because of their intrinsic absorption characteristics or the presence of absorbing impurities in the commercially available materials. Water is the only solvent that might be identified as readily suitable for such studies and, indeed, the only reports of the use of the ArF laser for solution phase laser flash photolysis studies (to our knowledge) have been carried out in aqueous solution (20, 21). Furthermore, the selection of potential transient quenchers suitable for use with 193 nm excitation is rather limited, since accurate determination of bimolecular rate constants by flash photolysis can only be carried out when the quencher does not absorb significantly at the excitation wavelength (over the concentration range necessary to detect the reaction kinetically). These limitations notwithstanding, our experience with the use of far-UV excitation sources for solution phase *steady state* photochemical studies (22) suggested that, in fact, it might very well be possible — even practical — to employ the ArF laser as an excitation source for flash photolysis experiments in nonaqueous solvents.

In this paper, we report the results of a nanosecond laser flash photolysis study of the chemistry of 1,1-dimethyl-1,3-(1-sila)butadiene (**2**) in hydrocarbon and acetonitrile solutions, using the 193 nm irradiation of 1,1-dimethyl-(1-sila)cyclobut-2-ene (**1**) to generate the silene under conditions where it can be detected directly. The photochemistry of **1** in solution has been reported previously (23), as has its gas phase thermolysis (24, 25). Under both sets of conditions, the formation of **2** as the major product has been demonstrated on the basis of chemical trapping experiments (e.g., eq. [1]). In this paper, we report absolute rate constants for the reaction of **2** with alcohols and oxygen in hexane and acetonitrile solution. An additional goal of this work was to determine rate constants and activation parameters for the thermal electrocyclic ring closure of **2** (which regenerates **1**) in solution at near ambient temperatures, to compare with previously reported data for the corresponding process in 1,1-dimethyl-2-phenyl-1,3-(1-sila)butadiene (**3**; eq. [2]) (7).



## Results and discussion

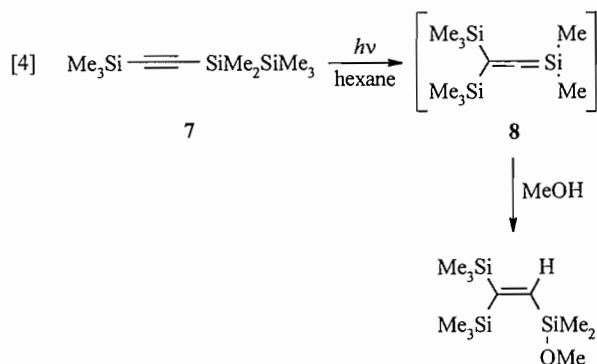
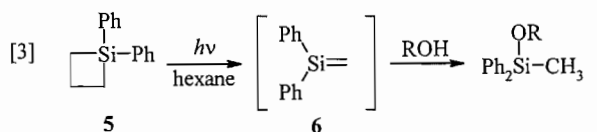
The laser flash photolysis experiments described below employed an ArF excimer laser (193 nm, ~15 ns, ~20 mJ, 1 Hz), a conventional front-face-excitation optical/detection system with nanosecond time resolution (26), and a 3 × 7 mm Suprasil quartz flow cell. Our system requires use of a single mirror to direct the excitation beam at the front face of the sample cell; for 193 nm experiments, the conventional Suprasil mirror that is used for longer wavelength excitation is replaced with a dichroic mirror manufactured specifically for 193 nm light. With a total travel distance of ~2 m through air, the intensity of the beam at the sample was reduced to about 50% of its value at the laser optic. The beam intensity was further reduced as required by use of stainless steel wire meshes as neutral density filters.

Various commercial solvents were examined for their potential suitability for 193-nm experiments. The main requirements are a low static absorbance at the laser wavelength (<0.1 through the path length of the sample cell is satisfactory), and the absence of absorbing transients in the 230-600 nm spectral range when the "pure" solvent is subjected to

<sup>2</sup> W.J. Leigh, C.J. Bradaric, G.W. Slugett, P.C. Venneri, R.T. Conlin, M.S.K. Dhurjati, and M.B. Ezhova. Unpublished results.

