

The one- and two-photon photochemistry of benzylsilacyclobutanes, acyclic benzylsilanes, and 1,1,2-triphenylsilacyclobutane

William J. Leigh and Thomas R. Owens

Abstract: The photochemistry of several α -silylbenzyl compounds has been investigated in hexane and in methanol solution. Direct photolysis of 1-benzyl-1-methylsilacyclobutane (**1**) in methanolic hexane solution produces 1-propyl-1-methyl-2,3-benzosilacyclobutene (**6**) in quantitative yield, by a sequential two-photon process involving the photoactive isotoluene derivative 1-methylene-6-(1-methylsilacyclobutyl)-2,4-cyclohexadiene (**13a**), which has been identified on the basis of its ^1H NMR and UV absorption spectra. In contrast, direct irradiation of 1-benzyl-1-phenylsilacyclobutane (**2**) under similar conditions results in the formation of a complex mixture of products consistent with the competing formation of 1-benzyl-1-phenylsilene and benzyl- and 1-phenylsilacyclobutyl radicals. The silene is a transient which has been detected directly by laser flash photolysis of **2** ($\lambda_{\text{max}} = 315$ nm, $\tau \sim 4.5$ μs). Free radical formation is shown to be due to secondary photolysis of a second primary product, 1-methylene-6-(1-phenylsilacyclobutyl)-2,4-cyclohexadiene (**13b**), which has also been detected and identified by static UV absorption ($\lambda_{\text{max}} = 335$ nm) and ^1H NMR spectroscopy. In a reaction with some analogy to the acid-catalyzed desilylation of allylsilanes, both **13a** and **13b** can be intercepted in neutral or acidic methanol solution to yield toluene and 1-methyl- or 1-phenyl-1-methoxysilacyclobutane, respectively. Direct photolysis of benzyldimethylphenylsilane (**4**) also leads to the formation of the corresponding isotoluene derivative, while benzyltrimethylsilane (**3**) exhibits negligible photoreactivity. The endocyclic benzylsilane 1,1,2-triphenylsilacyclobutane (**5**) is shown to undergo competing [2 + 2]-cycloreversion and [1,3]-silyl migration to yield a bicyclic isotoluene analogue, which reacts rapidly with methanol to yield the acyclic methoxysilane reported previously to be the main product of photolysis of this silacyclobutane in methanol solution. Relative quantum yields for isotoluene formation from photolysis of **1–4** and absolute rate constants for methanolysis of several of these compounds under neutral and acidic conditions have also been determined.

Key words: photochemistry, organosilicon, benzylsilane, silacyclobutane, silene, kinetics, isotoluene.

Résumé : On a étudié la photochimie de plusieurs composés α -silylbenzyles en solutions dans l'hexane ou dans le méthanol. La photolyse directe du 1-benzyl-1-méthylsilacyclobutane (**1**), en solution méthanolique d'hexane, conduit à la formation de 1-propyl-1-méthyl-2,3-benzosilacyclobutène (**6**) avec un rendement quantitatif; la réaction se produit par un processus séquentiel à deux photons impliquant le dérivé photoréactif isotoluène, 1-méthylène-6-(1-méthylsilacyclobutyl)cyclohexa-2,4-diène (**13a**) que l'on a identifié sur la base de son spectre RMN du ^1H et de son spectre d'absorption UV. Par ailleurs, l'irradiation directe du 1-benzyl-1-phénylsilacyclobutane (**2**) dans des conditions semblables conduit à un mélange complexe de produits qui pourraient résulter d'une compétition entre la formation des radicaux 1-benzyl-1-phénylsilène, et benzyl- et 1-phénylsilacyclobutyles. Le silène est une espèce transitoire que l'on a détectée directement par photolyse éclair à l'aide d'un laser du produit **2** ($\lambda_{\text{max}} = 315$ nm, $\tau \sim 4,5$ μs). On a démontré que la formation du radical libre est due à une photolyse secondaire d'un deuxième produit primaire, la 1-méthylène-6-(1-phénylsilacyclobutyl)cyclohexa-2,4-diène (**13b**) que l'on a aussi détecté et identifié par absorption UV statique ($\lambda_{\text{max}} = 335$ nm) et spectroscopie RMN du ^1H . Dans une réaction qui présente une certaine analogie avec la désilylation acidocatalysée des allylsilanes, on peut intercepter les composés **13a** ainsi que **13b**, en solutions méthanoliques tant neutre qu'acide, pour obtenir du toluène et respectivement du 1-méthyl- et du 1-phényl-1-méthoxysilacyclobutane. La photolyse directe du benzyldiméthylphénylsilane (**4**) conduit aussi à la formation du dérivé isotoluène correspondant alors que la photoréactivité du benzyltriméthylsilane (**3**) est négligeable. On a démontré que le benzylsilane endocyclique, 1,1,2-triphénylsilacyclobutane (**5**), est soumis à des réactions en compétition de cycloréversion [2 + 2] et de migration de silyle [1,3] qui conduisent à un analogue isotoluène bicyclique qui réagit rapidement avec le méthanol pour fournir le méthoxysilane acyclique reconnu antérieurement comme le produit principal de la photolyse de ce silacyclobutane en solution dans le méthanol. On a aussi déterminé les rendements quantiques

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This paper is dedicated to Professor Adrian Brook in honour of his many contributions to organosilicon chemistry.

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pour la formation de l'isotoluène par photolyse des composés **1–4** ainsi que les constantes de vitesse absolues de méthanolyse de plusieurs de ces composés dans des conditions neutres et acides.

Mots clés : photochimie, organosilicium, benzylsilane, silacyclobutane, silène, cinétique, isotoluène.

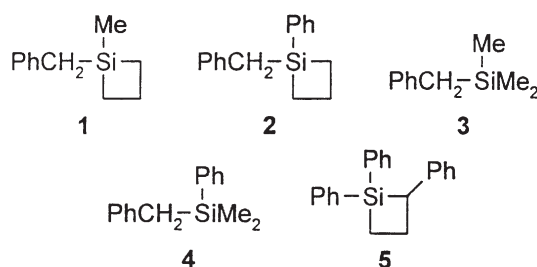
Introduction

Silacyclobutanes are well-known photochemical and thermal precursors to transient Si=C containing compounds ("silenes") (1–8), and are tremendously useful in experiments aimed at detecting these reactive intermediates directly and studying the kinetics and mechanisms of their various characteristic reactions (9–17). Photochemical silene formation proceeds with useful efficiencies from silacyclobutanes bearing a wide range of substituents at silicon, ranging from compounds in which the silacyclobutane ring is the primary chromophore (e.g., 1,1-dialkylsilacyclobutanes) to those in which the lowest excited state is localized more in the substituent (e.g., 1-arylsilacyclobutanes). The only known exception to this generalization is alkoxy-substituted derivatives; substituents of this type, either directly at silicon or on the aromatic rings of phenylated derivatives, renders the silacyclobutane moiety inert to photocycloreversion (13, 17).

Recent work in our laboratory has been directed at exploring the versatility of arylsilacyclobutanes as photochemical silene precursors, through systematic variation of the structure and photophysical properties of the aryl chromophore (18). These studies have also afforded new detail on the mechanism of silene photoextrusion from arylsilacyclobutanes. For example, the reaction proceeds from the lowest excited singlet state, probably via a 1,4-biradical intermediate that partitions between silene and the ground state of the silacyclobutane. If this mechanism is correct, then the overall quantum yield for reaction will be a function of two factors. The first is the partitioning of the silacyclobutane excited singlet state between Si—C bond cleavage and non-productive decay via internal conversion, intersystem crossing, and fluorescence; this tends to not vary dramatically as a function of aryl substituent, at least within the series of compounds that we have studied to date. The second is the partitioning of the biradical intermediate between silene and starting material. This does appear to vary as a function of substituent at silicon, most likely due to substituent-induced variations in the conformational properties of the biradical.

