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Reactions of Silenes with α,β-Unsaturated Aldehydes and Ketones

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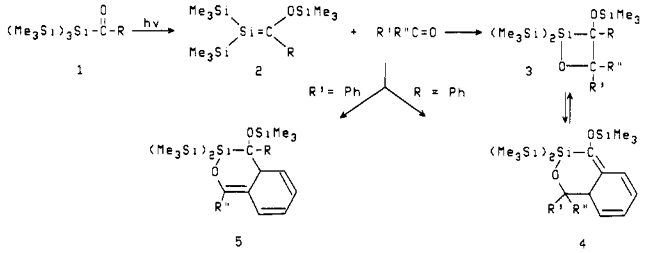
Silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (R = Ad, *t*-Bu, mesityl) react with unsubstituted α,β-unsaturated aldehydes and ketones in a [2 + 4] manner involving both possible regiochemistries, with the 1-sila-3-oxacyclohex-4-ene isomer as the major product. In contrast, α,β-unsaturated aldehydes and ketones having a β-substituent also react in a [2 + 4] manner but with the 1-sila-2-oxacyclohex-3-ene isomer predominating. In addition, the aldehydes, but not the ketones, often formed some of the [2 + 2] siloxetane isomer. The X-ray crystal structure of 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-2-(1-adamantyl)-4-methyl-1-sila-3-oxacyclohex-4-ene is reported, establishing the structure of the major product of the reaction of the adamantylsilene with methyl vinyl ketone. Mechanisms are proposed to account for the observed reactions.

It has previously been shown that relatively stable silenes **2** of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$, derived by photolysis of polysilylacylsilanes **1**, react with simple aldehydes and ketones to give [2 + 2] cycloadducts, the siloxetanes **3**. These species have been fully characterized by spectroscopy and by a crystal structure.[1] During the course of these studies it was occasionally observed, when either the R group of the silene was phenyl or an R group of the ketone R′R″C=O was aromatic (phenyl, *p*-tolyl, or mesityl), that nominal [2 + 4] cycloadditions occurred, yielding either 1-oxa-2-silacyclohex-3-enes (**4**) or 1-sila-2-oxacyclohex-3-enes **5** as the apparent initial products of the reactions, as shown in Scheme I. Thus, the four-π-electron component of the cycloaddition arose either from the Si=C bond and two electrons of an attached phenyl group or from the C=O bond and two electrons of an attached aromatic π system.

These results suggested that is would be of interest to investigate the behavior of the silenes with simple α,β-unsaturated compounds. The reaction of the silene $Me_2Si{=}CHPh$ with propenal at high temperatures has been described, and the results can be interpreted on the basis of competing [2 + 2] and [2 + 4] reactions.[2] The results described below reveal that the reactions of our silenes with α,β-unsaturated aldehydes and ketones may follow several modes, depending on the nature of the carbonyl compound employed.

Three silenes **2** were employed, having R = Ad, *t*-Bu, and mesityl,[2] and these were allowed to react with propenal, crotonaldehyde, or cinnamaldehyde, as representative α,β-unsaturated aldehydes and with methyl vinyl ketone (MVK) and benzalacetophenone as typical α,β-unsaturated ketones. The reactions were run in two modes: the first involved cophotolysis at wavelengths of 360 nm or longer of the appropriate acylsilane[3] precursor **1** of the desired silene **2** with 1 equiv of the carbonyl compound in deuteriobenzene solvent under argon for times varying from a few hours to 2 days. Essentially identical results were obtained if the acylsilane was prephotolyzed to the silene in deuteriobenzene and 1 equiv of the carbonyl compound was then added in the dark. Thus, it is clear that the cycloaddition reactions observed are "dark" reactions, independent of the radiation employed. Also, on the basis of the times required to complete the reactions under the two sets of conditions (the "dark" reaction between preformed silene and the carbonyl reagent was much faster than the cophotolysis method), it is evident that the conversion of the acylsilane to the silene is the rate-determining step.

Scheme I



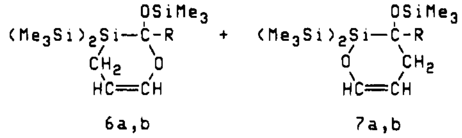
The products of the reactions were characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy and other analytical methods and, in one case, by a crystal structure determination to confirm the structure assigned on the basis of the NMR spectroscopy.

Results and Discussion

Reaction of the adamantyl- (**2a**) and *tert*-butylsilenes (**2b**) with propenal gave two isomeric products, in ratios of 5:1 or greater, as a result of [2 + 4] cycloadditions of the silene to the α,β-unsaturated O=C—C=C system with both possible regiochemistries. The major product in each case was the 1-sila-3-oxacyclohex-3-ene **6**, and the minor product was the 1-sila-2-oxacyclohex-3-ene **7**. The latter product might have been expected to be the major product formed on the basis of a consideration of the polarities of the reactants (eq 1). These results suggest that factors other than charge distribution play a significant role in

$$(Me_3Si)_2Si{=}C(OSiMe_3)R \;+\; CH_2{=}CH{-}CH{=}O \longrightarrow$$

2a R = Ad
2b R = t-Bu



(1)

6a,b 7a,b

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[1] Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorspohl, K. *Organometallics* 1987, *6*, 1246.

