

## The photochemistry of a potential diphenylsilylene precursor. Time-resolved spectroscopic studies of the reactivity of a transient vinylsilirane

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### Abstract

The photochemistry of 3,4-dimethyl-1,1-diphenylsilacyclopent-3-ene (**2**), a potential precursor to diphenylsilylene ( $\text{SiPh}_2$ ), has been studied in hydrocarbon and methanol solution by steady state and laser flash photolysis techniques. The results are consistent with the formation of three major photoproducts:  $\text{SiPh}_2$  (ca. 20%), 2,3-dimethyl-1,3-butadiene (DMB; ca. 20%), and 2-methyl-2-(1-methylethenyl)-1,1-diphenylsilirane (**9**; ca. 75%), the product of formal photochemical (1,3)-sigmatropic rearrangement of **2**. Attempts to detect the silylene by laser flash photolysis were unsuccessful, but the vinylsilirane could be easily detected as a long-lived transient exhibiting  $\lambda_{\text{max}} = 285 \text{ nm}$  and lifetime  $\tau = 1.3 \text{ s}$  in hexane at  $25^\circ\text{C}$ . The same spectrum is observed in neat methanol solution, where the lifetime of the species is shortened to  $\tau = 36 \text{ ms}$  and it is quenched by sodium methoxide and methanesulfonic acid with absolute rate constants of  $k_{\text{MeO}^-} = 2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{\text{H}^+} = 2.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. The photochemistry of **2** is compared to that of the corresponding germanium homologue (**1**), whose photolysis in solution has been previously shown to afford diphenylgermylene and DMB cleanly and in high yields. The corresponding vinylgermirane (**11a**), though not detectable as a primary photoproduct from **1** in solution, is the exclusive product of photolysis of **1** in a 3-methylpentane glass at  $78 \text{ K}$ , where it exhibits an essentially identical UV/vis spectrum to that of **9**. The rate constant for its unimolecular thermal isomerization to regenerate **1** is three orders of magnitude larger than that of the corresponding process in the homologous vinylsilirane (**9**) in hydrocarbon solution at  $25^\circ\text{C}$ .

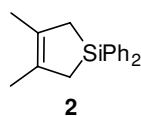
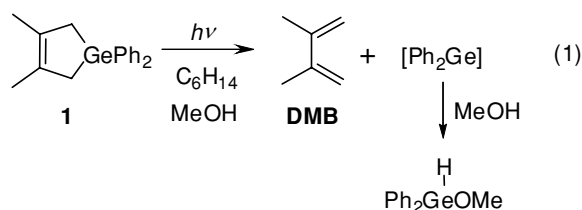
### Introduction

The chemistry of silylenes, the silicon analogues of carbenes, has been of great interest for more than 30 years [1–4]. In spite of this, relatively few quantitative data exist on the reactivity of simple transient derivatives in solution. The chemistry of the parent molecule,  $\text{SiH}_2$ , has been extensively characterized in the gas phase, chiefly by Walsh and his group [5], who have also carried out similar studies of  $\text{SiMe}_2$  [6–8]. The latter silylene has been studied in detail in solution by Das and Shizuka and their coworkers, who measured absolute rate constants for reaction of the species in cyclohexane solution with alcohols, ethers, alkenes, alkynes,  $\text{O}_2$ , trialkylsilanes, and tri-*n*-butylstannane and examined its

complexation with ethers, amines, and acetonitrile [9–12]. A time-resolved study of the reactivity of dimethylsilylene in hydrocarbon solvents has also been reported [13]. Flash photolysis studies of the reactivity of methylphenyl- and diphenylsilylene ( $\text{SiMePh}$  and  $\text{SiPh}_2$ , respectively) in solution had been reported somewhat earlier by Gaspar and coworkers [14–16], but several of the reported rate constants are so significantly different from those determined later for  $\text{SiMe}_2$  and  $\text{SiMe}_2$  with similar substrates that the basic assignments must be considered questionable [1]. The only comprehensive study of the UV-vis absorption spectra of transient aryl- and alkylsilylenes is that of Michalczyk et al., who reported the spectra of 22 simple silylenes in hydrocarbon matrices at  $77 \text{ K}$  [17]. The

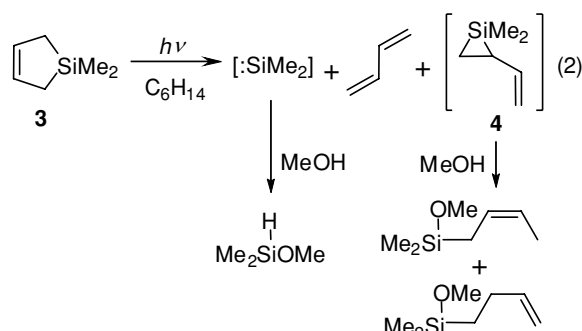
arylsilylenes studied in that work were all generated by photolysis of aryltrisilanes, analogous to the precursors employed by Gaspar and coworkers in their studies of SiMePh and SiPh<sub>2</sub> [14–16]. In fluid solution, compounds of this type are known to afford significant amounts of transient silenes, derived from 1,3-SiMe<sub>3</sub> migration into the ortho-position of a phenyl ring, in addition to the corresponding silylene [18–20]. Since silenes of this type generally absorb quite strongly in the same region as do arylalkyl- and diarylsilylenes [21], which should be quite weak absorbers [22], it is clear that an entirely different methodology is desirable for the generation of these fundamentally important reactive intermediates for study by time-resolved UV-vis spectroscopic methods in solution.

Recently, we reported the results of a study of the photochemistry of 3,4-dimethyl-1,1-diphenylgermacyclopent-3-ene (**1**) in hexane solution by steady state and laser flash photolysis methods (Equation (1)) [23]. Photolysis of the molecule proceeds very cleanly and with remarkably high efficiency ( $\Phi \sim 0.55$ ), producing 2,3-dimethyl-1,3-butadiene (DMB) and the expected trapping products of diphenylgermylene as the only detectable photolysis products under steady state conditions. The germylene proved to be readily detectable in laser flash photolysis experiments with **1** in hexane solution, allowing its reactivity toward a wide variety of reagents to be characterized in detail [24]. It occurred to us that the corresponding silicon compound (**2**) might prove to be similarly effective as a precursor to diphenylsilylene, for study in solution by laser flash photolysis techniques.