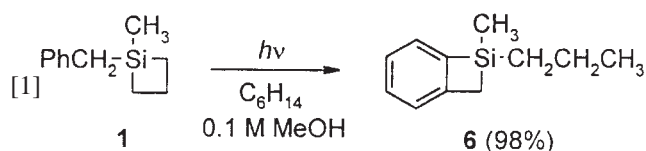
In this paper, we describe the results of a study of the photochemistry in solution of two 1-benzylsilacyclobutanes (**1** and **2**). These two compounds exemplify two different photophysical situations – one in which the benzyl group is the primary chromophore in the molecule (**1**) and one in which the role of primary chromophore is shared between it and the silacyclobutane ring via a second phenyl group at-

tached to silicon (**2**). Previous work suggests that benzylsilanes generally exhibit very low photoreactivity upon direct excitation in condensed phases (19). We thus wondered whether benzylsilacyclobutanes might show similar reactivity toward silene photoextrusion as is possessed by other simple silacyclobutane derivatives, with minimal complications from competing reactions due to the benzylic substituent. It quickly became clear that this is not the case, prompting us to expand our studies to include three additional benzylsilane derivatives, two of which have been studied previously: benzyltrimethylsilane (**3**) (19), benzyl-dimethylphenylsilane (**4**), and 1,1,2-triphenylsilacyclobutane (**5**) (4, 9, 20).



Results and discussion

Direct photolysis of 1-benzyl-1-methylsilacyclobutane (**1**; 0.05 M) in deoxygenated hexane solution containing methanol (0.1 M) with the light from a low pressure mercury lamp (254 nm) affords the single product **6** in quantitative (>98%) yield (eq. [1]). The same product was formed, again quantitatively, when the photolysis was conducted in the absence of methanol.



In contrast, photolysis of **2** as a deoxygenated 0.05 M solution in hexane containing 0.1 M methanol led to the more complex mixture of products shown in eq. [2]. Alkoxy-silane **7** is the product expected from trapping of 1-benzyl-1-phenylsilene (**12**) by methanol, while **8–10** are most likely the products of hydrogen abstraction or coupling of benzyl

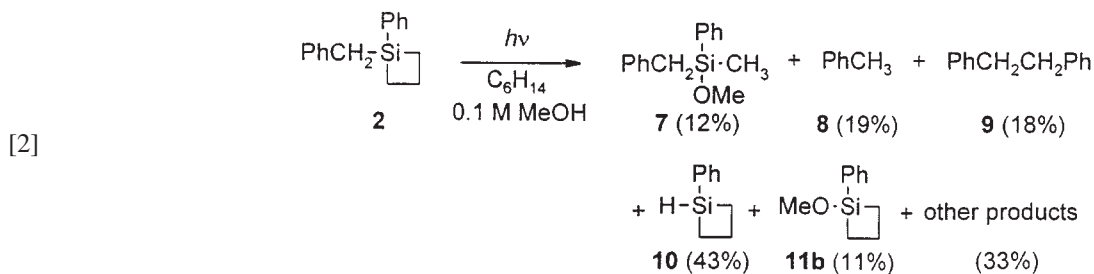
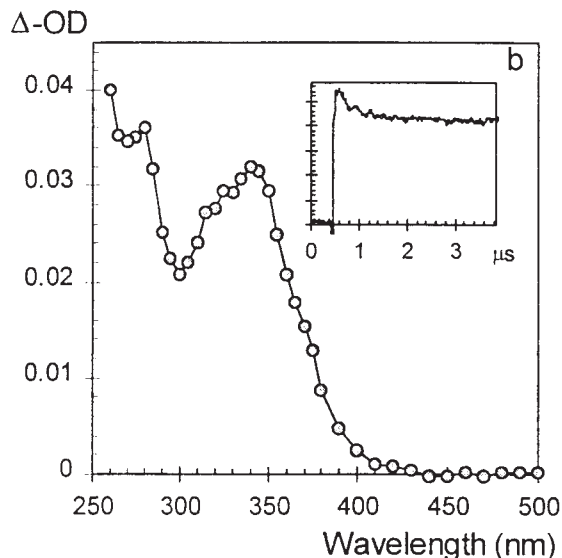
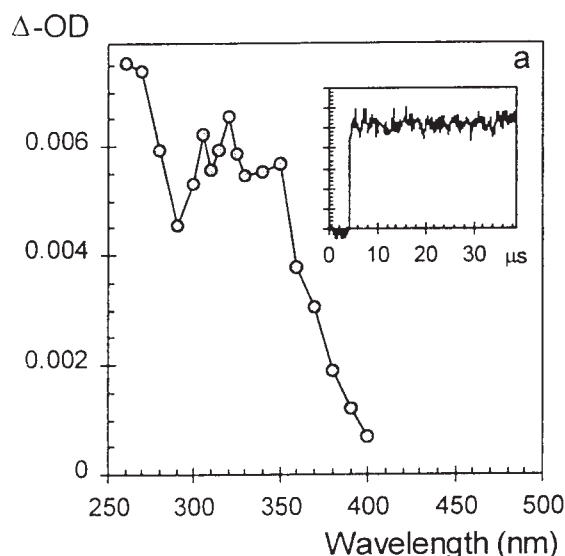


Fig. 1. UV absorption spectra, recorded by laser flash photolysis of deoxygenated hexane solutions of (a) 1-benzyl-1-methylsilacyclobutane (**1**; 0.002 M), 10–15 μs after the pulse and (b) 1-benzyl-1-phenylsilacyclobutane (**2**; 0.001 M), 3–3.5 μs after the pulse. The inserts show typical traces, recorded at 335 nm.



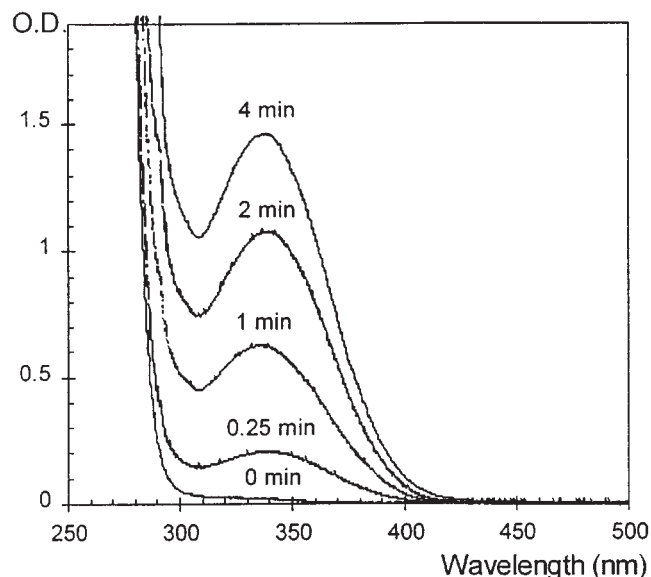
and phenylsilacyclobutyl radicals. Several other products were also formed, in yields which were too low to enable identification. The mass balance was $\sim 93\%$ at 20% conversion of **2**.