193-nm laser excitation. HPLC-grade hexane and isooctane ( $A_{193}^{3\text{-mm}} \sim 0.1$  in both cases) both proved to yield satisfactory results after a single distillation. Acetonitrile was somewhat more problematic; 193-nm laser flash photolysis of an HPLC-grade sample ( $A_{193}^{3\text{-mm}} \sim 0.2$ ) led to the formation of an unidentified transient species that absorbs more or less continuously over the 235–500 nm range and exhibits a lifetime of  $\sim 200$  ns. Several distillations of the solvent from phosphorus pentoxide substantially reduced both the static absorbance at 193-nm ( $A_{193}^{3\text{-mm}} \sim 0.06$ ) and the production of the transient absorption. The  $P_2O_5$ -distilled solvent contains small (ca.  $10^{-2}$  M) amounts of water or other hydroxylic impurities (vide infra). However, further treatment of the solvent by passage through activated alumina (which reduces the water concentration to ca.  $10^{-4}$  M (14)) reintroduced unacceptable levels of absorbing impurities.

A few initial experiments were carried out to establish the general reliability of far-UV laser flash photolysis data, by examining a couple of systems that were previously studied using a (248 nm) KrF excimer laser as the excitation source. For example, far-UV flash photolysis of a continuously deoxygenated hexane solution of 1,1-diphenylsilacyclobutane (**5**;  $3.4 \times 10^{-5}$  M) led to the formation of a transient whose decay characteristics, lifetime, and UV spectrum correspond very closely to those reported previously for 1,1-diphenylsilene (**6**;  $\tau > 5 \mu\text{s}$ ;  $\lambda_{\text{max}} = 325$  nm; see eq. [3]). The silene was quenched by methanol with a rate constant of  $k_q = (2.8 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , in excellent agreement with the value reported previously with 248 nm excitation and solutions of  $\sim 100$ -fold higher precursor concentrations (14). Similarly, a rate constant of  $k_q = (1.3 \pm 0.5) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  was determined for methanol quenching of 1,1-dimethyl-3,3-bis(trimethylsilyl)-1-silaallene (**8**), produced by 193-nm excitation of a deoxygenated hexane solution of (trimethylsilyl)ethynylpentamethyldisilane (**7**;  $6.3 \times 10^{-5}$  M; see eq. [4]). The transient absorption spectrum and quenching rate constant observed in this case are also in excellent agreement with those measured using 248-nm excitation (17).



Excitation of a deoxygenated hexane solution of **1** ( $8 \times 10^{-4}$  M,  $A_{193} \sim 0.6$ ) under similar conditions afforded readily detectable transient absorptions that decayed with mixed first-

and second-order kinetics on the microsecond time scale ( $\tau \sim 1.5 \mu\text{s}$ ). Reduction in the intensity of the excitation source with neutral density filters resulted in a change to clean pseudo-first-order decay kinetics and lengthening of the lifetime of the transient to a maximum of ca.  $5 \mu\text{s}$ . The UV absorption spectrum of the transient, recorded in point-by-point fashion 0.23–0.55  $\mu\text{s}$  after the pulse, is shown in Fig. 1 along with a typical decay trace. Similar results were obtained using distilled isooctane as the solvent.