Two solution phase studies have been reported on the photochemistry of 1-silacyclopent-3-ene

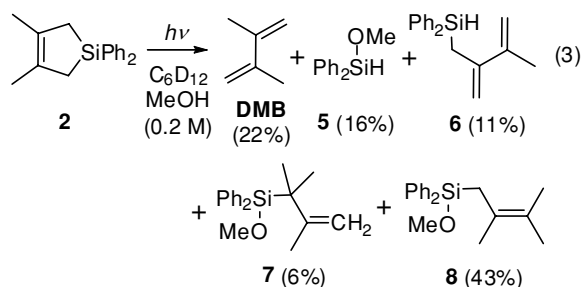
derivatives [25, 26]. Steinmetz and Yu reported that photolysis of 1,1-dimethylsilacyclopent-3-ene (**3**) in methanol (MeOH) or MeOH-hydrocarbon mixtures affords the OH insertion product of SiMe<sub>2</sub> in high yield, along with a mixture of products (in similar combined yield to the SiMe<sub>2</sub> adduct) assigned to reaction of MeOH with 1,1-dimethyl-2-vinylsilirane (**4**), the product of formal excited state (1,3)-sigmatropic rearrangement of the silacyclopent-3-ene (Equation (2)) [25]. They concluded that SiMe<sub>2</sub> was the major primary photoproduct, with a significant portion of the vinylsilirane that is also produced arising from a rapid cage reaction between the silylene and the diene co-product. More recently, Jiang and Gaspar showed that photolysis of a 1,1-bis(trialkylsilyl)silacyclopent-3-ene derivative in solution affords trapping products consistent with the formation of the corresponding bis(trialkyl)silylene as the major photoproduct [26]. These results seemed sufficiently encouraging that we decided to pursue a study of the photochemistry of the potential diphenylsilylene precursor, 3,4-dimethyl-1,1-diphenylsilacyclopent-3-ene (**2**) by steady state and laser flash photolysis methods, the results of which are reported in this paper.



## Results and discussion

Steady state photolysis of a deoxygenated 0.021 M solution of **2** in cyclohexane-*d*<sub>12</sub> containing MeOH (0.2 M) was carried out using low pressure mercury lamps (254 nm), with periodic monitoring of the photolysates by <sup>1</sup>H NMR spectroscopy. Photolysis resulted in the formation of the five major products shown in Equation (3). Methoxydiphenylsilane (**5**) was

identified by spiking the mixture with an authentic sample, while **6** and the methoxysilanes **7** and **8** were identified on the basis of their NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$ ), infrared, and mass spectra after chromatographic isolation from larger scale photolyses in hexane and methanol solution, respectively. The product yields shown in Equation (3) were determined relative to consumed **2**, from the initial slopes of concentration vs. time plots constructed for **2**, DMB, and **5–8** between 0 and ca. 40% conversion; the material balance was estimated to be ca. 85%. The quantum yield for consumption of **2** under these conditions was determined to be  $\Phi_{-2} = 0.31 \pm 0.05$  by 1,1-diphenylsilacyclobutane actinometry (see Experimental Section).

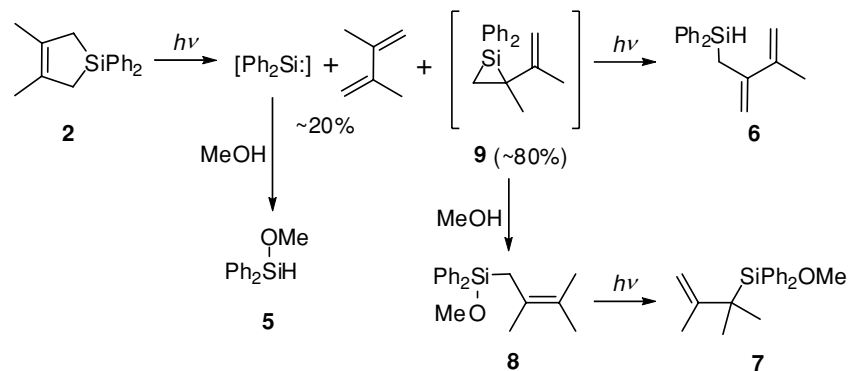


$^1\text{H}$  NMR spectra of the product mixture from photolysis of **2** as a 0.028 M solution in cyclohexane- $d_{12}$ , with no added MeOH, revealed the formation of DMB and **6** in roughly equal yields, along with substantial amounts of polymeric material that gave rise to a broad featureless resonance in the  $\delta$  7–8 region of the spectrum. The rate of consumption of **2** was approximately 35% lower than that in a parallel photolysis of a second solution of **2** (0.028 M) containing 0.11 M MeOH. The product distribution obtained under the latter conditions was considerably different than that obtained in the presence of 0.2 M alcohol; DMB, **5**, and **6** were formed in approximately the same yields, but the yields of **7** and **8** decreased to 2 and 12%, respectively. Compound **6** could not be detected at all in the product mixture from photolysis of **2** in neat methanol- $d_4$  solution, where the combined yield of **7** and **8** (as the  $d_4$  isotopomers) was 72% and DMB was present in 18% yield after 25% conversion of **2**. The yield of **7** rapidly increased at the expense of **8** with increasing photolysis

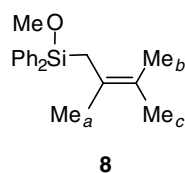
time under all three sets of conditions. Plots of the relative yields of the two products versus photolysis time showed quite clearly that the yield of **7** extrapolates to zero at zero% conversion, indicating that **7** is formed mainly via secondary photorearrangement of **8**. The two products were present in roughly equal amounts after photolysis to ca. 85% conversion of **2** in methanol- $d_4$  solution.