Flash photolysis of a deoxygenated hexane solution of **1** (0.007 M) with a KrF excimer laser (248 nm) led to the formation of a weakly absorbing species which was stable over 10 ms, the longest timescale able to be monitored with our system. The UV spectrum recorded 10–15 μs after laser excitation is shown in Fig. 1a, along with a ΔOD vs. time profile. No short-lived transient species could be detected at any monitoring wavelength between 260–600 nm from this compound. Similar experiments with **2** (0.008 M) led to the results shown in Fig. 1b: the formation of a long-lived species which exhibits a similar spectrum to that observed from **1**, on which is superimposed a weak transient absorption which decayed with pseudo-first order kinetics ($\tau \sim 4.5 \mu\text{s}$). Subtraction of the spectrum of the long-lived species from the spectrum recorded immediately after the laser pulse revealed an absorption centered at 310–315 nm, which can be associated with the short-lived transient species. The lifetime of this transient was shortened upon addition of methanol to the solution; a plot of k_{decay} vs. $[\text{MeOH}]$ according to eq. [3] was linear, with slope $k_{\text{MeOH}} = (9 \pm 2) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. The spectrum and sensitivity of the lifetime of this transient to the presence of methanol are consistent with its assignment to 1-benzyl-1-phenylsilene (**12**). Neither of the long-lived species formed from **1** and **2** were affected detectably by the addition of up to 0.1 M methanol, over the 10 ms timescale.

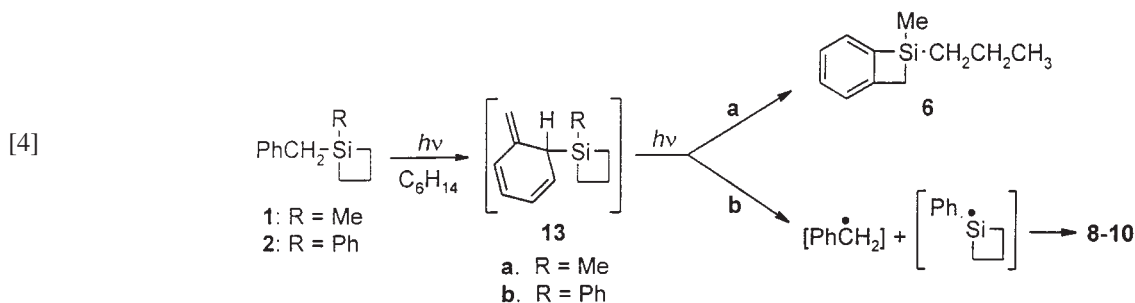
$$[3] \quad k_{\text{decay}} = k_0 + k_{\text{MeOH}}[\text{MeOH}]$$

The stable species produced in the flash photolysis experiments with **1** and **2** could also be detected by static UV absorption spectroscopy, and by ^1H NMR spectroscopy when the reactions were carried out in cyclohexane- d_{12} . For example, the static UV spectrum of a 0.017 M solution of **1** as a function of photolysis time is shown in Fig. 2. The ^1H NMR spectra of a cyclohexane- d_{12} solution of this compound after

Fig. 2. Static UV absorption spectra of a 0.017 M solution of **1** in hexane solution after various time intervals of photolysis with 254-nm light, illustrating the formation of isotoluene **13a** ($\lambda_{\text{max}} = 335 \text{ nm}$).



photolysis for similar periods of time showed the growth of a broad singlet at $\delta 3.18 \text{ ppm}$ and a number of resonances in the vinylic region which integrate to a total of six protons relative to the signal at $\delta 3.18$. These signals grow in during the early stages of the photolysis and then remain roughly constant in relative intensity upon continued irradiation, and can thus be identified as arising from the same initially-formed product that is responsible for the 335 nm UV absorption. On the basis of these data, we assign the structure of this product to 1-methylene-6-(1-methylsilacyclobutyl)-2,4-cyclohexadiene (**13a**; eq. [4]). The spectral data observed agree very well with those reported for other



isotoluene derivatives (21–24). Compounds of this type are surprisingly quite stable in non-nucleophilic solvents.

In the case of **1**, these experiments indicated **13a** to be the sole primary photolysis product, building up steadily in concentration over a conversion range of 0–15% to a level roughly 6% of that of the starting material, after which it decreased in parallel with **1** upon continued photolysis. Compound **6** could only be detected in significant yields after the formation of **13a** had nearly reached its initial plateau, suggesting that it is a secondary product resulting from photolysis of the latter species. This was verified by photolyzing a solution of **1** with 248 nm light to ca. 10% conversion, and then continuing the photolysis with 337 nm light; this caused **13a** to disappear, with concomitant formation of **6** and no further consumption of **1**, consistent with the fact that the latter is nonabsorbing above ~280 nm.

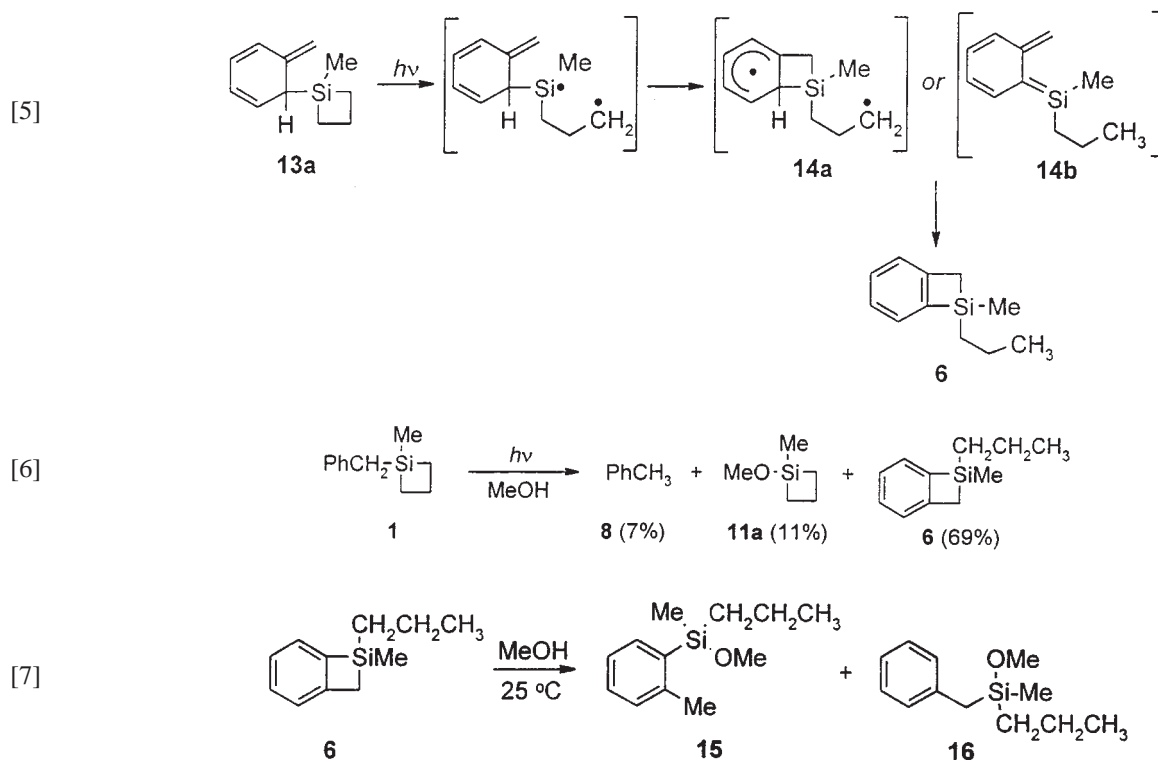
Similar experiments with **2** indicated that only alkoxy silane (**7**), ethylene, and a product identifiable as isotoluene **13b** are formed upon photolysis in hexane or cyclohexane-*d*₁₂ solution to low (<ca. 10%) conversions. Again, the isotoluene derivative could be detected by both static UV and ¹H NMR spectroscopy, and products **8–10** were found to be produced only after the concentration of **13b** rose to ~5% of that of **2**. Alternating 248 and 337 nm irradiation experiments verified that **8–10** are formed as a result of secondary photolysis of **13b**.

