

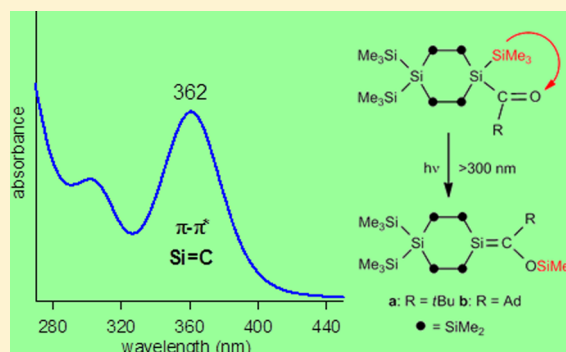
Photoinduced Brook-Type Rearrangement of Acylcyclopolysilanes

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S Supporting Information

ABSTRACT: Previously unknown 1,1,4-tris(trimethylsilyl)-4-acyldodecamethylcyclohexasilanes $(\text{Me}_3\text{Si})_2\text{Si}_6\text{Me}_{12}(\text{Me}_3\text{Si})\text{COR}$ (**16a**, $\text{R} = \text{tert-butyl}$; **16b**, $\text{R} = 1\text{-adamantyl}$) have been synthesized by the reaction of the potassium silanides $(\text{Me}_3\text{Si})_2\text{Si}_6\text{Me}_{12}(\text{Me}_3\text{Si})\text{K}$ with acid chlorides ClCOR , and their photochemical rearrangement reactions have been studied. The molecular structures of **16a,b** as determined by single-crystal X-ray diffraction analysis exhibit an unusual twist-boat conformation of the cyclohexasilane ring. When **16a,b** were photolyzed with $\lambda > 300 \text{ nm}$ radiation, they underwent Brook type $1,3\text{-Si} \rightarrow \text{O}$ migration reactions to generate the cyclohexasilanes **17a,b** with exocyclic $\text{Si}=\text{C}$ bonds along with smaller amounts of the ring-enlarged species **19a,b** with endocyclic $\text{Si}=\text{C}$ double bonds. While **17a,b** were stable enough to allow characterization by NMR and UV absorption spectroscopy, the less stable products **19a,b** could only be observed in the form of their methanol adducts.

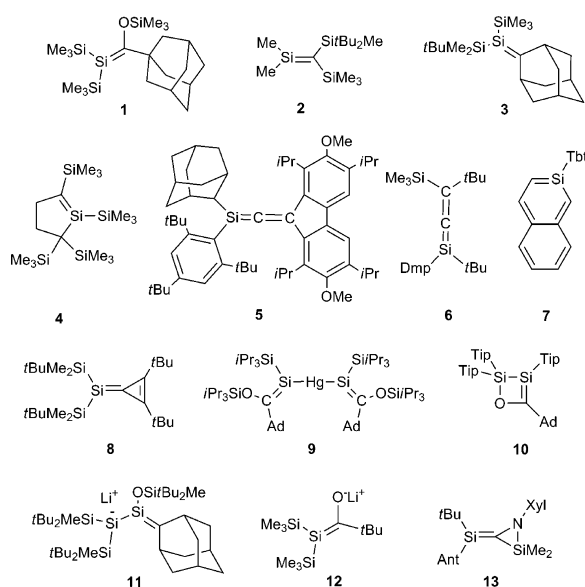


INTRODUCTION

Silenes with various structures have been isolated and characterized since Brook and subsequently Wiberg about 30 years ago reported on the first stable species which contain $\text{Si}=\text{C}$ double bonds (compare Chart 1).¹ Brook utilized a photochemical $1,3\text{-Si} \rightarrow \text{O}$ shift of a SiMe_3 group of the

acylpolsilane $(\text{Me}_3\text{Si})_3\text{SiCOAd}$ ($\text{Ad} = 1\text{-adamantyl}$) to generate the silene **1**,² while Wiberg obtained the donor-free species **2** by a route involving intramolecular lithium fluoride elimination.³ Further advances in $\text{Si}=\text{C}$ double-bond chemistry include the synthesis of the stable silene **3** by Apeloig and co-workers via a sila-Peterson type reaction⁴ and the synthesis of the endocyclic silene **4**, obtained by rearrangement of a silylene.⁵ In addition, stable 1-silaallenes **5** and **6** have been reported by the groups of West and Pietschnig,⁶ while Okazaki and Tokitoh published a series of papers on stable sila-aromatic compounds such as the 2-silaphthalene **7**.⁷ Only a few years ago, Kira et al. isolated and structurally characterized the 4-silatriafulvene **8**.⁸ Even more recently, the first example of the stable metal-substituted silene **9** was synthesized by Bravo-Zhivotovskii and Apeloig et al.,⁹ while Scheschkewitz and Sekiguchi et al. reported on the formation of the cyclic Brook-type silene **10** from the disilene $\text{Tip}_2\text{Si}=\text{SiTip}_2\text{Li}$ ($\text{Tip} = 2,4,6\text{-iPr}_3\text{C}_6\text{H}_2$) and AdCOCl .¹⁰ Charged silenes have been described by Sekiguchi et al., who synthesized the silyl anion substituted silene **11**,¹¹ and by Ottosson et al., who succeeded in the isolation of the first stable 2-silenolate **12**.¹² In the most recent paper, finally, Iwamoto et al. reported on the synthesis of the exocyclic silene **13** showing a distinct intramolecular charge transfer transition from the π orbital of the $\text{Si}=\text{C}$ double bond to the π^* orbital of the anthryl moiety.¹³

Data on substituted silenes clearly demonstrate that the stability of silenes is strongly influenced by the choice of the substituents attached to the $\text{Si}=\text{C}$ moiety.¹⁴ As already has been realized by Brook, the steric bulk of the substituents on

Chart 1. Selected Stable Silenes^a

^aAbbreviations: Tip, 2,4,6- $\text{iPr}_3\text{C}_6\text{H}_2$; Tbt, 2,4,6-bis(trimethylsilyl)-phenyl; Dmp, 2,6-dimesitylphenyl; Ad, 1-adamantyl; Ant, 9-anthryl.

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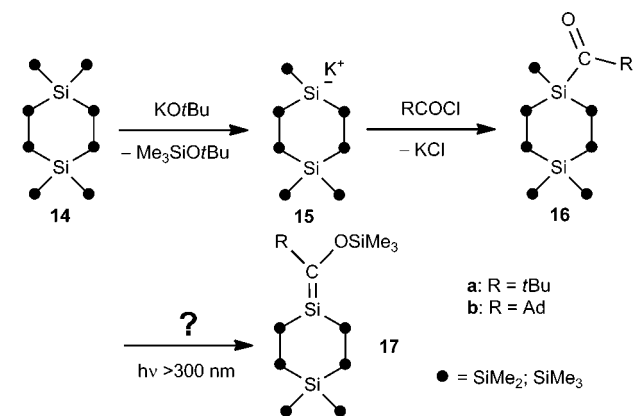
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the carbon atom is certainly a key factor in the kinetic stabilization of silenes with regard to dimerization. Additional stability is gained in silenes influenced by reversed ($\text{Si}^{\delta-}=\text{C}^{\delta+}$) bond polarization effected by π -donor substituents on the carbon atom.¹⁵ Reverse-polarized silenes such as the Brook-type silenes **1**, the silatrimfulvene **8**, or the transient 2-amino-2-siloxysilenes recently investigated by Ottosson et al.¹⁶ are less reactive toward moisture and alcohols than naturally polarized silenes ($\text{Si}^{\delta+}=\text{C}^{\delta-}$), and addition of alcohol often proceeds by C–O instead of Si–O bond formation. In contrast to the naturally polarized silenes, which give $[2 + 2]$ and ene adducts as well, the reverse-polarized silenes react selectively with dienes to yield only $[4 + 2]$ adducts.