The lifetime of the transient is shortened upon addition of methanol ( $\epsilon_{193} = (39 \pm 1) \text{ M}^{-1}\text{cm}^{-1}$ ), ethanol ( $\epsilon_{193} = (39 \pm 1) \text{ M}^{-1}\text{cm}^{-1}$ ), *tert*-butanol ( $\epsilon_{193} = (114 \pm 6) \text{ M}^{-1}\text{cm}^{-1}$ ) or oxygen<sup>3</sup> to the solution of **1**. Bimolecular rate constants for quenching of the transient by these compounds were obtained, as usual, from the slopes of plots of the rate constant for transient decay ( $k_{\text{decay}}$ ) versus quencher concentration according to eq. [5]. These were linear in every case; Fig. 2 shows representative plots for quenching by methanol and methanol-*O-d*. Table 1 summarizes the results of these experiments. We assign the structure of the transient observed in these experiments to 1,1-dimethyl-1,3-(1-sila)butadiene (**2**), based on its reactivity toward alcohols and oxygen,<sup>3</sup> and comparison of its UV absorption spectrum ( $\lambda_{\text{max}} = 312$  nm) to those of other transient silenes that have been reported — in particular, to that of 1,1-dimethyl-2-phenyl-1,3-(1-sila)butadiene (**3**) ( $\lambda_{\text{max}} = 338$  nm in cyclohexane), which was reported by Conlin et al. (7). The spectrum of **2** consists of a single, rather sharp, absorption band, which may indicate that the conformational distribution of the molecule lies largely in favour of a single conformer, most likely the *s-trans* (23).

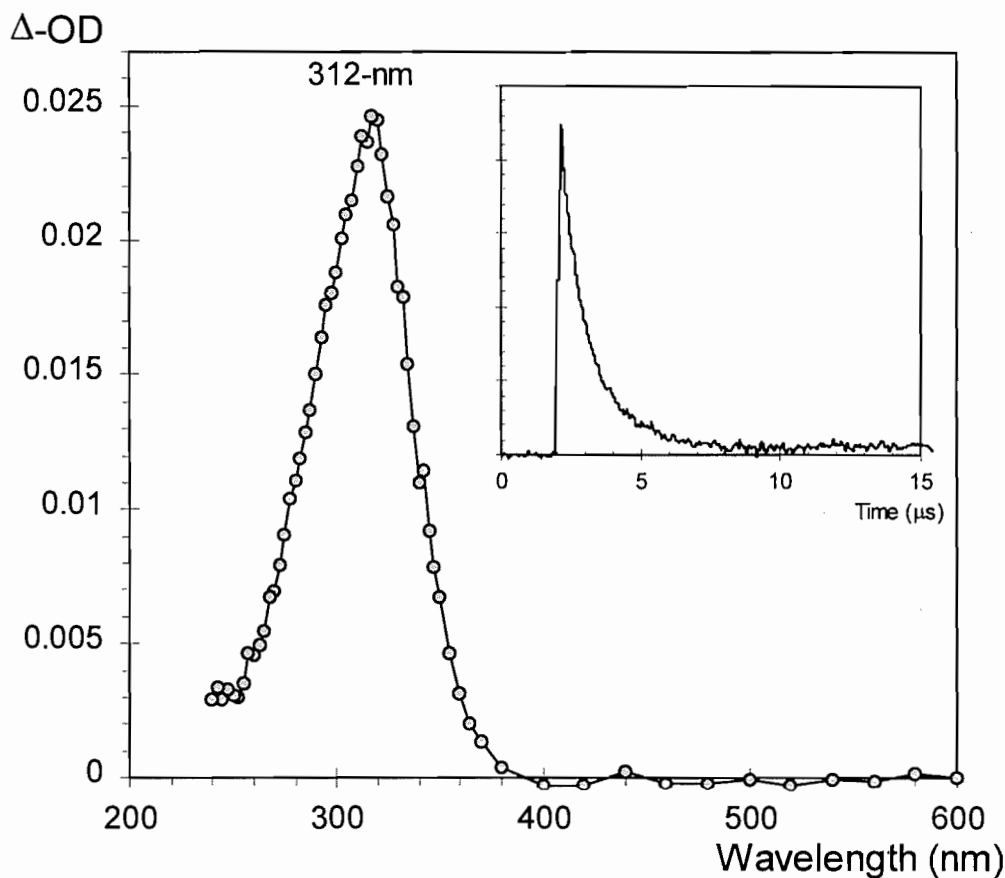
$$[5] \quad k_{\text{decay}} = k_d^0 + k_q[\text{Q}]$$

A solution of **1** (0.001 M) and *tert*-butanol (0.005 M) in hexane was deoxygenated and irradiated with the ArF laser (5 Hz repetition rate) in a  $10 \times 10$  mm Suprasil cuvette with vigorous stirring. GC-MS analysis of the solution after  $\sim 3\%$  conversion of **1** verified the formation of the major product reported by Steinmetz et al., from experiments carried out with a Zn resonance lamp (214 nm) (23). This experiment indicates that the photolysis of **1** with the ArF laser proceeds in the same manner as that with the 214-nm lamp, and supports our assignment of the transient species observed in time-resolved experiments to silene **2**.