The formation of **13a, b** as the major primary products of photolysis of **1** and **2** indicates that the photochemistry of these compounds is in both cases dominated by reactivity specific to the benzyl chromophore rather than the silacyclobutane moiety, unlike the case with other silacyclobutanes that have been studied. Silene formation competes significantly only in **2**, where the silacyclobutane ring bears a second phenyl chromophore which competes effectively with the benzyl group for direct light absorption. The reactive excited states in both **1** and **2** are most likely the lowest singlet states, since our flash photolysis experiments indicate that **13a, b** are both formed within the duration of the laser pulse (~25 ns), consistent with either a concerted sigmatropic rearrangement or a singlet radical-pair recombination mechanism for their formation. No evidence for the competing formation of benzyl radicals in the primary photochemical event could be obtained by flash photolysis in either case, which provides strong evidence against a mechanism for the formation of **13** which involves the triplet excited states of **1** and **2**. For that matter, no evidence for benzyl radical formation could be obtained either in two-laser flash photolysis experiments with **2**, where the second (337 nm) laser pulse was delivered 5–10 μs after **13b** was formed by the primary (248 nm) pulse. Since product studies clearly indicate that free benzyl radicals *must* be formed upon secondary photolysis of **13b**, this result merely suggests that the quan-

tum yield for photolysis of the intermediate is exceedingly low. This is also indicated by the fact that only slight irreversible bleaching of the 335 nm absorption due to **13b** could be detected in these experiments. Flash photolysis experiments carried out with optically matched (at 248 nm) solutions of **1** and **2** indicated that the quantum yield for formation of **13b** from **2** is only slightly higher than that for formation of **13a** from **1** ($\Phi_{13b}/\Phi_{13a} \sim 1.3$). This suggests that the main effect of replacing the methyl substituent in **1** with phenyl (in **2**) is to promote silene formation in minor amounts, via [2 + 2]-cycloreversion of the silacyclobutane ring. The spectra shown in Fig. 1 were recorded with solutions which were not optically-matched, and with different excitation laser intensities.

Interestingly, the identity of the second silyl substituent has a far more substantial effect on the photochemistry of the corresponding isotoluene derivatives **13a, b**. The formation of **6** from **13a** can be formulated in terms of a non-concerted mechanism involving rearrangement of the 1,4-biradical intermediate formed by cleavage of the one of the endocyclic silacyclobutyl Si—C bonds (eq. [5]). If this mechanism is correct, then the photochemistry of **13a** initially follows a course typical of 1-substituted methylsilacyclobutanes (**18**). Unlike other methylsilacyclobutane-derived 1,4-biradicals however, that derived from **13a** has available two possible reaction pathways that are both likely to be less energetically demanding than cleavage to the corresponding silene and ethylene: rearrangement to yield the more stable cyclohexadienyl biradical **14a** which can then aromatize to **6** via intramolecular disproportionation, or intramolecular abstraction of the cyclohexadienyl proton to form an *ortho*-silaxylylene intermediate (**14b**) followed by electrocyclic ring closure. We favour the former mechanism, on the basis of the fact that none of the expected trapping product of **14b** was observed in the photolysis of **1** in 0.3 M MeOH solution; however, its possible intermediacy in the formation of **6** from **13a** cannot be rigorously ruled out.

The photochemistry of **13b**, on the other hand, is evidently initiated by preferential cleavage of the weaker of the *exocyclic* silacyclobutyl Si—C bonds, yielding benzyl- and phenylsilacyclobutyl radicals. To our knowledge, no other examples of *exocyclic* Si—C bond cleavage are known in silacyclobutane photochemistry. One possible explanation for the difference in the photochemistry of **13a** and **13b** is that the latter has available to it a conformer in which a reasonable degree of π -overlap is possible between the methylcyclohexadienyl and phenyl rings; this could lead to preferential weakening of the *exocyclic* Si—C bond due to charge-transfer interactions between the two moieties in the lowest excited singlet state. While no evidence for such interactions could be obtained from the UV absorption spectra



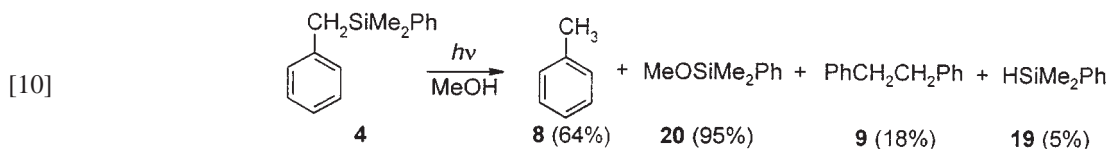
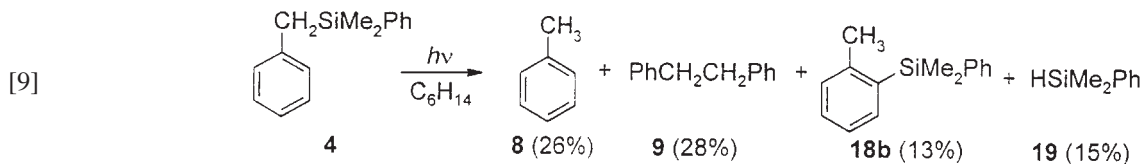
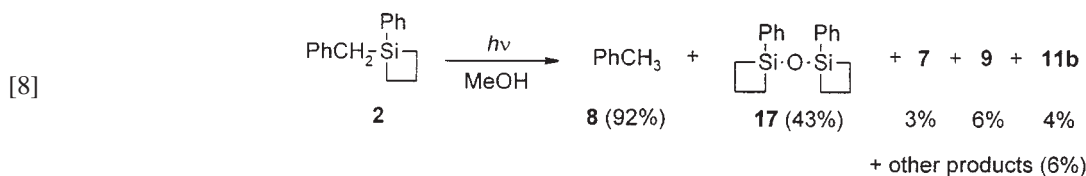
of the two compounds, the vinylic resonances in the ^1H NMR spectrum of **13b** appear at consistently lower fields than those in the spectrum of **13a**, indicative of significant deshielding of the vinyl protons by the phenyl ring. Neither compound appears to undergo the 4π electrocyclic ring closure that is typical of other isotoluene derivatives that have been studied (24), to any detectable extent.