Most silenes are acyclic molecules. To the best of our knowledge, in addition to the silaaromatics 1- and 2-silanaphthalene, 9-silaanthracene, and 9-silaphenanthrene, **4** and **10** are the only stable silenes with the unsaturated silicon atom incorporated into cyclic structures which have been isolated and structurally fully characterized so far. According to DFT calculations on small model compounds the slight pyramidalization of the tricoordinate Si atom in **10** is due to reverse ($\text{Si}^{\delta-}=\text{C}^{\delta+}$) bond polarization rather than steric congestion around the $\text{Si}=\text{C}$ double bond. In line with reverse polarization **10** turned out to be remarkably stable. In contrast to Brook's silene **1** it reacts only slowly with air and moisture and does not react with MeOH at any appreciable rate.¹⁰

Larger cyclopolsilanes containing either endo- or exocyclic $\text{Si}=\text{C}$ double bonds have not been described in the literature before. Because we are interested in substituent effects on polysilane frameworks in general,¹⁷ we now want to report on the outcome of our attempts to synthesize the previously unknown Brook-type cyclic silenes **17a,b** by the photolysis of the acylcyclohexasilanes **16a,b**, which we prepared successfully for the first time employing standard procedures for cyclopolsilane synthesis (Scheme 1).¹⁸

Scheme 1. Synthetic Approach toward Exocyclic Silenes



RESULTS AND DISCUSSION

Synthesis of Acylcyclohexasilanes. According to Scheme 1, the potassium silanide **15** cleanly reacts with equimolar amounts of acid chlorides ClCOR (R = tBu, Ad) in diethyl ether solution at -80°C to give the air-stable and crystalline acylcyclohexasilanes **16a,b** in yields of $>60\%$. Analytical data obtained for **16a,b** (see the Experimental Section) are consistent with the proposed structures. Substitution of one SiMe₃ group in **14** produces four magnetically nonequivalent

endocyclic silicon atoms. Thus, the ^{29}Si NMR spectra of **16a,b** exhibit two resonance lines near -38 ppm for the endocyclic SiMe₂ groups, one signal for the Si atom bearing the acyl group near -70 ppm, and one signal for the tertiary Si atom around -130 ppm.¹⁹ The methyl and SiMe₃ substituents, furthermore, can be attached either *cis* or *trans* relative to the acyl group, which leads to four nonequivalent methyl and three nonequivalent SiMe₃ groups. The resulting number of resonance lines actually appears in the experimental NMR spectra, although some ^1H signals are too close to each other to be completely resolved.

Single crystals suitable for X-ray structure analysis could be grown from compounds **16a,b**. The obtained molecular structures are depicted in Figures 1 and 2 together with

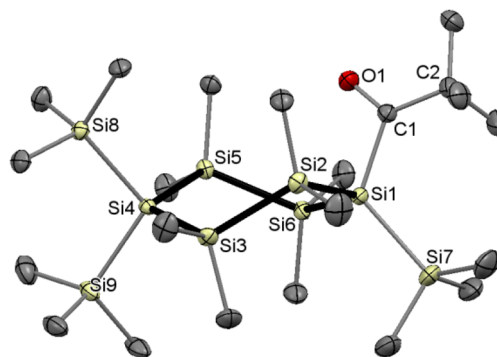


Figure 1. ORTEP diagram for compound **16a**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond and torsion angles (deg) with estimated standard deviations: Si–Si(mean) 2.356, C(1)–O(1) 1.213(2), Si(1)–C(1) 1.970(1), Si–C_{methyl}(mean) 1.880; Si(6)–Si(1)–Si(2) 111.73(2), Si(3)–Si(2)–Si(1) 111.88(2), Si(4)–Si(3)–Si(2) 113.50(3), Si(5)–Si(4)–Si(3) 112.03(2), Si(4)–Si(5)–Si(6) 113.04(2), Si(5)–Si(6)–Si(1) 114.46(2), O(1)–C(1)–C(2) 120.2(1), O(1)–C(1)–Si(1) 113.9(1), C(2)–C(1)–Si(1) 125.9(1), C(1)–Si(1)–Si(7) 120.8(5), C(1)–Si(1)–Si(6) 99.1(5), C(1)–Si(1)–Si(2) 101.2(5), C–Si–C(mean) 107.6; O(1)–C(1)–C(2)–Si(1) 177.2(2).

selected bond distances, bond angles, and dihedral angles. **16a,b** crystallize in the monoclinic space group $P2_1/n$ and in the triclinic space group $P\bar{1}$, respectively. In both structures the cyclohexasilane ring adopts a twist-boat conformation, which is rather unusual, because most cyclohexasilanes studied so far feature a chair conformation of the cyclopolsilane cycle.²⁰ The geometry around the endocyclic silicon atoms is approximately tetrahedral with Si–Si–Si bond angles close to the respective angles found in other cyclohexasilane structures,^{18,20,21} although Si(1) exhibits some distortion due to the steric bulk of the attached *t*-Bu or Ad group.

Si–Si bond lengths between 2.34 and 2.37 Å were observed; the average Si–Si bond distance of 2.36 Å is typical for Si–Si single bonds in cyclopolsilanes²² and agrees well with the Si–Si covalent bond length of 2.34 Å. The sum of the bond angles around the carbonyl C atom in **16a,b** is close to 360° and reflects the trigonal-planar geometry within the SiRC=O moiety. Unexceptional carbonyl C=O bond lengths of 1.21 and 1.23 Å were measured,²³ while the silicon carbonyl group bond distances at 1.97 and 1.96 Å are considerably elongated relative to the length of an average Si–C(sp³) bond,²⁴ as observed earlier for other acyl silanes.²⁵ In order to minimize steric congestion, the bulky *t*-Bu or Ad groups are oriented

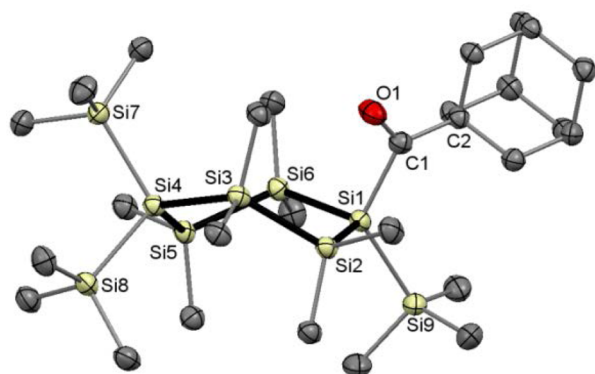


Figure 2. ORTEP diagram for compound **16b**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond and torsion angles (deg) with estimated standard deviations: Si–Si(mean) 2.358, C(1)–O(1) 1.226(3), Si(1)–C(1) 1.962(2), Si–C_{methyl}(mean) 1.883; Si(6)–Si(1)–Si(2) 111.73(3), Si(3)–Si(2)–Si(1) 115.54(3), Si(4)–Si(3)–Si(2) 113.61(3), Si(5)–Si(4)–Si(3) 111.67(3), Si(4)–Si(5)–Si(6) 114.40(3), Si(5)–Si(6)–Si(1) 112.18(3), O(1)–C(1)–C(2) 119.9(2), O(1)–C(1)–Si(1) 113.2(2), C(2)–C(1)–Si(1) 126.9(2), C(1)–Si(1)–Si(9) 121.78(7), C(1)–Si(1)–Si(6) 102.07(7), C(1)–Si(1)–Si(2) 99.12(7), C–Si–C(mean) 107.6; O(1)–C(1)–C(2)–Si(1) –176.9(3).

toward the outside of the molecules, which brings the carbonyl oxygen atoms in **16a,b** in rather close contact to the endocyclic Si–Si bond system, with nonbonding distances to the plane defined by Si(1), Si(2), and Si(6) of only 2.66 and 2.65 Å, respectively. This structural feature will gain importance because it can be used to rationalize the unprecedented course of the photolysis experiments described in the next section of this paper.