Far-UV flash photolysis of a deoxygenated  $8 \times 10^{-4}$  M solution of **1** in  $P_2O_5$ -treated acetonitrile afforded a transient with a similar absorption spectrum to that recorded for **2** in hexane solution, though it is considerably shorter-lived ( $\tau = (120 \pm 8)$  ns). Judging from the magnitude of the rate constant for quenching of **2** by methanol in hexane, the short lifetime of the silene in  $P_2O_5$ -treated acetonitrile can most likely be attributed

<sup>3</sup> **Note added in proof:** Saturation of hydrocarbon solutions of **1** with oxygen results in only small reductions in the initial strength of the transient absorbance due to **2** at 312 nm. However, new transient absorptions centered at  $\sim 250$  nm are also produced, probably through reaction of (directly) excited oxygen with the solvent (30). While the decay rate constant at 250 nm does not appear to depend on the presence of **1**, it is clear that oxygen is not generally appropriate for use as a transient quencher in 193 nm experiments.

**Fig. 1.** Transient UV absorption spectrum from far-UV (193 nm) laser flash photolysis of 1,1-dimethylsilacyclobut-2-ene (**1**;  $8 \times 10^{-4}$  M) in deoxygenated hexane solution at 23°C. The spectrum was recorded in point-by-point fashion, 0.1–0.3  $\mu$ s after the laser pulse. The insert shows a typical decay trace, recorded at a monitoring wavelength of 312 nm.



**Table 1.** Absolute rate constants for quenching of 1,1-dimethyl-1,3-(1-sila)butadiene (**2**) in deoxygenated hexane solution at  $23.0 \pm 0.2^\circ\text{C}$ .<sup>a</sup>

Quencher	MeOH	MeOD	EtOH	<i>t</i> -BuOH	<i>t</i> -BuOD	O <sub>2</sub>
$k_q/10^9 \text{ M}^{-1} \text{ s}^{-1}$	$3.6 \pm 0.1$	$2.8 \pm 0.2$	$2.41 \pm 0.06$	$1.8 \pm 0.1$	$1.24 \pm 0.04$	$0.30 \pm 0.12$

<sup>a</sup>From analysis of  $k_{\text{decay}}$  vs. concentration data according to eq. [5]. Errors are quoted as twice the standard deviation obtained from linear least-squares analysis of these data.

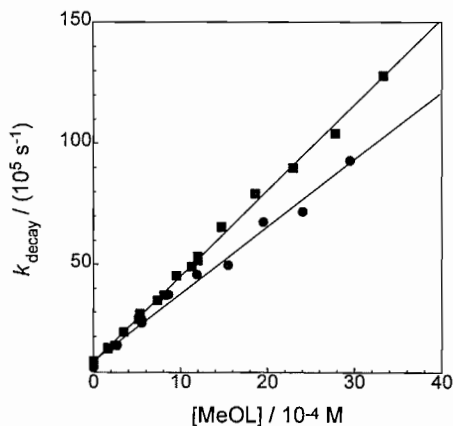
to the presence of small amounts of water or phosphoric acid (27). Because of the short lifetime of the silene in this solvent, determination of bimolecular quenching rate constants could not be carried out with the same level of precision as those determined for hexane solution. Nevertheless, values of  $k_q = (2.4 \pm 0.4) \times 10^9$  and  $(2.8 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for methanol and *tert*-butanol, respectively, were estimated from data recorded over a limited range of alcohol concentrations.