To gain additional evidence for the primary involvement of **13a, b** in the photochemistry of **1** and **2**, we examined the photolyses of the latter two compounds in neat methanol solution. One of the common properties of isotoluene derivatives is their sensitivity towards acid-catalyzed aromatization, the exact course of which (isomerization vs. solvolysis) depends on the nature of the substituents at the *bis*-allylic position of the methylenecyclohexadienyl ring (21, 24). Judging from the well-known reactivity of allylsilanes toward acid-catalyzed desilylation (25, 26), the present compounds should be expected to react readily with aliphatic alcohols to yield toluene and the corresponding methoxysilacyclobutane. Thus, it seemed very likely that the formation of the secondary products of photolysis of **1** and **2** might be suppressed in methanol solution due to interception of the primary products (**13**) by reaction with the solvent. This might also explain the formation of methoxyphenylsilacyclobutane (**11b**) in trace amounts in the photolysis of **2** in hexane containing 0.1 M methanol (eq. [2]).

As expected, photolysis of **1** in neat methanol produced **6** (69%), toluene (**8**; 7%), and 1-methoxy-1-methylsilacyclobutane (**11a**; 11%), as shown in eq. [6]. The reaction mixture was actually somewhat more complicated than this, because like other benzosilacyclobutenes (27), **6** reacts rapidly in methanol solution, in this case to yield two methoxysilanes in a 8:1 ratio. These were tentatively identified as **15** and **16**, respectively, on the basis of ^1H NMR and GC/MS evidence (eq. [7]). The actual amount of **6** detected in the photolysis

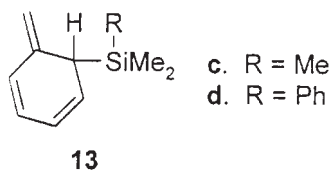
mixture therefore varied depending on the time taken between photolysis and GC analysis. The yields of **8** and **11a** increased to a combined yield of ~73% upon photolysis of a methanol solution of **1** containing 0.1 M HCl, and as expected (27), the relative yields of **15** and **16** changed to 1.4:1. Evaporation of the solvent after photolysis of a hexane solution of **1** to ca. 10% conversion and redissolution of the mixture in methanol confirmed that the formation of toluene (**8**) and 1-methoxy-1-methylsilacyclobutane (**11a**) are due to reaction of **13a** with the alcohol. Monitoring of this reaction by UV spectroscopy revealed that the isotoluene disappears with pseudo-first order kinetics and a rate constant of $k_{-13a} = (1.10 \pm 0.05) \times 10^{-3} \text{ s}^{-1}$ in neutral methanol solution at 25°C. In methanol containing 0.1 M HCl, disappearance of **13a** was too rapid for a rate constant to be measured by conventional UV absorption spectroscopy.

Steady state photolysis of **2** in deoxygenated methanol solution led to the formation of two main products, toluene (**8**) and disiloxane **17**, and only traces of bibenzyl (**9**) and the silene-derived methoxysilane **7** (eq. [8]). The mass balance in this experiment was ~92% after ca. 40% conversion of **2**. Disiloxane **17** most likely arises from condensation of **11b** due to the presence of small amounts of water in the solvent, a process which can be expected to proceed more readily in **11b** than in **11a** under neutral (as well as acidic) conditions (28). As before, evaporation of the solvent after photolysis of a hexane solution of **2** to ca. 10% conversion and redissolution of the mixture in methanol resulted in the disappearance of the 335 nm UV absorption due to **13b** and the formation of **8** and **17**. The reaction is complete within ~5 s under these conditions, but was found to be too slow for a rate constant to be obtained by flash photolysis. Thus, while an absolute rate constant for the reaction of **13b** with methanol could not be easily determined, it is clearly at least



two orders of magnitude greater than that for reaction of **13a** under similar conditions. The much higher reactivity of **13b** toward dark reaction with methanol more effectively lowers its steady-state concentration during the photolysis of **2** in this solvent, resulting in much lower yields of secondary photolysis products relative to what is observed in hydrocarbon solvents, compared to **13a**.

While the photoisomerization of **1** and **2** to the corresponding isotoluene derivatives has precedent in the photochemistry of other benzyl compounds (24), it has not been reported previously for benzylsilanes. Benzyltrimethylsilane (**3**) was first reported to be inert to photolysis in solution (20), but Kira et al. (19) later found that extended photolysis of the compound in hydrocarbon solution leads to the inefficient formation of *ortho*-tolyltrimethylsilane (**18a**), which they suggested to arise from a minor reaction of benzyl and trimethylsilyl radicals produced by homolysis of the benzyl carbon-silicon bond in the benzylsilane. More recently, spectroscopic evidence for the formation of free benzyl radicals upon photolysis of **3** in an ethanol matrix at 77 K has been reported by Hiratsuka et al. (29).

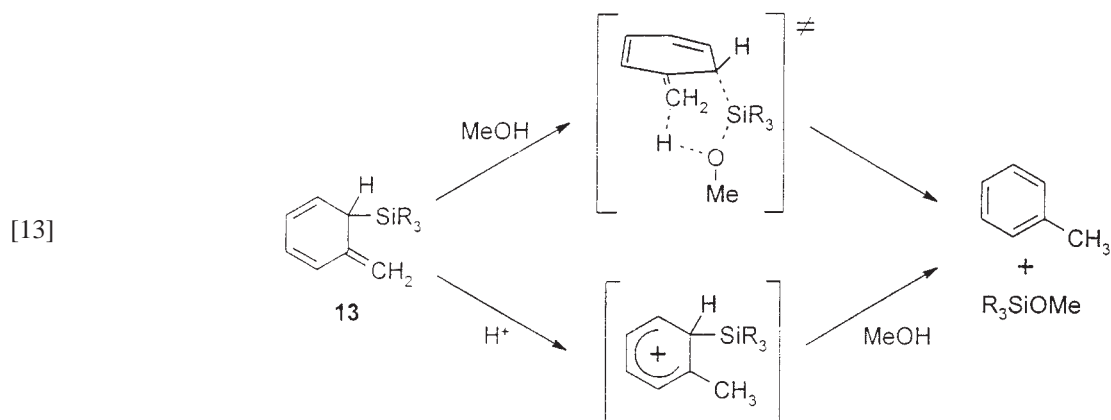
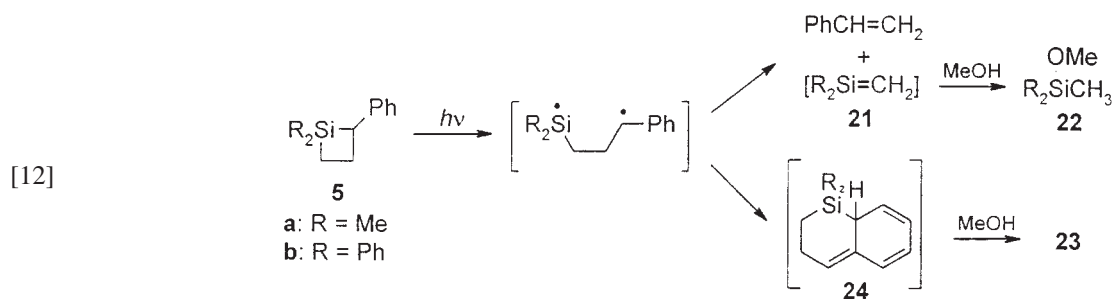
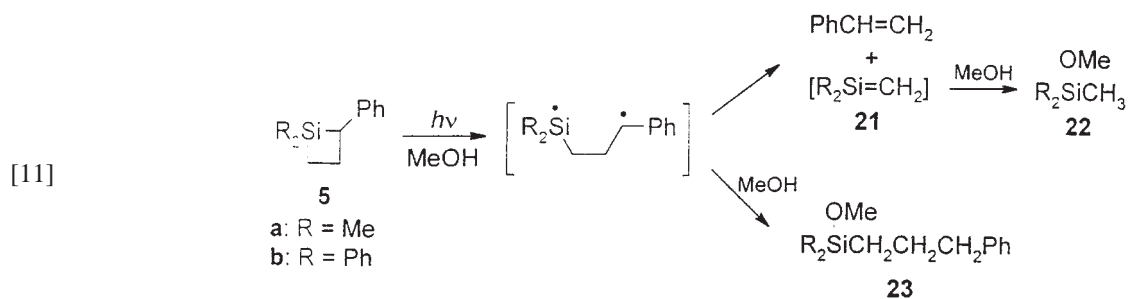


We also find that the parent benzylsilane exhibits very low photoreactivity in solution at room temperature. Extended photolysis of **3** in hexane with 254 nm light produces very weak UV absorptions on the long-wavelength edge of the absorption band due to **3**, but the ^1H NMR spectrum of the mixture shows no evidence of vinylic resonances consistent with the formation of isotoluene **13c** in detectable amounts. The quantum yield for formation of this product from **3** is thus no greater than ~5% of that for the formation of **13a** from **1** under similar conditions.