The results of these experiments are in close correspondence with those reported by Steinmetz and Yu for the 214 nm photolysis of the related silacyclopent-3-ene derivative **1** [25], as well as with previous studies of the reactions of transient silylenes with DMB and other dienes under photochemical conditions [18, 27–29]. The results are consistent with the formation of DMB,  $\text{SiPh}_2$ , and vinylsilirane **9** as the exclusive primary products of photolysis of **2**, as detailed in Scheme 1. In the presence of low ( $\leq 0.2\text{ M}$ ) concentrations of MeOH, **9** undergoes competing secondary photoisomerization to **6** and reaction with the alcohol to yield **8**, which then undergoes secondary photoisomerization to **7** via (1,3)-migration of the methoxydiphenylsilyl group [30, 31]. As expected, the yields of **7** and **8** increase relative to **6** with increasing MeOH concentration, consistent with competitive trapping and photoisomerization of **9**. As has been shown to be the case with other 2-methyl-2-vinylsilirane derivatives [18, 27, 28], **9** appears to react with methanol mainly via (1,4)-addition, yielding **8**. While we note that **7** is the formal product of (1,2)-addition of MeOH across the Si– $\text{C}_3$  bond in **9**, the variation in its yield relative to **8** with photolysis time indicates that very little, if any, of the compound is formed by this route. Furthermore, we could find no evidence for the formation of the other possible (1,2)-adduct (from addition of MeOH across the Si– $\text{C}_2$  bond in **9**), even at relatively high conversions of **2** [32]. The formation of hydrogen-migration products analogous to **6** has ample precedent in previous studies of the addition of arylsilylenes to DMB under photochemical conditions [18, 27–29], and has been shown to arise (along with the isomeric silacyclopent-3-ene derivative) via photoisomerization of the corresponding vinylsilirane, the main primary product of addition of silylenes to conjugated dienes [18]. Indeed, **2** and **6** are known to be the major products of photolysis of 1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisilane in a 4.0 M solution of DMB in hexane, and both were attributed to secondary reactions of vinylsilirane **9** [29].

Scheme 1.



Compounds **7** and **8** were isolated by a combination of column and semi-preparative gas chromatography from a larger scale photolysis in neat MeOH solution, and identified on the basis of their NMR, infrared, and mass spectra. The 600 MHz  $^1\text{H}$  NMR spectrum of **8** shows a two-proton singlet at  $\delta$  2.14, a three-proton singlet at  $\delta$  3.53 due to the methoxy protons, and three-proton singlets at  $\delta$  1.35, 1.56, and 1.58 that were assigned to the vinylic methyl groups  $\text{Me}_b$ ,  $\text{Me}_c$ , and  $\text{Me}_a$ , respectively, with the aid of  $^1\text{H}$  NOE experiments. Inspection of the NMR spectra obtained from the



photolysis of **2** in methanol- $d_4$  solution (*vide supra*) showed clear evidence of deuterium incorporation in the  $\text{Me}_b$  and  $\text{Me}_c$  groups in **8** and in the *gem*-dimethyl groups of compound **7**, by the presence of broad singlets that appeared at ca. 0.04 ppm lower frequency than the sharp singlets due to the corresponding fully protiated methyls; these are clearly assignable to  $\text{CH}_2\text{D}$  resonances. This was the major component of the  $\text{Me}_b$  resonance in the earliest stages of photolysis, and decreased in intensity relative to the sharp  $\text{CH}_3$  singlet as photolysis was continued. The opposite effect was noted for the relative intensities of the  $\text{CH}_2\text{D}$  and  $\text{CH}_3$  resonances associated with the  $\text{Me}_c$  group, indicating

that the  $\text{Me}_b$  and  $\text{Me}_c$  groups in **8** undergo photochemical exchange. At 85% conversion of **2**, the ratio of the intensities of the  $\text{CH}_2\text{D}$  resonances associated with  $\text{Me}_b$  and  $\text{Me}_c$  was ca. 2:1. The scrambling of deuterium between  $\text{Me}_b$  and  $\text{Me}_c$  can be attributed to *E,Z*-photoisomerization about the  $\text{C}=\text{C}$  bond in **8**; the initial rate of the scrambling process was approximately half that of the formation of the (1,3)-migration product **7**, for which the relative intensities of the  $\text{CH}_2\text{D}$  and  $\text{CH}_3$  components of the *gem*-dimethyl resonance remained constant as a function of photolysis time. We can thus conclude that the excited singlet state of **8** decays by competing torsional relaxation about the  $\text{C}=\text{C}$  bond and (1,3)-methoxydiphenylsilyl migration (producing **7**), with the two deactivation pathways contributing in nearly equal amounts.

We next carried out laser flash photolysis experiments, employing the pulses from a KrF excimer laser (248 nm, ca 100 mJ, 20–25 ns) for excitation and a flow system to replenish the solutions of **2** between laser pulses. Laser photolysis of a deoxygenated 0.004 M solution of **2** in anhydrous hexane gave rise to a very long-lived absorption centered at  $\lambda_{\text{max}} = 285$  nm that decayed to approximately half of its initial intensity over 0.9 s, the maximum time-window that can be monitored with our system. The decay was fit to first order kinetics, affording an estimate of  $\tau \sim 1.3$  s for the lifetime of the species under these conditions. A careful search of the transient spectrum within the first 0.05–2  $\mu\text{s}$  after the laser pulse revealed no short-lived transient absorptions over the 280–650 nm spectral range. The ca. 1.3 s lifetime of the species absorbing at 285 nm was confirmed by laser photolysis of a static deoxygenated hexane solution

of **2** in a conventional UV-vis spectrophotometer, where the decay of the species could be monitored over a longer time scale. This experiment also confirmed that the decay of the species proceeds with clean first-order kinetics.

The same species was observed upon laser photolysis of **2** in deoxygenated MeOH solution, where its lifetime is reduced to  $\tau = 36$  ms. Figure 1 shows a representative transient spectrum and decay trace obtained in the experiments in MeOH solution. The significantly reduced lifetime of the species in the neat alcohol is consistent with bimolecular reaction with the solvent, for which the lifetime affords an estimate of  $k_{\text{MeOH}} \sim 1.4 \text{ M}^{-1} \text{ s}^{-1}$  for the absolute rate constant, assuming the reaction is first order in alcohol under these conditions.