A deoxygenated 0.05 M pentane solution of **1** was irradiated (214 nm) in a merry-go-round apparatus along with a similar solution containing 0.15 M *tert*-butanol, with periodic monitoring of the two solutions by gas chromatography. Over the time period necessary for  $\sim 20\%$  consumption of **1** in the solution containing *tert*-butanol, there was no detectable destruction of **1** in the absence of the silene trap. This experiment

indicates that the predominant fate of siladiene **2** in the absence of silene traps is thermal electrocyclic ring closure to regenerate the silacyclobutene (**1**).

Decay rate constants for **2** were measured as a function of temperature in deoxygenated isooctane solution, using neutral density filters to reduce the laser intensity sufficiently to produce clean pseudo-first-order transient decays, and a lifetime at 23°C of  $\sim 5 \mu\text{s}$ . Interestingly, the decay rate constant varies only slightly with temperature over the 20–60°C range. The Arrhenius plot for the data obtained in isooctane solution is shown in Fig. 3; least-squares analysis of the data affords activation parameters of  $E_a = 0.5 \pm 0.2 \text{ kcal/mol}$  and  $\log A = 5.7 \pm 0.2$ . These values are too small for a thermal electrocyclic ring closure of an acyclic diene system, assuming that the reaction proceeds from the *s-cis* conformer and that the *s-trans*

**Fig. 2.** Plots of  $k_{\text{decay}}$  versus alcohol concentration for quenching of 1,1-dimethyl-1,3-(1-sila)butadiene (**2**) by methanol (■) and methanol-*O-d* (●) in deoxygenated hexane solution at 23°C.



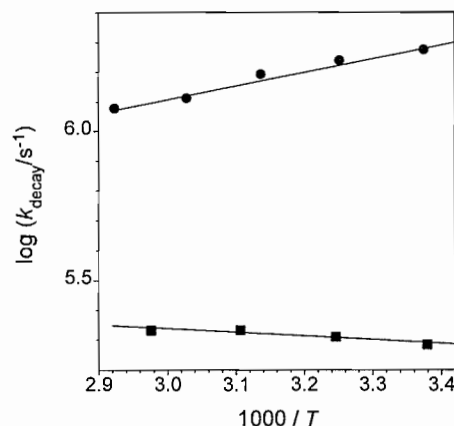
conformer is the thermodynamically favoured one in solution; in such cases, the minimum obtainable value for the activation energy for ring closure will be the difference in enthalpy between the nonreactive *s-trans* and the reactive *s-cis* conformers. AM1 calculations on the individual conformers of **1** predict the *s-trans* conformer to be  $\sim 3$  kcal/mol more stable than the *s-cis*, a result that is consistent with the results of ab initio calculations on the *s-cis* and *s-trans* conformers of 1,3-(1-sila)butadiene (23).

It is most likely that the pseudo-first-order rate constant for the decay of **2** in isooctane solution is at least partially controlled by impurity quenching, the most probable culprit being water. Assuming a quenching rate constant of  $k_q \sim 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , then a concentration of only  $10^{-4} \text{ M}$  water would be required to produce the observed lifetime of  $\sim 5 \mu\text{s}$ . It should be noted that the presence of such small concentrations of reactive impurities would *not* lead to appreciable consumption of **1** in steady state photolysis experiments, since the bulk concentration of **1** that was employed in these experiments was relatively high (0.05 M).

If this explanation is correct, then the unexpectedly low activation parameters for siladiene decay could result from the combination of a positive activation energy for ring closure with a *negative* activation energy for reaction with water. That the latter is reasonable can be inferred from the reported activation parameters for reaction of 1,1-diphenylsilene (**6**) with alcohols (13), which likely proceeds by an identical mechanism to that of the reaction with water (8). The negative  $E_a$  for alcohol addition to **6** has been explained in terms of a two-step mechanism involving reversible, exothermic formation of a silene-alcohol complex followed by rate-limiting proton transfer from oxygen to carbon (13).