Photolysis of Acylcyclohexasilanes. When the acylsilanes **16a,b** in *d*₆-benzene solution (*c* ≈ 0.07 M) in the absence of any other reactant were photolyzed with λ > 300 nm radiation, yellow solutions were obtained. NMR analysis performed after an irradiation time of 4 h showed the formation of the exocyclic silenes **17a,b** along with unreacted starting material. Figure 3 presents the ²⁹Si NMR spectrum of the photolysis product derived from **16b**, including the

assignment of the observed resonance lines. The remaining spectra can be found in the Supporting Information. ²⁹Si and ¹³C NMR chemical shift data of **17a,b** are summarized in Table 1. ¹³C and ²⁹Si NMR signals characteristic of Si=C were

Table 1. ¹³C and ²⁹Si Chemical Shift Data of Silenes **17a,b**^a

	R = <i>t</i> -Bu (17a)	R = 1-Ad (17b)
	¹³ C NMR	
Si=C	214.39	215.93
–R	42.70, 30.49	45.04, 42.15, 36.78, 29.03
–SiMe ₃	3.27, 1.17	3.29, 1.43
–SiMe ₂ –	–0.60, –1.49, –1.66, –2.54	–0.32, –1.43, –1.62, –2.47
	²⁹ Si NMR	
Si=C	37.00	37.45
–OSiMe ₃	13.16	13.27
–SiMe ₃	–8.79	–8.69
–SiMe ₂ –	–34.41, –36.81, –37.44, –37.58	–34.68, –36.75, –37.40, –37.48
SiSi ₄	–132.43	–132.38

^aIn C₆D₆ solution. All values are vs external TMS, in ppm.

observed near 215 and 37 ppm, respectively, while the ²⁹Si signal near 13 ppm is easily assigned to the OSiMe₃ moiety formed by the photochemical 1,3-trimethylsilyl shift. These values compare reasonably well with those measured for the acyclic Brook-type silenes (Me₃Si)₂Si=C(OSiMe₃)R (R = *t*-Bu, Ad).² The ¹H NMR spectrum of the photolysis product of **16a** contains, in addition to poorly resolved signals between δ 0.2 and 0.6 ppm for the SiMe₃ and SiMe₂ groups, absorptions at δ 1.26 and 0.96 ppm for the C(CH₃)₃ substituents in **16a** and **17a**, respectively. By integration of these signals a silene/acylsilane ratio of approximately 40/60 could be estimated.

The interesting observation that it is possible to generate **17a,b** photochemically with two competing chromophores in the acylcyclopolysilane, the cyclohexasilane moiety and the acyl group, can be rationalized on the basis of the UV spectra of **13** and **15**. While **14** does not absorb above 300 nm²⁶ **16a,b** exhibit weak absorption bands near 370 nm (*ε* ≈ 200 L mol^{–1} cm^{–1}), which are easily assigned to the n–π* transition of the C=O group in accordance with the literature.² Thus, the acyl group in **16** is selectively excited upon irradiation with 360 nm light, while the endocyclic σ(SiSi) electron system is not affected, which leads to the observed Brook type reaction course.

Further irradiation afforded increasing amounts of unidentified polymeric decomposition products at the expense of **17a,b**, illustrated by the appearance of broad signal groups typical for polymers containing (SiMe)_{*n*} (δ 0–0.6 ppm) and *t*-Bu (Ad) (δ 1.0–2.0 ppm) groups in the ¹H NMR spectra of the resulting photolysis solutions (compare Figure 4). Apparently **17a,b** are less stable under photolytic conditions than Brook's open-chain compounds, presumably as a consequence of the presence of the cyclohexasilane cycle. Cyclohexasilanes such as Si₆Me₁₂ have been shown earlier to undergo silylene extrusion and ring contraction reactions when photolyzed with 254 nm light.²⁷ Although experimental evidence is missing,²⁸ it is not unlikely that **16a,b** exhibit similar reactivity upon irradiation at 360 nm because the wavelength for the onset of the photoinduced silylene extrusion might be considerably red-shifted due to conjugation of the exocyclic π(Si=C) chromophore with the endocyclic σ(SiSi) system. Thus, Si₆Me₁₂ does not absorb light of wavelengths >270 nm, while the UV absorption spectra of

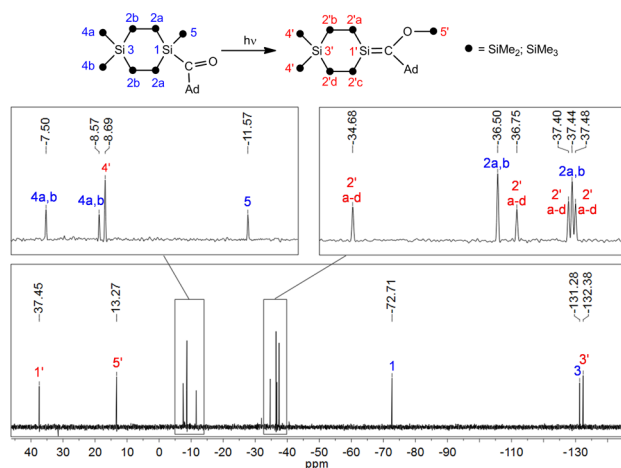


Figure 3. ²⁹Si NMR spectrum after photolysis of **16b** in C₆D₆ solution with a 150 W mercury lamp through Pyrex glass for 4 h at room temperature, including assignment of the resonance lines.

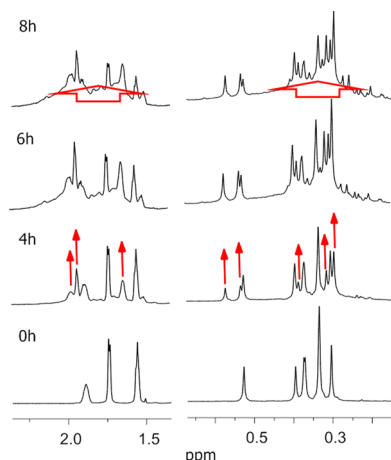


Figure 4. ^1H NMR spectrum after photolysis of **16b** with a 150 W mercury lamp through Pyrex glass for 0, 4, 6, and 8 h at room temperature.

17a,b show absorption bands at 362 and 302 nm of considerable intensity (Figure 5). It is also interesting to note

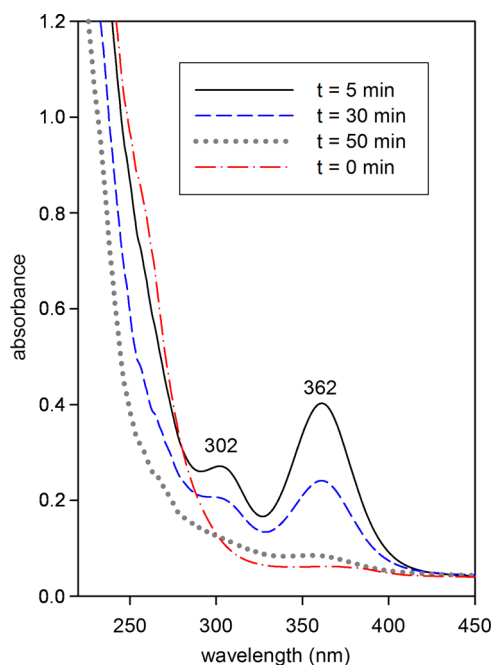


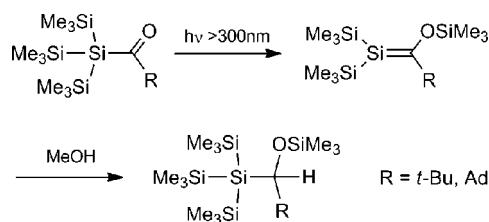
Figure 5. UV absorption spectra recorded after irradiation of a solution of **16b** in C_6H_{12} with a 4 W 366 nm lamp ($c = 5 \times 10^{-5}$ mol L^{-1} ; $t = 0, 5, 30, 50$ min).

that there is no evidence for the presence of head-to-head dimers arising from 2 + 2 cycloaddition reactions of **17a,b**, which are the decomposition products of most Brook-type silenes such as $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)t\text{-Bu}$.²⁹ This is conclusive, because the formation of head-to-head dimers of **17a,b** would cause severe steric strain due to the cyclic structure of the polysilane backbone, which apparently totally inhibits dimerization. Since no dimers were present in the photolysis mixtures, attempts were made to crystallize **17a,b** from the photolysis mixtures obtained after an irradiation time of 4 h. Removal of solvent in vacuo, however, gave viscous yellow oils which contained mainly polymeric material of undefined composition along with unreacted **16a,b**.