We assign the species observed in these experiments to vinylsilirane **9**, the major primary product of photolysis of **2** according to the steady state experiments described above. This is the only transient product that could be detected upon laser photolysis of **2**; in particular, we could not detect signs of a short-lived transient absorbing in the 500 nm region, where  $\text{SiPh}_2$  is known to absorb [17]. Our failure to detect transient absorptions assignable to  $\text{SiPh}_2$  is not unexpected, given that the quantum yield for formation of the silylene from **2** is on the order of only  $\Phi_{\text{SiPh}_2} \sim 0.06$ , as estimated from the quantum yield for total consumption

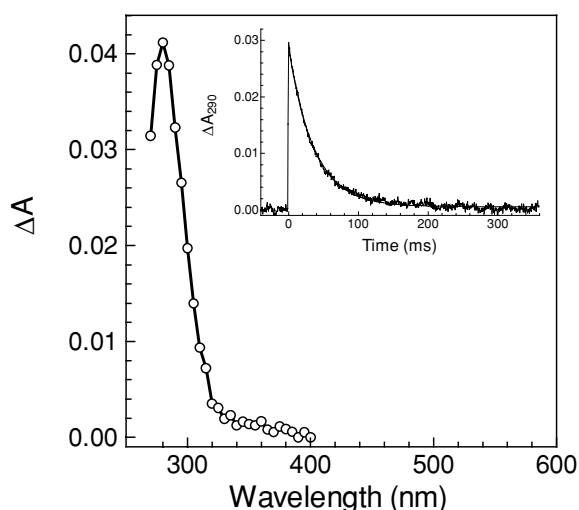
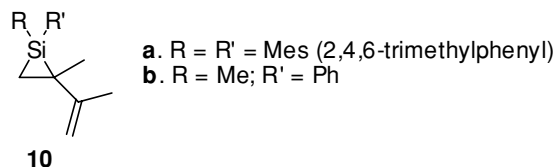


Figure 1. Time-resolved UV absorption spectrum from laser flash photolysis of a flowed, deoxygenated 0.004 M solution of **2** in methanol at 25 °C, recorded 0.31–0.33 ms after the laser pulse. The inset shows a typical decay trace recorded at a monitoring wavelength of 285 nm.

of **2** ( $\Phi_{-2} = 0.31$ ) and the chemical yields of DMB and **5** obtained in steady state photolysis experiments. Given the typical laser intensities used in our experiments and assuming that the extinction coefficient of  $\text{SiPh}_2$  at its absorption maximum is similar to that of  $\text{GePh}_2$  ( $\epsilon_{\text{max}} = 1850 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  [23]), this would result in an expected maximum transient absorbance of ca. 0.002, which would be barely distinguishable from noise under the conditions of our experiments.

The ca. 1.3 s lifetime determined for **9** in hexane is clearly long enough for it to build up in significant steady state concentrations under the conditions of our product studies, thus rendering it susceptible to secondary photolysis. We tentatively attribute the first order decay of the species to its thermal isomerization to **2**, accounting to some extent for the significantly lower efficiency with which **2** is consumed during its photolysis in cyclohexane- $d_{12}$  compared to that in the presence of MeOH under otherwise identical conditions (*vide supra*). This most likely represents only a portion of the decreased efficiency of the photolysis of **2** in the absence of MeOH, as Ishikawa and coworkers have shown that the vinylsilirane-silacyclopent-3-ene isomerization is also photochemically induced [18]. The lifetime of **9** under these conditions contrasts sharply with that of the 1,1-dimesityl derivative (**10a**), which has been shown by Zhang and Conlin to be stable for months under ambient conditions [33]. A more interesting comparison is with the 1-methyl-1-phenyl derivative **10b**; a quantitative estimate of its lifetime is not available, but the experimental protocol described by Ishikawa et al. in their successful trapping of the species with MeOH indicate that it must be at least an order of magnitude longer-lived than **9** in hydrocarbon solution at room temperature [18].



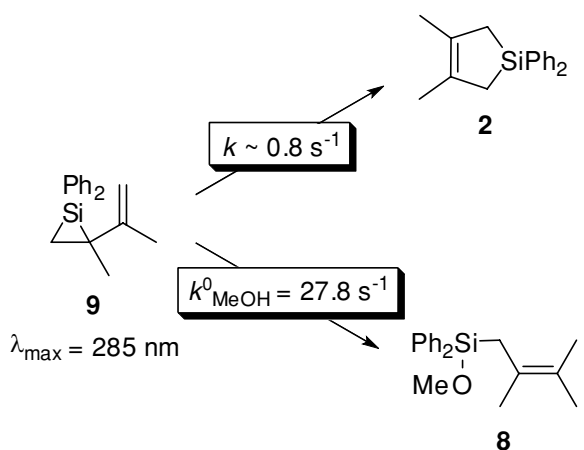
As might be expected, the lifetime of vinylsilirane **9** in MeOH is reduced substantially in the presence of added base or acid. Addition of sodium methoxide or methanesulfonic acid to methanol solutions of **2** resulted in enhancements of the pseudo-first order rate constant for decay of **9** ( $k_{\text{decay}}$ ) that varied linearly

according to Equation (4), where  $k_0$  is the  $k_{\text{decay}}$  value in pure MeOH solution and  $k_Q$  is the absolute second-order rate constant for reaction of the species with the added reagent ('Q'). Figure 2 shows the plot of  $k_{\text{decay}}$  vs. methoxide ion concentration that resulted from this experiment, from which was obtained a value of  $k_{\text{MeO}^-} = (2.0 \pm 0.1) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for the absolute rate constant. Quenching by added acid is much slower; a similar treatment of the variation in the decay rate constant of **9** in the presence of 0.02–0.6 M methanesulfonic acid afforded a rate constant of  $k_{\text{H}^+} = (2.6 \pm 0.3) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ .

$$k_{\text{decay}} = k_0 + k_Q[Q] \quad (4)$$

Scheme 2 summarizes the reactivity of vinylsilirane **9** in hydrocarbon and methanol solution at 25 °C, based on the results of the kinetic experiments described above.