This possible explanation was verified indirectly by measuring rate constants for decay of siladiene **2** in deoxygenated isooctane containing  $6 \times 10^{-4} \text{ M}$  methanol as a function of temperature, the results of which are included in Fig. 3. Under these conditions, the concentration of the alcohol is such that at least 90% of the observed pseudo-first-order decay rate constant is due to bimolecular reaction. The activation energy for

**Fig. 3.** Arrhenius plots for the pseudo-first-order decay of **2** in deoxygenated isooctane solution (■) and in deoxygenated isooctane containing  $6 \times 10^{-4} \text{ M}$  methanol (●) over the 20–60°C temperature range, measured by far-UV laser flash photolysis.



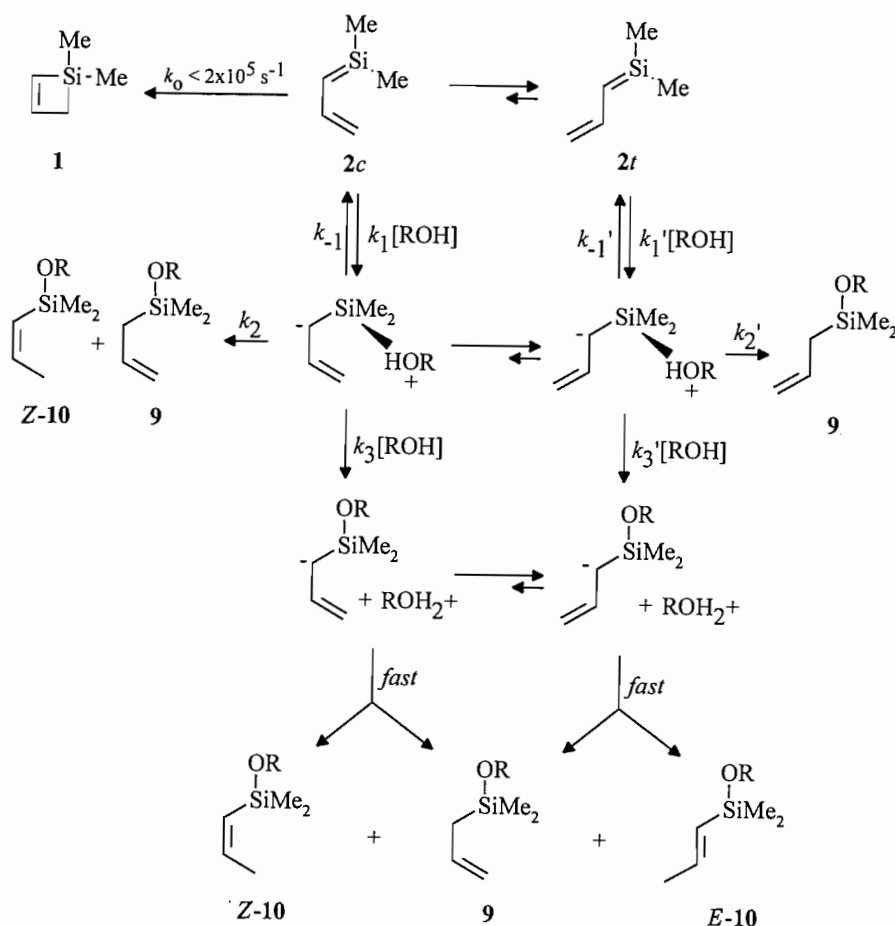
the reaction of **2** with methanol is indeed negative; an Arrhenius plot of the bimolecular quenching rate constants (calculated from the  $k_{\text{decay}}$  values) afford the activation parameters  $E_a = -2.6 \pm 0.3 \text{ kcal/mol}$  and  $\log A = 7.6 \pm 0.3$ .