[2] Valkovich, P. B.; Weber, W. P. *J. Org. Chem.* 1975, *40*, 229.

[3] Throughout this paper the various silenes and polysilylacylsilanes will be described in terms of the group attached to the sp^2-hybridized carbon of the silene or to the carbonyl group of the acylsilane; e.g. adamantylsilene for $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$ or mesitylacylsilane for $(Me_3Si)_3SiCO(mesityl)$.

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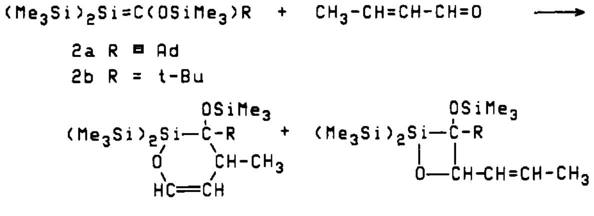
determining the regiochemistry of the products.

When crotonaldehyde was used as the reagent with the same silenes, the major product was the 1-sila-2-oxacyclohex-3-ene **8**, with the minor product being the siloxetane **9** arising from 1,2-addition of the silene across the C=O group (eq 2).



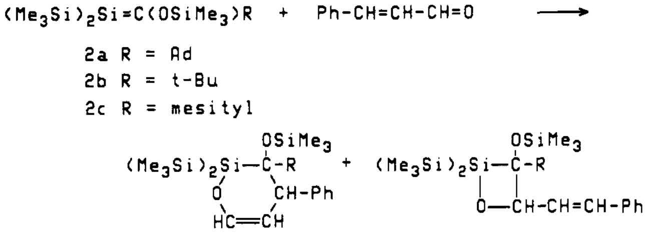
$(Me_3Si)_2Si{=}C(OSiMe_3)R + CH_3{-}CH{=}CH{-}CH{=}O \longrightarrow$

2a R = Ad
2b R = t-Bu

(2)

8a,b 9a

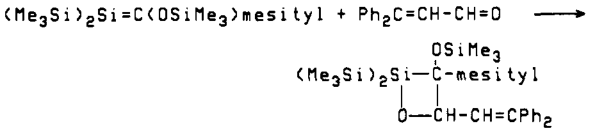
With use of cinnamaldehyde as reactant with the adamantyl- and *tert*-butylsilenes the same two types of products, the 1-sila-2-oxacyclohex-3-ene **10** and the siloxetane **11** were again formed, with **10** predominating, whereas the mesitylsilene gave only the siloxetane **11c** as a mixture of two diastereomers. Similarly, the mesitylsilene gave only the siloxetane **12c** when allowed to react with β-phenylcinnamaldehyde (eq 3).



$(Me_3Si)_2Si{=}C(OSiMe_3)R + Ph{-}CH{=}CH{-}CH{=}O \longrightarrow$

2a R = Ad
2b R = t-Bu
2c R = mesityl

10a,b 11a,b,c



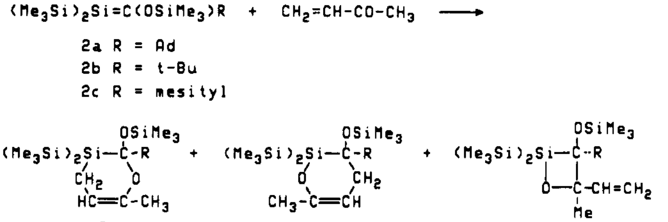
$(Me_3Si)_2Si{=}C(OSiMe_3)mesityl + Ph_2C{=}CH{-}CH{=}O \longrightarrow$

(3)

12c

Thus, whereas simple aldehydes were found to react exclusively with silenes to give siloxetanes,[1] we now find that siloxetanes are in most cases only minor products of the reaction of α,β-unsaturated aldehydes with these silenes and that [2 + 4] cycloaddition predominates. When the aldehyde bears a β-substituent, the major product is a 1-sila-2-oxacyclohex-3-ene, but in the absence of a β-substituent the opposite regiochemistry predominates. Before commenting further on these findings, it is best to discuss the results from reactions of α,β-unsaturated ketones with the same silenes.

When methyl vinyl ketone, an α,β-unsaturated ketone lacking a β-substituent, was used as the reactant with the adamantyl and *tert*-butylsilenes, the products again were the two regioisomers from 1,4-cycloaddition, the 1-sila-3-oxacyclohex-4-ene adducts **13a,b** and the 1-sila-2-oxacyclohex-3-enes **14a,b**, as shown in eq 4, with the former as major products.