As mentioned earlier, solutions of the silenes **17a,b** are yellow. UV absorption spectra recorded after irradiation of a diluted hydrocarbon solution of **16b** with λ 366 nm radiation in a quartz cuvette are presented in Figure 5. The quasi-identical spectra obtained for **16a** may be found in the Supporting Information. After an irradiation time of 5 min two absorption bands appear centered at $\lambda_{\text{max}} \sim 300$ and ~ 360 nm which were not present prior to photolysis. The latter band tailing into the visible region is easily assigned to a $\pi-\pi^*$ transition within the $\text{Si}=\text{C}$ fragment. Quite remarkably, it is shifted to the red by 20 nm with respect to the related acyclic silenes $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{R}$ ($\text{R} = t\text{-Bu, Ad}$), which have $\pi-\pi^*$ absorptions of around 340 nm.² The bathochromic shift of the $\pi-\pi^*$ absorption band observed for **17a,b** very likely might be explained by enhanced conjugation between the endocyclic $\sigma(\text{Si}-\text{Si})$ bond system with the exocyclic $\text{Si}=\text{C}$ double bond. The data presented in Figure 5, furthermore, also reflect the instability of **17a,b** under photolytic conditions. Upon prolonged irradiation the intensity of the 300 and 360 nm absorption bands decreases until nearly complete photo-bleaching occurs after about 20 and 50 min for **17a,b**, respectively. **17b**, therefore, seems to be slightly more stable, which is also evident from the relative intensities of the signals in the NMR spectra of the obtained photolysis solutions.

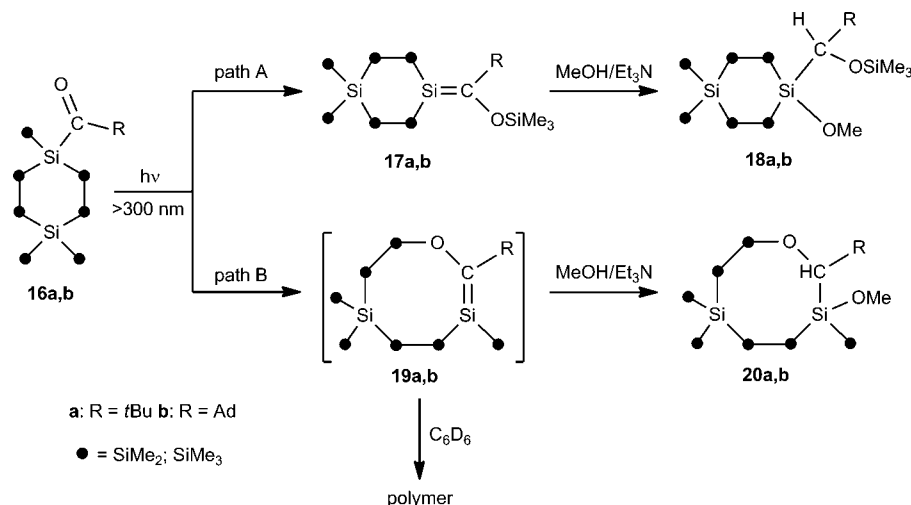
Trapping Experiments. Alcohols are known to be very effective trapping agents for Brook-type silenes.¹ Thus, photolysis of acyltris(trimethylsilyl)silanes in the presence of MeOH to which a trace of weak base such as pyridine or Et_3N has been added usually affords the 1,2-addition product across the $\text{Si}=\text{C}$ double bond with the $\text{RO}-$ group attached to silicon and the alcoholic H attached to carbon (Scheme 2). Earlier

Scheme 2. Photolysis of Acyltris(trimethylsilyl)silanes in the Presence of Methanol



work on the photolysis of acylsilanes has shown that in the absence of base subsequent acid-catalyzed C–O or Si–O bond cleavage reactions of the initially formed trapping products occur, which lead to the formation of complex mixtures of “solvolysis” products.³⁰ The acid catalysts appeared to be byproducts of the photolysis reaction. In contrast to the behavior described in Scheme 2, photolysis of the cyclic acyl silanes **16a,b** in 2.5/1 $\text{C}_6\text{D}_6/\text{MeOH}$ gave only about 80% of the adducts **18a,b** expected from trapping of the silenes **17a,b** which already have been observed in the absence of trapping reagents. Rather surprisingly, about 20% of the cyclosiloxanes **20a,b** was also obtained, which are the trapping products of the silenes **19a,b**.

These results are presented in Scheme 3 and clearly indicate that photochemical rearrangement of acylcyclohexasilanes to species containing $\text{Si}=\text{C}$ double bonds can occur in two different ways. In addition to the “normal” Brook-type rearrangement including a 1,3-Si \rightarrow O trimethylsilyl shift to give silenes **17a,b** with exocyclic $\text{Si}=\text{C}$ bonds (reaction path A), an unprecedented rearrangement takes place, including ring

Scheme 3. Photolysis of Acylcyclohexasilanes **16a,b** in the Presence of Methanol/ Et_3N 

scission and a 1,3-Si \rightarrow O dimethylsilyl shift with formation of the ring-enlarged silenes **19a,b** with endocyclic Si=C double bonds (reaction path B). Likely the formation of **19a,b** can be interpreted as arising from the molecular structure of the acyl silanes **16a,b**, because reaction path B might become a favorable process, due to last but not least the close proximity of the carbonyl oxygen atom to the adjacent endocyclic Si-Si bonds already mentioned above (compare Figures 1 and 2). Furthermore, it is obvious that **19a,b** are not stable under photolytic conditions in the absence of trapping reagents because they were not detected when the photolysis was carried out in pure hydrocarbon solvents.

Pure **18a** and **20a** could be isolated from the crude photolysis solution by column chromatography over silica gel with heptane as an eluant followed by crystallization from acetone. Pure **18b** was obtained as the less soluble product from the mixture with **20b** by repeated crystallization from acetone. Slightly impure crystals of **20b** were isolated in low yield from the combined mother liquors after concentration and repeated crystallization from acetone at -30°C . Nevertheless, the identity of the individual adducts **18a,b** and **20a,b** was established by NMR and high-resolution mass spectroscopy. Analytical data are summarized in the Experimental Section, and experimental ^1H NMR spectra can be found in the Supporting Information. All adducts showed nine ^{29}Si resonances, in line with the presence of nine magnetically inequivalent silicon atoms. For the six-membered cycles **18a,b** four signals for the endocyclic SiMe_2 groups between -32 and -41 ppm, two SiMe_3 resonances near -6 and -9 ppm, and one signal for the OSiMe_3 group near $+15$ ppm were detected. The isomers **20a,b**, in contrast, had three SiMe_2 signals between -32 and -44 ppm and one signal for the OSiMe_2 group at significantly lower field ($\sim +19$ ppm), while three SiMe_3 signals appeared near -8.5 (two signals) and -19 ppm. In ^{13}C NMR eight lines appear at the high-field end of the spectra for the magnetically nonequivalent methyl groups attached to the endocyclic silicon atoms.