We conclude that the rapidity with which **2** reacts with trace amounts of hydroxylic impurities precludes a reliable determination of the rate constant for unimolecular reaction of the siladiene in solution, although our data indicate that it is significantly smaller than  $2 \times 10^5 \text{ s}^{-1}$  at near-ambient temperatures. It is relevant to note that a similar rate constant was reported for the decay of the phenyl-substituted analogue (**3**; see eq. [2]) at ambient temperature and attributed to that of electrocyclic ring closure (7). Clearly, the reported Arrhenius parameters for ring closure of **3**, which were estimated from the single rate constant, are not likely to be meaningful.

The reaction of silenes with alcohols is thought to proceed by a mechanism initiated by reversible nucleophilic attack at silicon to yield a zwitterion (or  $\sigma$ -complex), which collapses to product by competing intra- and intermolecular proton transfer, the latter involving a second molecule of alcohol (8, 11, 13, 14, 28). Arrhenius data and kinetic isotope effect studies for the reaction of methanol and *tert*-butanol with 1,1-diphenylsilene indicate that the first step is exothermic and the intramolecular proton-transfer step, though slower than return of the zwitterion to starting materials, proceeds with a low enough activation enthalpy that the overall reaction exhibits a negative activation energy (13). The kinetic and Arrhenius data reported here for the reaction of siladiene **2** with methanol and *tert*-butanol are entirely consistent with this mechanism.

Intermolecular proton transfer from the zwitterion to a second molecule of alcohol competes with the intramolecular process at high alcohol concentrations, and can lead to concentration-dependent product distributions in appropriate cases (11, 14, 28). The intervention of this pathway in the reaction of **2** with *tert*-butanol was deduced by Steinmetz et al., from a careful study of the variation in product distribution with alcohol concentration (23). A detailed mechanism, illustrating the evolution of the various products of reaction of **2** with *tert*-butanol, is shown in Scheme 1. In terms of product

Scheme 1.



formation, the most important aspect of this mechanism is the fact that adduct **E-10** can *only* be formed by a pathway involving two or more molecules of alcohol. Indeed, the yield of **E-10** was found to increase quite significantly with increasing *tert*-butanol concentration (23). This result is also consistent with *s-trans* **2** being the favoured conformer in solution, as is suggested by theoretical calculations as well as the UV spectrum reported in the present work.

## Conclusions

Despite the limited selection of solvents and quenchers that can be employed with 193-nm excitation, the far-UV nanosecond laser flash photolysis technique is clearly of considerable potential utility. It provides a method for studying the chemistry of a number of small, fundamentally important, reactive intermediates in solution, in cases where the most desirable precursor is devoid of absorption in the spectral range accessible with longer wavelength pulsed lasers, or where its absorption spectrum overlaps substantially with that of the reactive intermediate of interest. In the latter cases, the use of 193 nm excitation allows one to employ solutions of substantially lower concentration than are required for longer wavelength excitation, so that the 200–300 nm spectral range is not screened by the precursor, and transient decay pathways involving reaction with the precursor can be minimized. The

ability to employ very low precursor concentrations is also advantageous in cases where it is difficult to obtain the compound in large enough quantities for study by conventional laser flash photolysis techniques. In cases where “kinetic identification” of a transient is required, it must exhibit substantial (i.e.,  $k_q \geq 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) reactivity toward water, aliphatic alcohols, silanes, or other reagents that exhibit low absorptivity at the excitation wavelength. A number of reactive intermediates in organic and organosilicon chemistry satisfy this requirement, and are under investigation in our laboratory.

## Experimental

<sup>1</sup>H NMR spectra were recorded on a Bruker AC200 spectrometer in chloroform-*d* solution. Low-resolution mass spectra were recorded on a Hewlett–Packard 5890II gas chromatograph equipped with an HP-5971A mass selective detector and a DB5 fused silica capillary column (30 m × 0.25 mm; Chromatographic Specialties, Inc.). Ultraviolet absorption spectra were recorded on a Perkin Elmer Lambda 9 spectrometer interfaced to a Pentium™ microcomputer. 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 DB-1 megabore capillary column (15 m × 0.53 mm; Chromatographic Specialties, Inc.).