Scheme 2.



$$k_{\text{MeOH}} / \text{s}^{-1} = k_{\text{MeOH}}^0 + k_{\text{MeO}^-}[\text{MeO}^-] + k_{\text{H}^+}[\text{H}^+]$$

$$k_{\text{MeO}^-} = 2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}; k_{\text{H}^+} = 2.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

The photochemical behavior of **2** contrasts sharply with that of the germanium homologue (**1**), whose photolysis yields  $\text{GePh}_2$  and DMB cleanly and with a quantum yield  $\Phi = 0.55$  under similar conditions (Equation (1)) [23]. It is difficult to determine with certainty whether or not the corresponding vinylgermirane (**11a**) is also formed in the photolysis of **1** in fluid solution; while no evidence for its formation could be obtained from steady state trapping studies, our subse-

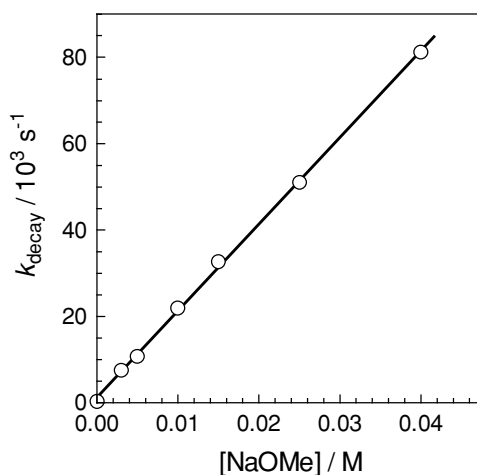
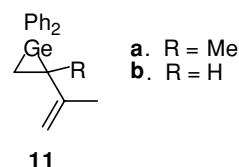


Figure 2. Plot of the pseudo-first order rate constant for decay of vinylsilirane **9** ( $k_{\text{decay}}$ ) vs. the concentration of added NaOMe in methanol at 25 °C.

quent studies of the reactions of  $\text{GePh}_2$  and  $\text{GeMePh}$  with isoprene and DMB [24, 34] show that if it were formed as a primary photochemical product, it would dissociate to  $\text{GePh}_2$  and DMB too rapidly for it to be trapped efficiently under typical experimental conditions [35]. Nevertheless, a closely related species could be detected by flash photolysis of **1** in the presence of 3–50 mM isoprene [24]. The UV/vis absorption spectrum of the species, which was assigned to vinylgermirane **11b**, is nearly identical to that of **9**, as might be expected. It exhibits a lifetime  $\tau \sim 500 \mu\text{s}$  in the presence of 50 mM added diene, which was proposed to reflect the rate of (thermal) isomerization to the isomeric germacyclopent-3-ene derivative [24], the ultimate product of the reaction of  $\text{GePh}_2$  with isoprene [23, 36, 37].



A species assignable to vinylgermirane **11a** can be detected as a product of photolysis of **1**, provided that the photolysis is carried out under conditions where the compound is rendered incapable of dissociation to free germylene and diene, such as in a rigid matrix at low temperatures. For example, Figure 3 shows a static UV/vis difference spectrum recorded from a solution of

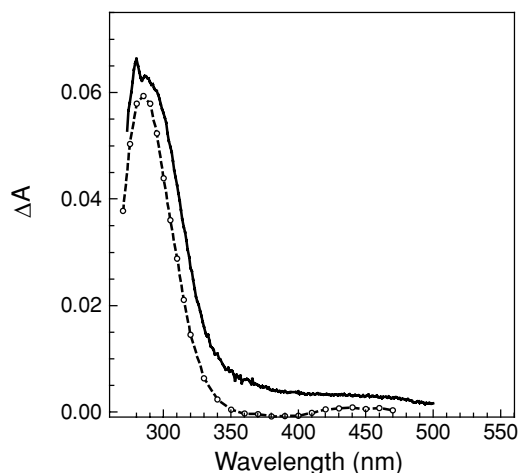


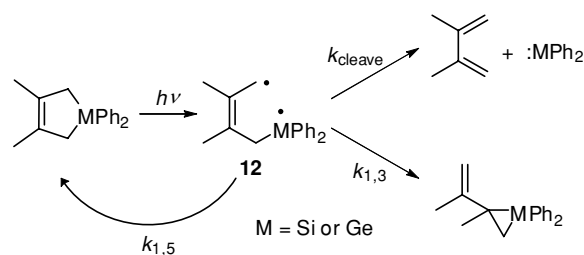
Figure 3. UV/vis absorption spectra of vinylgermiranes **11a** (—) and **11b** (---). That shown for **11a** is the difference spectrum obtained from a solution of **1** in a 3-methylpentane (MP) glass at 78 K, before and after brief irradiation with 254 nm light, while that of **11b** is the transient absorption spectrum recorded at 25 °C by flash photolysis of **1** in hexane containing 50 mM isoprene. The latter spectrum was reprinted with permission from [24]; copyright 2005 American Chemical Society.

**1** in a 3-methylpentane (MP) glass at 78 K after brief irradiation with 254 nm light. It is not clear whether the species is formed under these conditions via direct photorearrangement of **1** or via back reaction of  $\text{GePh}_2$  with the diene co-product in the rigid solvent cage; nevertheless, its spectrum is essentially identical to that of the transient product (**11b**) obtained by laser flash photolysis of **1** in solution in the presence of isoprene [24], which is also shown in the figure. No absorptions assignable to free  $\text{GePh}_2$  could be detected in the low temperature experiment, in contrast to the situation in fluid solution at ambient temperatures. As expected, warming the matrix to the softening point resulted in the rapid disappearance of the absorption. Photolysis of **2** in a MP glass under similar conditions to those above also resulted in the formation of new absorptions at wavelengths between ca. 270 and 300 nm, but they appeared as an edge absorption on that due to the precursor and did not exhibit the same distinctive, well-defined absorption band as was observed from **2** in laser flash photolysis experiments (*vide supra*). We suspect that the spectrum due to **9** is obscured in this experiment owing to secondary photolysis, as significant new absorptions were also produced in the 254 nm region of the spectrum. This was not the case in the matrix photolysis of **1**.

The differences in the photochemical behavior of **1** and **2** in solution can be understood on the basis

of a mechanistic model in which the primary photochemical process for both molecules is cleavage of the  $\text{M}-\text{C}_{2(5)}$  bond to yield the corresponding (singlet) 1,5-biradicals, **12**, as shown in Scheme 3. Once formed, these species can be expected to undergo competing cleavage of the second  $\text{M}-\text{C}$  bond and ring-closure, to yield the free metallylene, vinylmetallirane and original metallacyclopent-3-ene derivative with the individual rate constants  $k_{\text{cleave}}$ ,  $k_{1,3}$ , and  $k_{1,5}$ , respectively. The much higher yield of cleavage products obtained when  $\text{M} = \text{Ge}$  can then be understood as the result of a much larger value of  $k_{\text{cleave}}$  for the germanium-centered biradical compared to that for the silicon-centered one, as expected on the basis of the higher divalent state stabilization energies of germylenes compared to silylenes [38, 39]; this is equivalent to stating that the  $\text{C}-\text{Ge}$  bond in **12** ( $\text{M} = \text{Ge}$ ) is weaker than the  $\text{C}-\text{Si}$  bond in **12** ( $\text{M} = \text{Si}$ ). An alternate mechanism involving competing  $\text{MPH}_2$  extrusion and rearrangement directly from the excited states of **1** and **2**, without the intermediacy of biradical **12**, cannot be ruled out, however.