On the other hand, photolysis of benzyltrimethylphenylsilane (**4**) in hexane results in the fairly efficient formation of a long-wavelength absorbing species which can be identi-

fied as the isotoluene derivative **13d** on the basis of its UV and ^1H NMR spectra. This compound, the only detectable product at low (<5%) conversion of **4**, is formed with a similar quantum yield to that for formation of **13b** from **2**. It also behaves similarly to **13b** with respect to secondary photolysis and reaction with methanol. For example, eqs. [9] and [10] show the product mixtures obtained from photolysis of **4** in deoxygenated hexane and methanol solutions, respectively, to 40–50% conversion of the starting material. Interestingly, a product tentatively identified as *ortho*-tolyltrimethylphenylsilane (**18b**) could be detected in significant yield by GC/MS analysis of the hexane photolyzate. It is barely resolved from **4** under our GC/MS conditions, and coelutes with **4** under those employed for our GC/FID analyses. A closer inspection of the product mixture from photolysis of **2** in hexane revealed that an analogous isomeric product is formed in this case as well, but in yields of less than 10%. These products are most likely formed by a free radical pathway initiated by hydrogen abstraction from **13b/d** by benzyl radicals, since they are not formed in detectable yields in methanol solution, where the steady state concentration of **13** is substantially lower due to reaction with the solvent. As was found with **13b**, dissolution of **13d** in neutral methanol results in its immediate disappearance and the concomitant formation of **8** and **20**. It is possible that the higher photoreactivity of **4** compared to **3** with respect to isotoluene formation is due to similar factors as those suggested above to explain the different photoreactivities of **13a, b**. However, we are at a loss to explain why the methylsilylcyclobutyl derivative **1** is also more reactive than **3** toward this photorearrangement.

The results reported above provide a reasonable explanation for one or two unusual aspects of the photochemistry of 2-phenylsilylcyclobutanes (**5**) which have been reported previously (4, 9, 20). Both 1,1-dimethyl-2-phenyl- and 1,1,2-triphenylsilylcyclobutane (**5a** and **5b**, respectively), yield styrene and the corresponding silene **21a, b** upon photolysis in methanol solution, as evidenced by the formation of the methoxysilane (**22**) expected from trapping of the silene by the solvent (eq. [11]) (4, 20). Also formed are the methoxysilanes **23a, b**, which were originally ascribed to nucleophilic trapping of the 1,4-biradical/zwitterion formed



by cleavage of a single carbon—silicon bond in the excited state of the silacyclobutane (eq. [11]). The formation of these products was offered as the first evidence for a stepwise reaction mechanism for the formal [2 + 2]-photocycloreversion of silacyclobutanes (4, 20).

Our results for **1–4** suggest that a more likely explanation for the formation of **23** is that it arises from reaction of methanol with the isotoluene derivative (**24**) formed by [1,3]-silyl migration into the *ortho*-position of the 2-phenyl ring in **5** (eq. [12]). The isotoluenes **24a, b** would be expected to be stable enough that they should build up to significant concentrations, at least in non-nucleophilic solvents. However, their secondary photolysis should result mainly in reversion to the biradical precursor, so no additional products that might have signalled their presence would be expected.

In fact, we have already published evidence consistent with this interpretation, although we failed to recognize it at the time (9). Laser flash photolysis of **5b** in isooctane leads to the formation of a transient species identified as 1,1-diphenylsilene (**21b**), whose absorptions ($\lambda_{\text{max}} = 325 \text{ nm}$) are superimposed on those due to a species which is stable over the timescale of our experiment and exhibits $\lambda_{\text{max}} \sim 335 \text{ nm}$. We originally reported that this species did

not persist over a timescale of several minutes, but this conclusion was based on examination of photolyzed solutions containing small amounts of methanol. In fact, inspection of photolyzed hexane or cyclohexane- d_{12} solutions of **5b** in the absence of added methanol reveals that the species is quite stable, and exhibits a ^1H NMR spectrum consistent with isotoluene **24b**. The compound reacts within $\sim 5 \text{ s}$ upon dissolution in neutral methanol to yield the previously reported methoxysilane **23**.

The three phenylsilyl-substituted isotoluenes (**13b, 13d**, and **24b**) all react with methanol under neutral conditions at least two orders of magnitude faster than the trialkylsilyl derivative **13a**. This difference in reactivity, which has been documented previously in other systems (25, 30), suggests that desilylation proceeds by an $\text{S}_{\text{N}}2$ mechanism under these conditions, probably with simultaneous protonation at the exocyclic double bond of the leaving group (eq. [13]).

On the other hand, little difference in reactivity as a function of substitution at silicon is observed in acidic methanol solution. For example, **13a, 13b, 13d**, and **24b** were all found (by laser flash photolysis) to have lifetimes in the 12–17 ms range in methanol containing 0.3 M HCl. This suggests that under acidic conditions, the rate-determining step for reaction is protonation of the exocyclic double bond,

Table 1. Pseudo-first order rate constants for decay of isotoluenes in methanol and methanol containing 0.3 M HCl at 23°C.

	k_{decay} (s^{-1})			
	13a	13b	13d	24b
MeOH	0.0011±0.0001	>0.2	>0.2	>0.2
0.3 M HCl–MeOH	85 ± 1	61 ± 2	77 ± 1	58 ± 4

the rate of which is not expected to depend on substitution at silicon. The resulting β -silyl-substituted cyclohexadienyl carbenium ion then undergoes rapid methanol-assisted desilylation (30) to yield toluene and the corresponding methoxysilane. The pseudo-first-order rate constants for decay of the four isotoluenes in methanol and methanol containing 0.3 M HCl are summarized in Table 1.