The molecular structures of **18b** and **20a,b** in the solid state as determined by single-crystal X-ray diffraction are presented in Figures 6–8 together with selected bond distances, bond angles, and dihedral angles. **18b** crystallizes in the monoclinic space group $P2_1/c$ with the cyclohexasilane ring in a slightly distorted chair conformation and unexceptional bond lengths

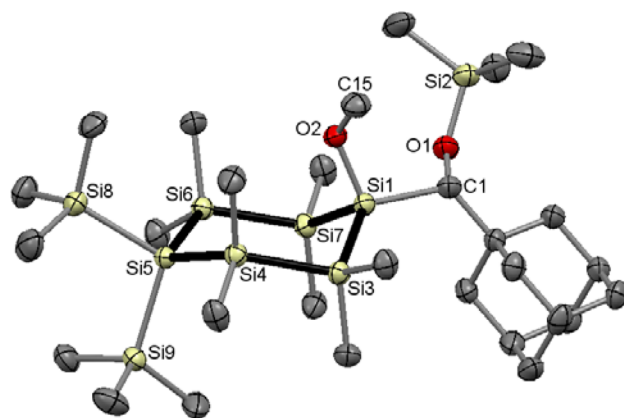


Figure 6. ORTEP diagram for compound **18b**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: Si-Si(mean) 2.362, C(1)-O(1) 1.434(3), Si(1)-O(2) 1.679(2), Si(2)-O(1) 1.651(2), Si(1)-C(1) 1.930(3), Si-C_{methyl}(mean) 1.877; Si(7)-Si(1)-Si(3) 110.14(3), Si(1)-Si(3)-Si(4) 107.90(3), Si(3)-Si(4)-Si(5) 115.20(4), Si(4)-Si(5)-Si(6) 112.25(3), Si(5)-Si(6)-Si(7) 117.05(3), Si(6)-Si(7)-Si(1) 107.56(3), Si(1)-O(2)-C(15) 121.7(2), C(1)-O(1)-Si(2) 128.4(2), C-Si-C(mean) 107.8.

and angles. **20a,b** crystallize in the triclinic space group $P\bar{1}$. The eight-membered heterocycle adopts a boatlike conformation. The most prominent feature of the molecular structures of **20a,b** is the position of the endocyclic oxygen atom, which is oriented toward the center of the ring in order to allow an exocyclic arrangement with minimum steric congestion for the bulky R group at C(1). **20a,b** contain two chiral centers. In both cases one molecule of the S,S and one molecule of the R,R enantiomer are present in the unit cell, which are related by an inversion center (compare Figure 9). Obviously the diastereomeric species with R,S and S,R configuration were not formed, because otherwise a second set of NMR signals should have been observed.

Photolysis of Acylbicyclo[2.2.2]octasilanes. In contrast to the behavior described above for the acylcyclohexasilanes **16a,b** the photolysis of the 1-trimethylacyl-4-(trimethylsilyl)-dodecamethylbicyclo[2.2.2]octasilane cage **21** in a MeOH/ C_6D_6 mixture gave rise to the formation of the silene-methanol

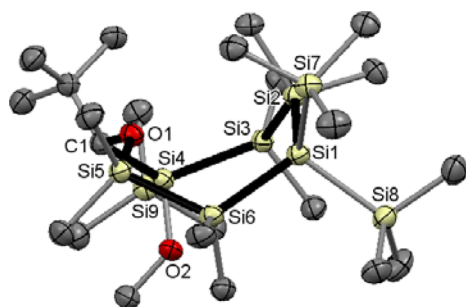


Figure 7. ORTEP diagram for compound **20a**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond and torsion angles (deg) with estimated standard deviations: Si–Si(mean) 2.359, C(1)–O(1) 1.448(3), Si(4)–O(2) 1.672(2), Si(5)–O(1) 1.657(2), Si(4)–C(1) 1.929(2), Si–C_{methyl}(mean) 1.879; Si(6)–Si(1)–Si(2) 112.35(3), Si(1)–Si(2)–Si(3) 119.26(3), Si(2)–Si(3)–Si(4) 122.98(3), Si(5)–Si(6)–Si(1) 115.00(3), Si(4)–O(2)–C(23) 124.0(2), C(1)–O(1)–Si(5) 128.4(2), C–Si–C(mean) 107.4; Si(1)–Si(6)–Si(5)–O(1) –41.4(1), Si(3)–Si(4)–C(1)–O(1) 38.0(1).

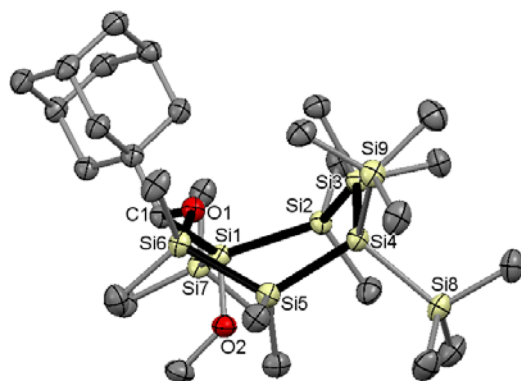


Figure 8. ORTEP diagram for compound **20b**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond and torsion angles (deg) with estimated standard deviations: Si–Si(mean) 2.361, C(1)–O(1) 1.458(3), Si(1)–O(2) 1.673(2), Si(6)–O(1) 1.654(2), Si(1)–C(1) 1.925(3), Si–C_{methyl}(mean) 1.883; Si(1)–Si(2)–Si(3) 123.28(4), Si(2)–Si(3)–Si(4) 120.49(4), Si(3)–Si(4)–Si(5) 111.26(4), Si(4)–Si(5)–Si(6) 114.57(4), Si(1)–O(2)–C(20) 124.6(2), C(1)–O(1)–Si(6) 128.5(2), C–Si–C(mean) 107.6; Si(4)–Si(5)–Si(6)–O(1) 44.2(1), Si(2)–Si(1)–C(1)–O(1) –37.9(2).

adduct **22** along with polymeric material of unknown structure, with no evidence for the presence of products derived from photochemically induced Me₃Si migration (Scheme 4). When it was photolyzed in pure C₆D₆, **21** reacted very slowly to give unidentified polymeric decomposition products. This finding is not surprising, because **21** does not contain a Me₃Si group in a position α to the acyl functionality. A Brook-type 1,3-SiMe₃ shift under formation of an exocyclic silene, thus, is simply not possible.

Although pure **22** could not be isolated from the obtained crude product mixture, its structure has been established by NMR and GC-MS analysis. Analytical data are summarized in the Experimental Section. GC-MS showed only one volatile product with a signal corresponding to the molecular ion at *m/e* 594. Due to the presence of nine inequivalent silicon atoms, nine ²⁹Si resonances were found at –130.5 (SiSi₄), –43.7, –43.5, –40.5, –37.4, and –36.7 (SiMe₂), –5.6 (SiMe₃), +8.6 (SiOMe), and +18.3 ppm ((SiMe₂)O). Consistent with the

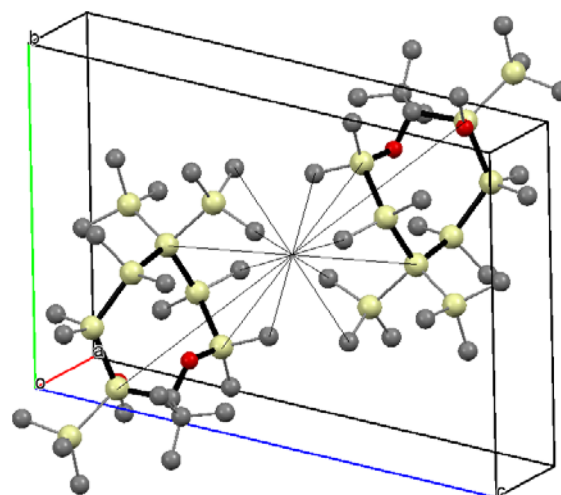
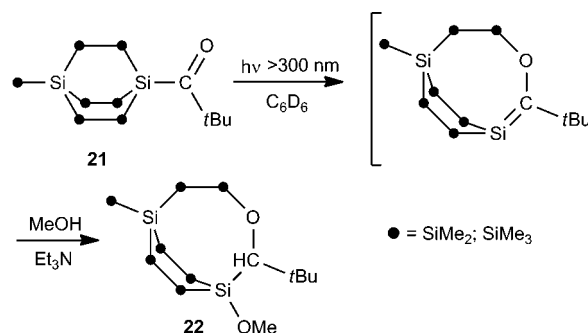


Figure 9. Unit cell of compound **20a** containing one *S,S* and *R,R* enantiomeric pair, which can be interconverted through an inversion center between the molecules.