Scheme 3.



## Summary and conclusions

The results of this work indicate that 1-silacyclopent-3-ene derivatives will likely not show the same general suitability as their germanium [23, 24, 34, 40] and tin [41] homologues as photochemical precursors to reactive metallylenes for study by time-resolved UV/vis absorption methods in solution. Nevertheless, they clearly show considerable potential as precursors for more detailed kinetic studies of the chemistry of reactive vinylsiliranes, the key primary intermediates in the reaction of silylenes with conjugated dienes [18, 27, 28, 42–44].

The present work provides the first quantitative study of the reactivity of a vinylsilirane derivative in solution, detailing the kinetics of its bimolecular reaction

with methanol under neutral, basic, and acidic conditions and of its thermal decomposition at ambient temperatures, presumably via rearrangement to the stable 1-silacyclopent-3-ene isomer. The latter proceeds ca. 2,000 times more slowly than does the corresponding reaction of the germanium homologue of otherwise identical structure.

## Experimental

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra were recorded on Bruker AV200, DRX500 or AV600 spectrometers in deuteriochloroform solution unless otherwise noted;  $^1\text{H}$  and  $^{13}\text{C}$  spectra were referenced to the residual solvent proton and  $^{13}\text{C}$  signals, respectively.  $^{29}\text{Si}$  resonances were obtained via  $^1\text{H}$ – $^{29}\text{Si}$  HMBC NMR spectroscopy using  $\text{SiMe}_4$  as reference. Low and high resolution mass spectra were obtained with a Micromass TofSpec 2E mass spectrometer using electron impact ionization (70 eV). Infrared spectra were recorded as thin-films on sodium chloride plates using a Bio-Rad FTS-40 FTIR spectrometer. Semi-preparative gas chromatographic (GC) separations employed a Varian 3330 gas chromatograph equipped with a 0.25 in.  $\times$  6 ft. stainless steel column (3% OV-17 on 80/100 Chromosorb W HP; Supelco, Inc.). Analytical GC separations employed a Hewlett-Packard 5890 Series II gas chromatograph equipped with a HP3396A integrator, a flame ionization detector and a DB-5 column (30 m, 0.25  $\mu\text{m}$ ; Chromatographic Specialties, Inc.), or a Varian Saturn 2200 GC/MS/MS system equipped with a VF-5ms capillary column (30 m  $\times$  0.25 mm; 0.25  $\mu\text{m}$ ; Varian, Inc.). Steady state photolyses were carried out in a Rayonet<sup>®</sup> photochemical reactor (Southern New England Ultraviolet Co.) equipped with a merry-go-round and 2-6 RPR-2537 lamps (254 nm). Melting points were determined using a Mettler FP82 hot stage mounted on a polarizing microscope and are uncorrected. Low temperature UV/vis spectrophotometry employed 2 cm  $\times$  1 cm  $\times$  1 cm cuvettes constructed from Suprasil quartz tubing (Vitro Dynamics, Inc.) and an Oxford Optistat<sup>™</sup> liquid nitrogen cryostat equipped with an Oxford ITC601 temperature controller.

Hexanes (EMD OmniSolv), diethyl ether (Caledon Reagent) and tetrahydrofuran (Caledon Reagent) were dried by passage through activated alumina under nitrogen using a Solv-Tek solvent drying system (Solv-Tek, Inc.). Trichlorosilane (Gelest), diphenylchlorosilane (Gelest), 2,3-dimethyl-1,3-butadiene (Aldrich), magnesium (Fisher Scientific),

methanol (Sigma-Aldrich Spectroscopic grade), methanesulfonic acid (Sigma-Aldrich), and bromobenzene (Sigma-Aldrich) were used as received from the suppliers. Deuterated solvents were used as received from Cambridge Isotope Laboratories. 1,1-Dichloro-3,4-dimethylsilacyclopent-3-ene was synthesized according to the method of Kang et al. [45].

### *Synthesis of methoxydiphenylsilane (5)*

Diphenylchlorosilane (0.50 g, 2.2 mmol) was dissolved in THF (10 mL) and a solution of sodium methoxide (prepared from 0.05 g sodium (2.2 mmol) and 1 mL methanol) was added dropwise at 0 °C. The resulting mixture was stirred at room temperature for 2 h, the solvent was removed on the rotary evaporator, and the residue was dissolved in hexane. The solid salts were removed by filtration through Celite, and the solvent was again removed on the rotary evaporator to afford a colorless oil (0.42 g) containing **5** (ca. 50%), dimethoxydiphenylsilane (ca. 40%), and several other minor products. Kugelrohr distillation afforded a mixture of **5** (ca. 60%) and dimethoxydiphenylsilane ( $\text{Ph}_2\text{Si}(\text{OMe})_2$ ; ca. 40%). The two compounds were identified by comparison of their  $^1\text{H}$  NMR spectra to the reported spectra [46] and by GC/MS. **5**,  $m/z$  (I) = 214.1(8), 213.1(20), 184.1(7), 183.1(15), 138.1(9), 136.0 (100), 107.0 (9), 105.1(13), 92.1(12), 91.2(13);  $\text{Ph}_2\text{Si}(\text{OMe})_2$ ,  $m/z$  (I) = 245.1(5), 244.0(16), 213.2(23), 168.1(15), 167.0(100), 166.1(27), 154.2(30), 137.2(36), 107.0(18), 105.2(13).