Summary and conclusions

The direct photolysis of benzylsilanes in solution results mainly in the formation of the corresponding 6-silylisotoluene derivatives, which are sufficiently stable in hydrocarbon solvents that they build up in concentration and start to compete with the precursor for light absorption after conversions of only 5–6%. Secondary photolysis of the isotoluene derivatives is responsible for the formation of most of the products of benzylsilane photolysis that are detected chromatographically. Isotoluene formation results formally from a photochemically allowed [1,3]-sigmatropic rearrangement, although a singlet radical pair recombination mechanism cannot be ruled out, and is generally more efficient in benzyldialkylphenylsilanes than in benzyltrialkylsilanes. Phenyl substitution at silicon also affects the photochemistry of the corresponding 6-silylisotoluene derivative, promoting Si—C bond homolysis to yield benzyl and silyl free radicals. The isotoluene derivatives undergo rapid desilylation in neutral or acidic methanol solution, which allows the formation of secondary photolysis products to be suppressed. The rate of solvolysis under neutral conditions is at least two orders of magnitude greater for the phenylsilyl derivatives, suggesting that it proceeds by an $\text{S}_{\text{N}}2$ mechanism in neutral methanol. The rates are accelerated by up to five orders of magnitude in methanol containing 0.3 M HCl and show no dependence on silyl substituent, consistent with protonation being the rate determining step for isotoluene desilylation under acidic conditions. The photochemical [1,3]-rearrangement also occurs in “masked” benzylsilanes such as 1,1,2-triphenylsilylacyclobutane and accounts for the formation of silylacyclobutane-ring-opening products in the photolyses of 2-phenylsilylacyclobutanes in methanol solution.

Experimental

^1H , ^{13}C , and ^{29}Si NMR spectra were recorded using Bruker AC200, Bruker AC300, or DRX500 NMR spectrometers. Infrared spectra were recorded on a BioRad FTS-40 FT/IR spectrometer and are reported in wavenumbers (cm^{-1}). Ultraviolet absorption spectra were recorded on Cary–Varian Model 50 or Model 400 spectrometers. Gas chromatographic separations employed a Hewlett–Packard 5890 gas chromatograph equipped with a 3396A integrator, flame ion-

ization detector, a conventional splitless injector (heated), and a DB-1 fused silica capillary column (15 m \times 0.2-mm; Chromatographic Specialties, Inc.). Low resolution mass spectra were recorded using a Hewlett–Packard 5890 gas chromatograph equipped with a HP-5971A mass selective detector and a DB-5 fused silica capillary column (30 m \times 0.25 mm; Chromatographic Specialties, Inc.). High-resolution electron impact mass spectra and exact masses were determined using a VGH ZABE mass spectrometer.

Radial chromatographic separations were carried out using a Chromatotron[®] (Harrison Research, Inc.), with 2 or 4 mm silica gel 60 thick layer plates using hexane as the eluant.

Hexanes and methanol (BDH Omnisolv), cyclohexane- d_{12} (Cambridge Isotope Laboratories), benzyl bromide (Aldrich), benzyltrimethylsilane (**3**, Aldrich), dimethylphenylsilane (**19**, Aldrich), and chlorodimethylphenylsilane (Aldrich) were used as received from the suppliers. Tetrahydrofuran (BDH) was distilled from sodium. 1-Chloro-1-methylsilylacyclobutane (**31**), 1-chloro-1-phenylsilylacyclobutane (**32**), and benzyldimethylphenylsilane (**4**) (**33**) were prepared as previously described. 1,1,2-Triphenylsilylacyclobutane (**5**) (**9**), 1-methoxy-1-methylsilylacyclobutane (**11a**) (**17**), 1-phenylsilylacyclobutane (**10**) (**18**), and dimethylmethoxyphenylsilane (**20**) (**18**) were available from previous studies. Benzylmethoxymethylphenylsilane (**7**) was prepared by reaction of benzylmethylphenylsilane with methanol in the presence of PdCl_2 (**17**).

1-Benzyl-1-methylsilylacyclobutane (**1**) (**34**) was synthesized as follows. Magnesium filings (2.55 g, 0.105 g-atom) were placed in a 500 mL 2-neck round bottom flask fitted with an addition funnel, reflux condenser with nitrogen inlet, and magnetic stirrer. The entire apparatus was flame-dried under nitrogen and after cooling, anhydrous diethyl ether (100 mL) and 1-chloro-1-methylsilylacyclobutane (4.0 mL, 2.75 g, 0.0299 mol) were added. Benzyl bromide (3.3 mL, 2.29 g, 0.0136 mol) was dissolved in anhydrous ether (50 mL) and added dropwise over a 30 min period with stirring. The mixture was stirred for 48 h at room temperature, during which time it turned a light gray color. Ice water (30 mL) was added slowly, and the resulting mixture was then filtered. The filtrate was placed in a 500 mL separatory funnel, the aqueous layer was removed, and the ether solution was washed with cold water (3 \times 50 mL). After drying with anhydrous magnesium sulfate and filtering, the solvent was removed on a rotary evaporator to afford a slightly yellow oil (2.01 g). Compound **1** (1.04 g, 0.006 mol, 29%) was isolated as a colourless oil in >99% purity by radial chromatography on silica gel using hexane as eluant, and identified on the basis of the following spectroscopic data: ^1H NMR, δ = 0.289 (s, 3H), 1.03 (m, 2H), 1.09 (m, 2H), 2.08 (m, 2H), 2.36 (s, 2H), 7.13 (m, 3H), 7.26 (d, 1H), 7.28 (d, 1H); ^{13}C NMR, δ = -1.79, 13.8, 17.85, 22.68, 26.56, 31.61, 124.16, 128.02, 128.29, 128.60, 139.40; ^{29}Si NMR, δ = 18.85; 3082(s), 3062(s), 3027(s), 2964(m), 2926(w), 2798(m), 1934(m), 1868(m), 1801(m), 1600(s), 1494(s), 1452(s), 1410(m), 1250 (s), 1206(s), 1152(s), 1121(m), 1055(s), 1031(s), 903(s), 873(s), 755(s), 698(m), 653(s); UV (λ_{max}) = 220, 260 nm; MS (EI), m/z (I) = 176 (27), 148 (100), 133 (68), 119 (18), 107 (17), 105 (28), 91 (40), 85 (95), 65 (38), 43 (47); HRMS calcd. for $\text{C}_{11}\text{H}_{16}\text{Si}$: 176.1022; found: 176.1025.

1-Benzyl-1-phenylsilacyclobutane (**2**) was synthesized and purified by a similar procedure to the one given above for **1**. It was isolated as a colourless oil and identified on the basis of the following spectroscopic data: ^1H NMR, δ = 0.90 (s), 0.98 (t), 1.33 (m, 2H), 1.96 (m, 2H), 2.64 (t, 2H), 7.17 (m, 3H), 7.29 (m, 3H), 7.46 (m, 2H), 7.63 (m, 2H); ^{13}C NMR, δ = 12.88, 18.05, 22.68, 25.32, 31.59, 124.40, 127.88, 128.30, 128.36, 129.51, 133.67, 137.20, 138.74; ^{29}Si NMR, δ = 12.00; 3067(w), 3025(m), 2969(m), 2924(w), 1954(m), 1881(m), 1816(m), 1600(s), 1493(s), 1428(s), 1395(m), 1207(s), 1184(s), 1152(m), 1117(m), 1056(s), 1030(s), 999(s), 924(s), 902(s), 858(m), 820(s), 801(s), 766(m), 735(s), 697(w); UV (λ_{max}) = 262, 222; MS (EI), m/z (I) = 238 (33), 210 (25), 161 (25), 147 (48), 132 (60), 105 (100), 93 (60), 91 (67), 65 (25), 53 (55); HRMS calcd. for $\text{C}_{16}\text{H}_{18}\text{Si}$: 238.1179; found: 238.1177.