Scheme 4. Photolysis of Acylbicyclo[2.2.2]octasilane **21** in the Presence of Methanol/Et₃N



proposed structure, ¹H NMR showed a one-proton singlet at δ 3.68 ppm (HCOMe), a three-proton singlet at δ 3.47 ppm (OCH₃), a nine-proton singlet at δ 0.99 ppm (C(CH₃)₃), and a poorly resolved signal group at δ 0.18–0.32 ppm (SiCH₃) in addition to some minor impurities and some polymeric background.

CONCLUSIONS

In summary, we have demonstrated that acylcyclohexasilanes which contain a Me₃Si group in a position α to the acyl substituent upon photolysis undergo Brook-type rearrangement reactions to give products with Si=C double bonds. In contrast to the behavior of branched open-chain substrates as studied extensively by Brook et al. in the past, however, we observed the formation of two products: a cyclohexasilane with an exocyclic Si=C double bond arising from a 1,3-Si \rightarrow O shift of a SiMe₃ group and a ring-enlarged silene with an endocyclic Si=C double bond arising from an unprecedented rearrangement including ring scission and insertion of the Si=C–O fragment into the cyclohexasilane ring. The exocyclic product was stable enough to allow detection by NMR and UV absorption spectroscopy, while the less stable endocyclic product could only be observed in the form of its methanol adduct. Photolysis experiments involving acylbicyclo[2.2.2]-octasilane cages, furthermore, indicated that in the absence of α -SiMe₃ groups exclusively the endocyclic product is obtained.

Further studies with the primary aim to isolate related species with enhanced stability are currently underway.

EXPERIMENTAL SECTION

General Considerations. All experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried using a column solvent purification system.³¹ Commercial KO-*t*-Bu (97%), ClCO-*t*-Bu (99%), and ClCOAd (98%) were used as purchased, Et₃N (99%) was dried by distillation from solid KOH, and commercial anhydrous MeOH was dried with 3 Å molecular sieves. **14** and **15** were synthesized as previously reported.¹⁸ ¹H (299.95 MHz), ¹³C (75.43 MHz), and ²⁹Si NMR spectra (59.59 MHz) were recorded on a Varian INOVA 300 spectrometer in C₆D₆ or CDCl₃ solution and referenced versus TMS using the internal ²H-lock signal of the solvent. Mass spectra were run either on an HP 5971A/5890-II GC/MS coupling (HP 1 capillary column, length 25 m, diameter 0.2 mm, 0.33 μm polydimethylsiloxane) or on a Kratos Profile mass spectrometer equipped with a solid probe inlet. Infrared spectra were obtained on a Bruker Alpha-P Diamond ATR spectrometer from the solid sample. Melting points were determined using a Büchi 535 apparatus and are uncorrected. Elemental analyses were carried out on a Hanau Vario Elementar EL apparatus. Photolyses were performed by using a 150 W medium-pressure mercury lamp (Heraeus TQ 150). Sample solutions were photolyzed under an atmosphere of nitrogen in Pyrex Schlenk or NMR tubes immersed in cold water to ensure ambient sample temperature and to prevent irradiation with light of wavelengths λ < 300 nm. UV absorption spectra of **17a,b** were recorded on a PerkinElmer Lambda 5 spectrometer after irradiation of diluted cyclohexane solutions of **16a,b** (c = 5 × 10⁻⁵ mol L⁻¹) with a 4 W 366 nm lamp at room temperature in quartz cuvettes.

Synthesis of 1-Trimethylacyloctamethyl-1,4,4-tris(trimethylsilyl)cyclohexasilane (16a). A solution of **15** in 20 mL of DME was freshly prepared from 1.74 g (3.0 mmol) of **14** and 0.37 g (3.3 mmol) of KO-*t*-Bu and slowly added to a solution of 0.40 g (3.3 mmol) of ClC-*Ot*-Bu in 50 mL of diethyl ether at -80 °C. Subsequently the mixture was stirred for another 30 min at -80 °C, warmed to room temperature, and finally stirred for an additional 60 min. After aqueous workup with 100 mL of 3% sulfuric acid the organic layer was separated and dried over Na₂SO₄ and the solvents were stripped off with a rotary evaporator. Drying in vacuo (0.02 mbar) and crystallization from acetone solution by slow evaporation of the solvent at room temperature afforded 1.37 g (77%) of analytically pure **16a** as colorless crystals.

Mp: 159–161 °C. Anal. Found: C, 44.15; H, 9.82. Calcd for C₂₂H₆₀OSi₉: C, 45.52; H, 10.19. ²⁹Si NMR (C₆D₆, TMS, ppm): -7.77, -8.62, -11.55 (SiMe₃); -37.04, -38.02 (SiMe₂); -71.86 (SiC*Ot*Bu); -131.46 (Si(SiMe₃)₂). ¹³C NMR (C₆D₆, TMS, ppm): 245.41 (SiC=O); 48.77 (C(CH₃)₃); 24.75 (C(CH₃)₃); 3.75, 3.70, 2.55 (Si(CH₃)₃); -0.74, -0.87, -2.20, -2.26 (Si(CH₃)₂). ¹H NMR (C₆D₆, TMS, ppm, relative intensity): 0.96 (9H, s, C(CH₃)₃); 0.50, 0.36, 0.35, (6H each, s, Si(CH₃)₂); 0.32 (15H, s, Si(CH₃)₂ + Si(CH₃)₃); 0.29, 0.28 (9H each, s, Si(CH₃)₃). IR (neat): ν(C=O) 1623 (m) cm⁻¹. UV absorption (hexane solution): λ₁ 367 nm (ε₁ = 190 mol⁻¹ cm⁻¹), absorption shoulder at 255 nm (ε₂ = 11000 mol⁻¹ cm⁻¹). HRMS: calcd for [C₂₂H₆₀OSi₉]⁺ (M⁺) 592.2568, found 592.2603.

Synthesis of 1-Adamantylcarbonyloctamethyl-1,4,4-tris(trimethylsilyl)cyclohexasilane (16b). The procedure followed was that used for **16a** with 2.91 g (5.0 mmol) of **14**, 0.62 g (5.5 mmol) of KO-*t*-Bu, and 0.99 g (5.0 mmol) of ClCOAd. Yield: 2.02 g (60%) of analytically pure **16b** as colorless crystals.