### *Synthesis of 3,4-dimethyl-1,1-diphenyl-1-silacyclopent-3-ene (2)*

In a two-neck, 250 mL round-bottom flask fitted with a dropping funnel, condenser, and nitrogen inlet were placed magnesium turnings (2.5 g, 100 mmol) and anhydrous THF (20 mL). The dropping funnel was charged with 1,1-dichloro-3,4-dimethyl-1-silacyclopent-3-ene (4.7 g, 26 mmol), bromobenzene (12.4 g, 79 mmol), and anhydrous THF (25 mL). A ca. 10 mL portion of the solution from the dropping funnel was added and the solution was stirred until the reaction initiated, at which point the remainder of the solution was added at a rate appropriate to sustain reflux. After the addition was complete, additional anhydrous THF (30 mL) was added and the resulting solution was refluxed for 2 days. The progress of the reaction was monitored by  $^{13}\text{C}$  NMR spectroscopy; aliquots were



removed at appropriate time intervals, dissolved in hexane, filtered, evaporated to dryness, and then dissolved in  $\text{CDCl}_3$ . The spectra showed the initial development of a peak at  $\delta$  27.12 assignable to the monophenylated intermediate, which was gradually replaced by a peak at  $\delta$  24.31 due to the final product. Once the reaction was complete, hexane (100 mL) was added and the resulting solids removed by vacuum filtration. The filtrate was evaporated to dryness, yielding the crude product as a pale-yellow oil. The oil was passed through a standard silica column (with hexanes) to remove polar contaminants. The solvent was evaporated to dryness, yielding a colourless oil (6.2 g, 23 mmol, 88%), which eventually crystallized. Further purification was achieved by multiple, slow recrystallizations from hexanes to yield a white solid (mp 46.6–47.8 °C). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR and mass spectra of the compound were similar to those previously reported [47, 48].

#### Photolysis of **2** in hexane

A solution of **2** (0.46 g, 1.9 mmol) in hexane (80 mL) was placed in a 100 mL quartz tube. The solution was deoxygenated with a fine stream of argon for 30 min, the tube was sealed with a rubber septum, and then irradiated with  $6 \times 254$  nm lamps for 85 min. The solvent was removed under vacuum to yield a pale-yellow oil. Compound **6** was isolated, free of polymeric materials and small amounts of residual **2**, by column chromatography on silica gel (230–400 mesh) using pentane as the eluant. The solvent was removed under vacuum to yield a colorless oil, which was identified as 2-methyl-3-diphenylsilylmethyl-1,3-butadiene (**6**) on the basis of the following spectroscopic data: IR,  $3070\text{ cm}^{-1}$  (m), 3051 (m), 3012 (m), 2133 (s), 1592 (s), 1429 (s), 1117 (s), 886 (s), 809 (s), 699 (s);  $^1\text{H}$  NMR,  $\delta$  1.88 (s, 3H), 2.37 (d,  $J = 3.8$  Hz, 2H), 4.83 (s, 1H), 4.92 (t,  $J = 3.7$  Hz, 1H), 4.98 (s, 1H), 5.02 (s, 1H), 5.11 (s, 1H), 7.34–7.43 (m, 6H), 7.56–7.59 (m, 4H);  $^{13}\text{C}$  NMR,  $\delta$  19.97, 21.17, 112.52, 113.93, 128.04, 129.73, 134.53, 135.16, 143.23, 144.20; MS,  $m/z$  (I) = 266.1 (3), 265.1 (6), 264.1 (19), 186.1 (25), 184.1 (14), 183.1 (100), 181.0 (34), 105.1 (31); HRMS: calc. for  $\text{C}_{18}\text{H}_{20}\text{Si}$  264.1334, found 264.1314.

#### Photolysis of **2** in methanol

A solution of **2** (0.15 g, 0.06 mmol) in methanol (18 mL) was divided equally into two quartz tubes (15 mm diameter), deoxygenated with a fine stream of

argon for 15 min, and then sealed with rubber septa. The solutions were irradiated with  $6 \times 254$  nm lamps for 1 h, combined, and the solvent was removed by vacuum distillation. The  $^1\text{H}$  NMR spectrum of the residue showed ca. 85% conversion of the starting material to a mixture of four methoxylated products, identifiable as **7** (33%), **8** (51%), **5** (3%), and  $\text{Ph}_2\text{Si}(\text{OMe})_2$  (13%). Column chromatography on silica gel using 2% ethyl acetate in hexanes as eluant afforded two fractions. The first contained **2**, while the second contained **7**, **8**,  $\text{Ph}_2\text{Si}(\text{OMe})_2$ , and small amounts of residual **2**. The components of the second fraction were isolated by semi-preparative gas chromatography, which afforded (in order of increasing retention time)  $\text{Ph}_2\text{Si}(\text{OMe})_2$ , **7**, **8** and **2** as colorless oils; **7** eventually crystallized to a colorless solid.

A control experiment, in which a 1.5 mM solution of **2** in deoxygenated MeOH containing dodecane (0.1 mM) was photolyzed to  $\sim 65\%$  conversion with periodic monitoring by GC/MS, showed that  $\text{Ph}_2\text{Si}(\text{OMe})_2$  is a secondary photoproduct whose yield relative to **5** and **8** increases with increasing photolysis times; the experiment also verified that the same is true of **7**. Allowing the photolyzed solution to stand in the dark for several hours resulted in the eventual complete decomposition of **5**.

Compounds **7** and **8** were identified on the basis of the following spectroscopic data: 2,3-Dimethyl-3-(methoxydiphenylsilyl)-1-butene (**7**; mp 107.2–108.4 °C): IR ( $\text{cm}^{-1}$ ), 3067 (m), 2960 (s, br), 2835 (s), 1623 (m), 1429 (s), 1377 (m), 1187 (m), 1113 (s), 1083 (s), 889 (m), 879 (m), 701 (s);  $^1\text{H}$  NMR,  $\delta$  1.20 (s, 6H), 1.75 (s, 3H), 3.48 (s, 3H), 4.56 (s, 1H), 4.77 (s, 1H), 7.35–7.43 (m, 6H), 7.67–7.74 (m, 4H);  $^{13}\text{C}$  NMR,  $\delta$  22.74, 23.79, 31.43, 52.24, 109.94, 127.70, 129.82, 133.43, 135.94, 151.98;  $^{29}\text{Si}$  NMR,  $\delta$  -6.6; MS,  $m/z$  (I) = 297.2 (4), 296.2 (16), 215.1 (18), 214.1 (80), 213.0 (100), 185.1 (7), 184.1 (22), 183.0 (89), 181.0 (56); HRMS, calc. for  $\text{C}_{19}\text{H}_{24}\text{SiO}$ , 296.1596, found, 296.1597. 2,3-Dimethyl-1-(methoxydiphenylsilyl)-2-butene (**8**): IR ( $\text{cm}^{-1}$ ), 3070 (m), 2920 (s, br), 2834 (m), 1429 (s), 1168 (m), 1117 (s), 1086 (s), 736 (s), 700 (s);  $^1\text{H}$  NMR,  $\delta$  1.35 (s, 3H), 1.56 (s, 3H), 1.58 (s, 3H), 2.14 (s, 2H), 3.53 (s, 3H), 7.35–7.43 (m, 6H), 7.57–7.60 (m, 4H);  $^{13}\text{C}$  NMR,  $\delta$  20.58, 20.90, 21.11, 22.89, 51.64, 122.88, 122.98, 127.85, 129.76, 134.91, 135.00;  $^{29}\text{Si}$  NMR,  $\delta$  -5.6; MS,  $m/z$  (I) = 297.2 (4), 296.2 (15), 215.1 (8), 214.1 (50), 213.0 (100), 184.1 (9), 183.0 (61), 181.0 (25); HRMS, calc. for  $\text{C}_{19}\text{H}_{24}\text{SiO}$ , 296.1596; found, 296.1590.