Compound **6** was isolated from a semi-preparative scale photolysis of a hexane solution of 1-benzyl-1-methylsilacyclobutane (**1**, 0.22 g, 1.25 mmol) in hexane (20 mL). The solution was placed in a quartz photolysis tube, sealed with a rubber septum, deoxygenated with dry argon, and then irradiated in a Rayonet reactor fitted with seven RPR-2537 lamps. The photolysis was monitored periodically by GC, and terminated after ca. 95% conversion of **1** (59 hs). After evaporation of the solvent, the single product was isolated by radial chromatography, further purified by silica gel column chromatography (hexane as eluent), and identified as 1-methyl-1-propyl-3,4-benzosilacyclobutene (**6**; 0.023 g, 0.125 mmol, 10%) on the basis of the following spectroscopic data: ^1H NMR, δ = 0.43 (s, 3H), 0.93 (t, 2H), 0.97 (t, 3H), 1.48 (m, 2H), 2.11 (d, 1H), 2.14 (d, 1H), 7.13 (d, 1H), 7.16 (d, 1H), 7.24 (d, 1H), 7.30 (d, 1H); ^{13}C NMR, δ = -2.173, 17.39, 17.66, 18.35, 19.08, 126.12, 126.82, 130.30, 130.57, 145.71, 150.95; ^{29}Si NMR, δ = 10.82; IR (neat), 3078(m), 2969(m), 2938(w), 2875(m), 2360(m), 2313(m), 1718(s), 1703(s), 1671(s), 1625(s), 1546(s), 1531(s), 1500(s), 1422(s), 1407(m), 1375(s), 1281(s), 1250(m), 1125(m), 1063(m), 1047(m), 812(s), 750(w); MS (EI), m/z (I) = 176(8), 161(3), 134(14), 119(15), 105(4), 85(43), 56(76), 57(74), 43(91), 41(100); HRMS calcd. for $\text{C}_{11}\text{H}_{16}\text{Si}$: 176.1022; found: 176.0995.

Steady state photolysis experiments were carried out in a Rayonet reactor fitted with 6–10 RPR-2537 lamps, on argon-saturated solutions contained in quartz tubes. In some cases, KrF excimer (248 nm) or nitrogen (337 nm) lasers, operated at 0.5 Hz with the intensity reduced using neutral density filters, were employed as excitation sources. Product yields were estimated in small scale runs, from the GC peak areas relative to that of an internal standard (usually decane). These were not corrected for differences in FID response factors.

The products of photolysis of **1** in deoxygenated methanol solution containing 0.1 M HCl were identified by GC/MS and GC coinjection with authentic samples. The major product of dark reaction of **6** with methanol was tentatively identified as methylmethoxy(*o*-tolyl)(1-propyl)silane (**15**; 76%) by ^1H NMR and GC/MS, on the crude mixture obtained from stirring a sample of **6** (0.1 g) in methanol (5 mL) for fourteen hours at 25°C, followed by evaporation of the solvent and redissolution in CDCl_3 . The ^1H NMR spectrum of the compound exhibited singlets at δ 0.41 (SiCH_3), 2.46

(*o*-tolyl CH_3), and 3.41 (OCH_3) and resonances assignable to the *n*-propyl group (δ 0.90 (t, 2H), 0.95 (t, 3H), 1.38 (m, 2H)), and the following mass spectrum: m/z (I) = 208 (4), 193 (2), 165 (100), 151 (12), 135 (33), 119 (12), 105 (18), 91 (11), 59 (20). Both the photolysis and dark reaction mixtures also contained a second minor isomer in the same yield relative to **15** (1:8) which was tentatively identified as benzylmethylmethoxy(1-propyl)silane (**16**, 21%) on the basis of its mass spectrum: m/z (I) = 208 (17), 165 (15), 151 (10), 133 (12), 117 (90), 91 (30), 75 (100), 59 (30)). The latter clearly shows the fragmentation pattern expected for a benzylsilane.

The products of steady state photolysis of **2–4** in hexane, hexane containing 0.1 M methanol, or neat methanol were identified by GC coinjection with authentic samples. In the few cases where these were not available, tentative identification was made on the basis of GC/MS. For example photolysis of **2** in hexane yielded an isomer in ~10% yield, which was barely resolved from **2** under our GC/MS conditions. It exhibited the following mass spectral data: MS, m/z (I) = 226 (7), 211 (100), 195 (7), 181 (10), 165 (15), 148 (67), 133 (15), 105 (22), 91 (10). An analogous product was formed in ~35% yield from photolysis of **4** in hexane solution, and tentatively identified as dimethylphenyl(*o*-tolyl)silane (**18b**) m/z : (I) = 226 (7), 211 (100), 195 (7), 181 (10), 165 (15), 148 (67), 133 (15), 105 (22), 91 (10). Disiloxane **17** from photolysis of **2** in methanol solution was identified on the basis of its ^1H NMR (δ 1.45 (m, 8H), 1.67 (m, 2H), 2.06 (m, 2H), 7.41 (m, 6H), 7.61 (m, 4H)) and mass spectrum: m/z (I) = 310 (3), 282 (25), 269 (100), 254 (50), 241 (78), 227 (27), 197 (36), 195 (28), 181 (39), 119 (27), 105 (59), 93 (16), 78 (19) (35).

The toluene derivatives **13a**, **b**, **d**, and **24b** were detected by UV absorption and ^1H NMR spectroscopy on the crude mixtures from 254-nm photolysis of **1–5** (0.01–0.02 M) to 5–10% conversion in hexane or cyclohexane- d_{12} . The four compounds exhibited identical UV spectra (λ_{max} = 335 nm; see Fig. 1 for **13a**) and the following ^1H NMR spectra: **13a** (from **1**; silacyclobutyl Hs excluded), δ = 0.49 (s, 3H), 3.18 (m, 1H), 4.12 (s, 1H), 4.46 (s, 1H), 5.74 (m, 3H), 5.97 (d, 1H, J = 8.7 Hz); **13b** (from **2**; phenyl and silacyclobutyl Hs excluded), δ = 3.34 (m, 1H), 4.42 (s, 1H), 4.58 (s, 1H), 5.60 (m, 1H), 5.72 (m, 2H), 5.94 (d, 1H, J = 6.3 Hz); **13d** (from **4**; phenyl Hs excluded), δ = 3.33 (m, 1H), 4.41 (s, 1H), 4.76 (s, 1H), 5.82 (m, 1H), 5.86 (m, 2H), 6.14 (d, 1H, J = 7.4 Hz); **24b** (from **5**; phenyl Hs excluded), δ = 3.20 (m, 1H), 4.55 (m, 1H), 5.75 (m, 1H), 5.94 (m, 2H), 6.08 (d, 1H, J = 7.5 Hz). Photolysis of a 0.01 M solution of **3** under the same conditions resulted in the appearance of weak edge absorptions in the 300–340 nm range, even after photolysis for roughly 5 times longer than the other compounds. The ^1H NMR spectrum of the photolysate (after evaporation of the solvent and redissolution in cyclohexane- d_{12}) showed no evidence of absorptions in the 3–6 ppm range.

Nanosecond laser flash photolysis experiments employed the pulses (248 nm; ca. 25 ns; 70–140 mJ) from a Lambda Physik Compex 120 excimer laser filled with F_2 -Kr mixtures in neon, and a microcomputer-controlled detection system (36). The laser beam was unfocussed, and its intensity was reduced to 10–15 mJ at the cell using a series

of stainless steel wire meshes as neutral density filters. Solutions were prepared at concentrations such that the absorbance at the excitation wavelength was ca. 0.7 ($\sim 8 \times 10^{-4}$ M), and were flowed continuously through a 3×7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir. Nitrogen was bubbled continuously through the reservoir throughout the experiments.

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