Mp: 148–151 °C. Anal. Found: C, 49.91; H, 9.72. Calcd for C₂₈H₆₆OSi₉: C, 50.07; H, 9.91. ²⁹Si NMR (CDCl₃, TMS, ppm): -7.60, -8.30, -10.90 (SiMe₃); -36.80, -37.96 (SiMe₂); -72.06 (SiCOAd); -131.32 (Si(SiMe₃)₂). ¹³C NMR (CDCl₃, TMS, ppm): 248.22 (SiC=O); 51.50 (AdCCO); 36.99, 36.69 (Ad-CH₂); 28.03 (Ad-CH); 3.86, 3.83, 2.83 (Si(CH₃)₃); -0.69, -0.92, -1.68, -2.01 (Si(CH₃)₂). ¹H NMR (CDCl₃, TMS, ppm, relative intensity): 2.06 (3H, b, Ad-CH); 1.72, 1.67 (6H each, b, Ad-CH₂); 0.35, 0.30 (6H each, s, Si(CH₃)₂); 0.28, 0.25 (15H each, s, Si(CH₃)₃ + Si(CH₃)₂);

0.23 (9H, s, Si(CH₃)₃). IR (neat): ν(C=O) 1621 (m) cm⁻¹. UV absorption (hexane solution): λ₁ 371 nm (ε₁ = 200 mol⁻¹ cm⁻¹), absorption shoulder at 250 nm (ε₂ = 12000 mol⁻¹ cm⁻¹). HRMS: calcd for [C₂₈H₆₆OSi₉]⁺ (M⁺) 670.3037, found 670.3065.

Photolysis of 16a,b in Hydrocarbon Solution. A solution of 0.05 mmol of the acylsilane **16a** or **16b** in 0.7 mL of d₆-benzene in an NMR tube was photolyzed with a 150 W mercury lamp at 25 °C for 4 h. At this time ¹H and ²⁹Si NMR analysis showed the formation of the silene **17a** or **17b**, respectively, along with unreacted starting material. For **16a/17a** a silene/acylsilane ratio of approximately 40/60 in the resulting yellow solution was estimated by integration of the C(CH₃)₃ signals in the ¹H NMR spectra. Further irradiation afforded increasing amounts of polymeric decomposition products at the expense of **17a,b**. Attempted removal of the solvent in vacuo after an irradiation time of 4 h also gave rise to extensive product decomposition.

Data for **17a** are as follows. ²⁹Si NMR (C₆D₆, TMS, ppm): 37.00 (Si=C), 13.16 (OSiMe₃), -8.79 (Si(SiMe₃)₂), -34.41, -36.81, -37.44, -37.58 (SiMe₂), -132.43 (Si(SiMe₃)₂). ¹³C NMR (C₆D₆, TMS, ppm): 214.39 (Si=C), 42.70 (C(CH₃)₃), 30.49 (C(CH₃)₃), 3.27 (Si(Si(CH₃)₃)₂), 1.17 (OSi(CH₃)₃), -0.60, -1.49, -1.66, -2.54 (Si(CH₃)₂). ¹H NMR (C₆D₆, TMS, ppm, relative intensity): 1.26 (s, C(CH₃)₃); 0.55–0.28 (several overlapping signals, Si(CH₃)).

Data for **17b** are as follows. ²⁹Si NMR (C₆D₆, TMS, ppm): 37.45 (Si=C), 13.27 (OSiMe₃), -8.69 (Si(SiMe₃)₂), -34.68, -36.75, -37.40, -37.48 (SiMe₂), -132.38 (Si(SiMe₃)₂). ¹³C NMR (C₆D₆, TMS, ppm): 215.93 (Si=C), 45.04, 42.15, 36.78, 29.03 (Ad-C), 3.29 (Si(Si(CH₃)₃)₂), 1.43 (OSi(CH₃)₂), -0.32, -1.43, -1.62, -2.47 (Si(CH₃)₂). ¹H NMR (C₆D₆, TMS, ppm, relative intensity): 1.98 (b, Ad-CH); 1.89, 1.65 (b, Ad-CH₂); 0.57–0.29 (several overlapping signals, Si(CH₃)).

Photolysis of 16a/Methanol. A solution of 0.50 g (0.84 mmol) of **16a** and 3 drops of anhydrous Et₃N in 5 mL of benzene and 2 mL of methanol was photolyzed with a 150 W mercury lamp at 25 °C over 10 h. At this time NMR analysis showed that the starting material had been completely consumed. After removal of the volatile components on a rotary evaporator, 20 mL of pentane was added and the resulting solution was filtered over silica gel. Evaporation of pentane afforded 0.46 g of a semisolid residue containing approximately 80% of **18a** and 20% of **20a**. Pure and colorless crystals of **18a** and **20a** could be isolated from the crude product by column chromatography (heptane, silica gel) followed by crystallization of the individual components from acetone at -30 °C.

Data for **18a** are as follows. Yield: 0.1 g (20%). Mp: 124–127 °C. ²⁹Si NMR (C₆D₆, TMS, ppm): 16.13, 14.95 (SiOMe, OSiMe₃); -6.49, -9.23 (Si(SiMe₃)₂); -33.06, -33.23, -39.57, -41.02 (SiMe₂); -132.22 (Si(SiMe₃)₂). ¹³C NMR (C₆D₆, TMS, ppm): 80.12 (CH(*t*-Bu)OSi); 53.40 (OCH₃); 35.07 (CCH₃)₃; 28.33 (C(CH₃)₃); 3.96, 3.92, 0.85 (Si(CH₃)₃); -0.25, -0.54, -1.34, -1.54, -3.02, -3.15, -3.23, -3.81 (Si(CH₃)₂). ¹H NMR (C₆D₆, TMS, ppm, relative intensity): 3.55 (1H, s, CH(*t*-Bu)OSi); 3.28 (3H, s, OCH₃); 0.93 (s, 9H, C(CH₃)₃); 0.55, 0.47, 0.41, 0.405, 0.37, 0.31, 0.30, 0.28 (3H each, s, Si(CH₃)₂); 0.35, 0.345, 0.252 (9H each, s, Si(CH₃)₃). HRMS: calcd for [C₂₃H₆₄O₂Si₉]⁺ (M⁺) 624.2830, found 624.2814.

Data for **20a** are as follows. Yield: 0.05 g (10%). Mp: 136–138 °C. ²⁹Si NMR (C₆D₆, TMS, ppm): 19.61, 16.78 (OSiMe₂, SiOMe); -8.41, -8.45 (Si(SiMe₃)₂); -19.67 (MeOSiSiMe₃); -32.25, -41.54, -43.11 (SiMe₂); -130.64 (Si(SiMe₃)₂). ¹³C NMR (C₆D₆, TMS, ppm): 80.96 (OCHSi-*t*-Bu); 53.39 (OCH₃); 34.61 (CCH₃)₃; 28.92 (CCH₃)₃; 3.72, 3.54, 1.48 (Si(CH₃)₃); 3.22, -0.10, -1.105, -1.11, -1.50, -2.10, -2.78, -4.11 (Si(CH₃)₂). ¹H NMR (C₆D₆, TMS, ppm, relative intensity): 3.55 (1H, s, OCHSi-*t*-Bu); 3.28 (3H, s, OCH₃); 0.93 (s, 9H, C(CH₃)₃); 0.55, 0.47, 0.41, 0.405, 0.37, 0.31, 0.30, 0.28 (3H each, s, Si(CH₃)₂); 0.35, 0.345, 0.25 (9H each, s, Si(CH₃)₃). HRMS: calcd for [C₂₃H₆₄O₂Si₉]⁺ (M⁺) 624.2830, found 624.2855.

Photolysis of 16b/Methanol. A solution of 0.40 g (0.60 mmol) of **16b** and 3 drops of anhydrous Et₃N in 5 mL of benzene and 2 mL of methanol was photolyzed at 25 °C with a 150 W mercury lamp over 10 h. At this time NMR analysis showed that the starting material had been completely consumed. After removal of the volatile components on a rotary evaporator 20 mL of pentane was added and the resulting

solution was filtered over silica gel. Evaporation of pentane afforded 0.38 g of a semisolid residue containing approximately 80% of **18b** and 20% of **20b**. Small amounts of pure and colorless crystals of **18b** could be isolated as the less soluble product after repeated recrystallization from acetone solution. White crystals of slightly impure **20b** were isolated in low yield from the combined mother liquors after concentration and repeated crystallization from acetone at $-30\text{ }^{\circ}\text{C}$.