Analytical scale photolyses were carried out in 5 mm quartz NMR tubes and monitored at periodic time intervals by  $^1\text{H}$  NMR spectroscopy, over total conversions ranging between 40 and 75% of **2**. Product yields were calculated relative to consumed **2** from the initial slopes of concentration vs. time plots, constructed for **2** and each of the products using the residual solvent protons or hexamethyldisilane as internal integration standard. The quoted yields are considered accurate to within  $\pm 20\%$  of the nominal values (e.g. the yield of DMB in the experiment of Equation (3) is  $(22 \pm 5)\%$ ).

Laser flash photolysis experiments employed the pulses from a Lambda Physik Compex 120 excimer laser, filled with  $\text{F}_2/\text{Kr}/\text{Ne}$  (248 nm;  $\sim 25$  ns;  $100 \pm 5$  mJ) mixtures, and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously [23]. Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was between ca. 0.7 and 0.9, and were flowed continuously through a thermostatted  $7 \times 7$  mm Suprasil flow cell connected to a calibrated 100 mL reservoir, fitted with a glass frit to allow bubbling of nitrogen or argon gas through the solution for at least 30 min prior to and then throughout the duration of each experiment. The glassware, sample cells, and transfer lines used for these experiments were stored in a  $65^\circ\text{C}$  vacuum oven when not in use, and the oven was vented with dry nitrogen just prior to assembling the sample-handling system at the beginning of an experiment. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple inserted directly into the flow cell. Transient decay and growth rate constants were calculated by non-linear least squares analysis of the absorbance-time profiles using the Prism 3.0 software package (GraphPad Software, Inc.) and the appropriate user-defined fitting equations, after importing the raw data from the Luzchem mLFP software. Reagents were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Rate constants were calculated by linear least-squares analysis of decay rate-concentration data (5–7 points) that spanned at least a factor of 100 in  $k_{\text{decay}}$ . Errors are quoted as twice the standard deviation obtained from the least-squares analyses.

The quantum yield for photolysis of **2** was determined by merry-go-round photolysis of deoxygenated solutions of **2** (0.021 M) and 1,1-diphenylsilacyclobutane (0.019 M) in cyclohexane- $d_{12}$  containing MeOH (0.2 M) and hexamethyldisilane (ca. 0.001 M) as internal integration standard, using a Rayonet photochemical reactor fitted with  $6 \times 254$  nm

lamps. The photolyses were monitored as a function of time between 0 and ca. 20% conversion of **2** by 600 MHz NMR spectroscopy. The quantum yield ( $\Phi_{-2} = 0.31 \pm 0.05$ ) was calculated from the relative slopes of concentration vs. time plots for **2** and 1,1-diphenylsilacyclobutane, and the reported quantum yield for the latter reaction ( $\phi = 0.21 \pm 0.02$  [49]).

For low temperature UV/vis absorption spectra, solutions of **1** or **2** (ca. 0.001 M;  $A_{254\text{nm}} 0.8$ ) in 3-methylpentane (Aldrich spectrophotometric grade) was sealed in a Suprasil quartz cuvette with a rubber septum and degassed by bubbling with a fine stream of argon for 5 min. The sample was placed in the cryostat, which was then cooled to 78 K. The entire assembly was placed in a Rayonet photochemical reactor equipped with 4–10 RPR-2537 lamps in order to irradiate the sample, with UV/vis spectra being obtained before and during the photolysis procedure at selected time intervals. The spectrum shown in Figure 3 is a result of subtracting the UV spectrum obtained prior to photolysis from that obtained after irradiation.

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35. We base this conclusion on the fact that GePh<sub>2</sub> reacts with isoprene reversibly, with forward rate and equilibrium constants of  $k_Q = 5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $K_{eq} = 6000 \pm 2500 \text{ M}^{-1}$ , respectively [24]. These dictate a lifetime on the order of ca. 1  $\mu\text{s}$  for the primary product of the reaction, vinylgermirane **11a**, if it were formed by photorearrangement of the germacyclopent-3-ene in the absence of added diene. Formation of GePh<sub>2</sub> by this route should be revealed in flash photolysis experiments by a fast growth component in the transient absorption due to the germylene and a rapidly decaying prompt signal at 285 nm due to **11a**. The germylene signals do, in fact, generally exhibit a distinct (50–80 ns) growth that lags slightly behind the laser pulse; the transient absorptions in the 270–300 nm range are very difficult to sort out because they consist of contributions from at least three species of varying lifetimes [23]. Subsequent studies of the reactions of GeMePh with isoprene and DMB indicate that the forward rate constants are similar for the two dienes, but the equilibrium constant for addition to DMB is significantly lower than that for addition to isoprene [34]. This suggests that the rate constants for dissociation of DMB-derived vinylgermiranes are somewhat greater than those of isoprene-derived derivatives, all else being equal. It is thus possible that the fast growth component of the germylene signals observed in flash photolysis experiments with **1** and related derivatives is due to formation of the germylene by this route, with the growth component appearing faster than it really is due to its superposition on the relatively fast subsequent decay of the germylene due to dimerization.
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