Semi-preparative gas chromatographic separations were carried out using a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and one of the following two columns (Supelco, Inc.): (a) 20% TCEP on 80/100 Chromosorb PNAW (10 ft  $\times$  4-mm i.d. glass); (b) 3.8% UCW982 on 80/100 Supelcoport (24 ft  $\times$  0.25 in. stainless steel).

Hexane (BDH Omnisolv) and 2,2,4-trimethylpentane (isooctane; BDH Omnisolv) exhibited absorbances of  $<0.2$  at 193 nm in a 3-mm cell, and were distilled once before use. Acetonitrile (Aldrich HPLC) exhibited an absorbance at 193 nm of 0.2 in a 3-mm cell after a single distillation. Purification by reflux over phosphorus pentoxide for several hours followed by distillation (repeating the procedure six times, or until no discolouration of the solvent occurred during the initial reflux period) reduced the absorbance at 193 nm to 0.06 in a 3-mm cell. Methanol, methanol-*O-d*, ethanol, *tert*-butanol, and *tert*-butanol-*O-d* were of the highest purity available and were used as received from Aldrich Chemical Co.

1,1-Dimethyl-(1-sila)cyclobut-2-ene (**1**) was prepared by flash vacuum pyrolysis of dimethyldiallylsilane according to the published method (23, 29). The compound was isolated and obtained in  $>99\%$  purity (as estimated by capillary GC analysis) after sequential semi-preparative gas chromatography on columns (a) and (b). The spectral and analytical data for the compound were in excellent agreement with those reported previously (23, 29).

Analytical-scale photolyses were carried out using a zinc resonance lamp (214 nm; Philips 93106E), with solutions contained in Suprasil quartz cuvettes (10 mm  $\times$  10 mm) and mounted in a merry-go-round apparatus, or the ArF laser (5 Hz repetition rate), with solutions contained in similar cuvettes and clamped  $\sim 2$  m from the light source. In the latter case, the solutions were stirred during irradiation with a small magnetic stirrer. In all cases, the solutions were deoxygenated prior to photolysis with a stream of dry argon, and sealed with rubber septums. In each case, the course of the photolysis was monitored periodically by GC and (or) GC-MS analysis.

Nanosecond laser flash photolysis experiments employed the pulses (193 nm; ca. 15 ns; 20 mJ) from a Lumonics 510 excimer laser filled with F<sub>2</sub>-Ar-He mixtures, and a microcomputer-controlled detection system (26). The laser beam was focussed on the front face of the sample compartment using a single 193-nm dichroic mirror and a Suprasil lens. The total travel distance of the excitation beam is ca. 2 m, which results in a loss of  $\sim 50\%$  in power between the source and the sample compartment; the intensity of the beam was reduced to  $<2$  mJ at the cell using a series of stainless steel wire meshes as neutral density filters. The system incorporates a brass sample holder whose temperature is controlled to within 0.1°C by a VWR 1166 constant temperature circulating bath. Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (193 nm) was ca. 0.7 ( $\sim 8 \times 10^{-4}$  M), and were flowed continuously through a 3  $\times$  7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir. Nitrogen or nitrogen-oxygen mixtures were bubbled continuously through the reservoir throughout the experiments; the composition of the gas was controlled using a Matheson 7351-600 gas proportioner. Solution temperatures were measured with a Teflon-coated copper-constantan thermocouple that was inserted directly into the flow cell. Quenchers were added directly to the reservoir by microlitre syringe as aliquots of

standard solutions. Rate constants were calculated by linear least-squares analysis of decay rate – concentration data (six or more points) which spanned at least one order of magnitude in the transient decay rate. Errors are quoted as twice the standard deviation obtained from the least-squares analysis in each case.

## Acknowledgments

We wish to thank the Natural Sciences and Engineering Research Council of Canada for financial support, the Max-Planck-Gesellschaft zur Förderung der Wissenschaften and the Deutsche Forschungsgemeinschaft for fellowships to C.K., and the Reactive Intermediates Student Exchange (RISE) for a summer scholarship to M.B.

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