Data for **18b** are as follows. Mp: $186\text{--}188\text{ }^{\circ}\text{C}$. ^{29}Si NMR (CDCl_3 , TMS, ppm): 16.26, 14.82 (SiOMe , OSiMe_3); -6.06 , -9.08 ($\text{Si}(\text{SiMe}_3)_2$); -32.55 , -32.74 , -39.23 , -40.66 (SiMe_2); -131.93 ($\text{Si}(\text{SiMe}_3)_2$). ^{13}C NMR (CDCl_3 , TMS, ppm): 81.45 ($\text{CH}(\text{Ad})\text{OSi}$), 53.50 (OCH_3); 40.87, 37.15, 37.10, 28.66 (Ad); 4.10, 4.07, 1.06 ($\text{Si}(\text{CH}_3)_3$); -0.13 , -0.57 , -1.38 , -1.53 , -2.82 , -2.93 , -3.29 , -3.94 ($\text{Si}(\text{CH}_3)_2$). ^1H NMR (CDCl_3 , TMS, ppm, relative intensity): 3.74 (1H, s, $\text{CH}(\text{Ad})\text{OSi}$); 3.37 (3H, s, OCH_3); 1.99 (3H, b, Ad-CH), 1.7–1.5 (12H, b, Ad-CH_2); 0.35 (3H, s, $\text{Si}(\text{CH}_3)_2$), 0.30 (6H, b, $\text{Si}(\text{CH}_3)_2$); 0.27, 0.25 (3H each, s, $\text{Si}(\text{CH}_3)_2$); 0.26 (15H, s, $\text{Si}(\text{CH}_3)_3$ + $\text{Si}(\text{CH}_3)_2$); 0.22 (12H, s, $\text{Si}(\text{CH}_3)_3$ + $\text{Si}(\text{CH}_3)_2$); 0.125 (9H, s, $\text{Si}(\text{CH}_3)_3$). HRMS: calcd for $[\text{C}_{29}\text{H}_{70}\text{O}_2\text{Si}_9]^+$ (M^+) 702.3300, found 702.3335.

Data for **20b** are as follows. ^{29}Si NMR (CDCl_3 , TMS, ppm): 19.30, 16.69 (OSiMe_2 , SiOMe); -8.37 , -8.45 ($\text{Si}(\text{SiMe}_3)_2$); -19.74 (MeOSiSiMe_3); -32.23 , -41.36 , -42.93 (SiMe_2); -130.52 ($\text{Si}(\text{SiMe}_3)_2$). ^{13}C NMR (CDCl_3 , TMS, ppm): 81.85 ($\text{SiCH}(\text{Ad})\text{OSi}$); 53.66 (OCH_3); 41.30, 37.00, 36.72, 28.63 (Ad); 3.83, 3.62, 1.81 ($\text{Si}(\text{CH}_3)_3$); 3.62, -0.02 , -1.05 , -1.14 , -1.38 , -2.15 , -2.88 , -3.94 ($\text{Si}(\text{CH}_3)_2$). ^1H NMR (CDCl_3 , TMS, ppm, relative intensity): 3.47 (1H, s, $\text{CH}(\text{O})\text{Ad}$); 3.41 (3H, s, OCH_3); 1.97 (3H, b, Ad-CH); 1.7–1.4 (12H, b, Ad-CH_2); 0.38, 0.31, 0.27, 0.20, 0.17 (3H each, s, $\text{Si}(\text{CH}_3)_2$); 0.25 (6H, b, $\text{Si}(\text{CH}_3)_2$); 0.28, 0.26 (9H each, s, $\text{Si}(\text{CH}_3)_3$), 0.24 (12H, s, $\text{Si}(\text{CH}_3)_3$ + $\text{Si}(\text{CH}_3)_2$). HRMS: calcd for $[\text{C}_{29}\text{H}_{70}\text{O}_2\text{Si}_9]^+$ (M^+) 702.3300, found 702.3348.

Photolysis of 1-Trimethylacetyl-4-(trimethylsilyl)-dodecamethylbicyclo[2.2.2]octasilane (21) in Methanol. A solution of 40 mg (0.071 mmol) of **21** and 3 drops of anhydrous Et_3N in 0.3 mL of benzene and 0.3 mL of methanol in an NMR tube was photolyzed with a 150 W mercury lamp at $25\text{ }^{\circ}\text{C}$ for 10 h. At this time NMR and GC-MS analysis showed the formation of methanol adduct **22**. Attempted purification by crystallization of the oily crude product obtained after evaporation of the solvents failed to yield a crystalline solid.

^{29}Si NMR (CDCl_3 , TMS, ppm): 18.35 (OSiMe_2), 8.63 (SiOMe), -5.65 (SiMe_3); -36.71 , -37.38 , -40.48 , -43.54 , -43.75 (SiMe_2); -130.53 (SiSi_4). ^{13}C NMR (CDCl_3 , TMS, ppm): 76.31 ($\text{CH}(\text{O})\text{-t-Bu}$); 54.53 (OCH_3); 35.50 ($\text{C}(\text{CH}_3)_3$); 28.17 ($\text{C}(\text{CH}_3)_3$), 3.82 ($\text{Si}(\text{CH}_3)_3$), 3.75, -0.05 , -0.25 , -0.36 , -0.66 , -1.08 , -1.48 , -1.68 , -2.23 , -3.32 , -3.85 , -4.07 ($\text{Si}(\text{CH}_3)_2$). ^1H NMR (CDCl_3 , TMS, ppm, relative intensity): 3.68 (1H, s, $\text{CH}(\text{O})\text{tBu}$); 3.47 (3H, s, OCH_3); 0.99 (9H, s, $\text{C}(\text{CH}_3)_3$); 0.32, 0.30, 0.29, 0.27, 0.24, 0.18 (3H each, s, $\text{Si}(\text{CH}_3)_2$); 0.31 (6H, s, $\text{Si}(\text{CH}_3)_3$ + $\text{Si}(\text{CH}_3)_2$), 0.28 (9H, s, $\text{Si}(\text{CH}_3)_3$ + $\text{Si}(\text{CH}_3)_2$), 0.26 (12H, s, $\text{Si}(\text{CH}_3)_3$ + $\text{Si}(\text{CH}_3)_2$). MS (m/e (relative intensity)): 594 (0.7%, M^+).

X-ray Crystallography. For X-ray structure analysis suitable crystals were mounted onto the tip of glass fibers using mineral oil. Data collection was performed on a Bruker Kappa Apex II CCD diffractometer at 100 K using graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073\text{ \AA}$) radiation. Details of the crystal data and structure refinement are provided as Supporting Information. The SHELX version 6.1 program package was used for the structure solution and refinement.³² Absorption corrections were applied using the SADABS program.³³ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the refinement at calculated positions using a riding model as implemented in the SHELXTL program. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-964365 (**16a**), CCDC-964366 (**16b**), CCDC-964367 (**18b**), CCDC-964368 (**20a**), and CCDC-964369 (**20b**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12

Union Road, Cambridge CB2 1EZ, U.K. (fax (internat.), +44-1223/336-033; e-mail, deposit@ccdc.cam.ac.uk).

■ ASSOCIATED CONTENT

Supporting Information

Figures giving ^1H , ^{13}C , and ^{29}Si NMR spectra of **16a** after photolysis in C_6D_6 , the ^{13}C NMR spectrum of **16b** after photolysis, the UV absorption spectrum of the photolysis mixture derived from **16a**, and ^1H , ^{13}C , and ^{29}Si NMR spectra of compounds **18a,b**, **20a,b**, and **22** and tables and CIF files giving crystal, collection, and refinement data for the structures of compounds **16a,b**, **18b**, and **20a,b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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