$(Me_3Si)_2Si{=}C(OSiMe_3)R + CH_2{=}CH{-}CO{-}CH_3 \longrightarrow$

2a R = Ad
2b R = t-Bu
2c R = mesityl

13a,b,c 14a,b,c 15c

(4)

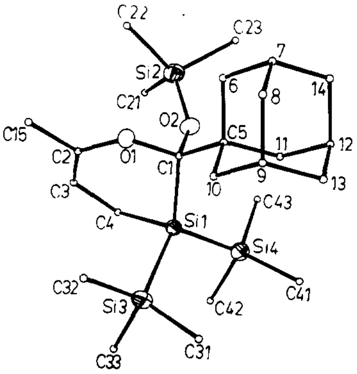
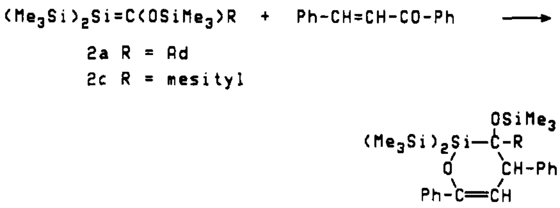


Figure 1. View of **13a** showing the atomic labeling scheme. Thermal ellipsoids are at the 25% probability level. For the sake of clarity, hydrogen atoms have been omitted and carbon atoms have been assigned as spheres or arbitrary radius.

With the mesitylsilene two diastereomers of the siloxetane **15c** were also formed as part of a complex mixture.

The major product from the reaction of MVK with the adamantylsilene was obtained crystalline, and its crystal structure confirmed the identity of the molecule as **13a**. The ORTEP diagram of **13a** is shown in Figure 1.

In contrast to the above, when benzalacetophenone reacted with the adamantylsilene **2a**, the major reaction product (>95%) was the 1-sila-2-oxacyclohex-3-ene **16a**, as shown in eq 5. With the mesitylsilene **2c**, the only



$(Me_3Si)_2Si{=}C(OSiMe_3)R + Ph{-}CH{=}CH{-}CO{-}Ph \longrightarrow$

2a R = Ad
2c R = mesityl

(5)

16a,c

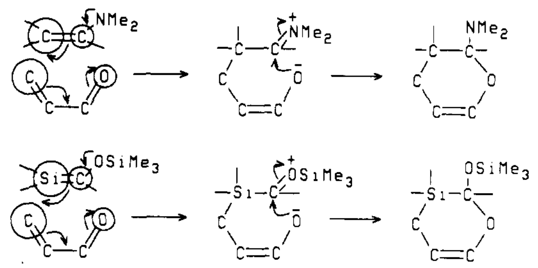
product was the 1-sila-2-oxacyclohex-3-ene **16c**. Thus, with α,β-unsaturated ketones as well, the preferred regiochemistry was reversed when the ketone carried a β-substituent.

These results indicate that [2 + 4] cycloaddition is preferred to [2 + 2] cycloaddition with either α,β-unsaturated aldehydes or ketones and that [2 + 2] cycloaddition is less important with α,β-unsaturated ketones than with α,β-unsaturated aldehydes. This latter finding seems reasonable in light of the known general behavior of α,β-unsaturated aldehydes and ketones.

In explanation of the variable regiochemistries observed in the above [2 + 4] cycloaddition reactions it is possible that there are two different competing mechanism involved. The formation of the siloxetanes and of the 1-sila-2-oxacyclohex-3-enes derived from the α,β-unsaturated aldehydes and ketones can be regarded as [2 + 2] and [2 + 4] cycloadditions, respectively, where the regiochemistry is strongly influenced by the well-known silaphilic character of oxygen and the anticipated polarities of the reactants, i.e. $Si^{\delta+}{=}C^{\delta-}$ and $C^{\delta+}{=}C{-}C{=}O^{\delta-}$. Whether these processes are truly concerted or whether, as seems reasonable, silicon–oxygen bond formation precedes the carbon–carbon bond formation required to close the ring is not known and is difficult to demonstrate.

All of the above [2 + 4] reactions can also be classified as cyclizations involving a heterodiene and a heterodienophile bearing an electron-releasing group, the Me_3SiO group, on the carbon atom of the silene. It has been well documented that the regiochemistries of heterodiene cyclizations involving species such as propenal and methyl vinyl ketone are unusual.[4] Their [2 + 4] cycloaddition

Scheme II



reactions have been discussed by Fleming[5] in terms of frontier orbital theory. Calculations have shown that the energetically favored pathway for reaction involves the interaction of the LUMO of the heterodiene with the HOMO of the dienophile, either by a concerted path or by a stepwise ionic process. The symmetry of these molecular orbitals, i.e. +−−+ for the LUMO and ++ for the HOMO, allows formation of products with either of the possible regiochemistries. The energetically favored regioisomer (i.e. the major product) is normally derived from the interaction between the atom in each reactant that has the larger orbital coefficient. Particularly relevant to the present case is the regiochemistry reported for the reaction of methyl vinyl ketone with an enamine, as shown in Scheme II. Here, cyclization directed by the dominant interaction of the frontier orbitals having the larger coefficients, which are located on the terminal carbon atom of propenal and the carbon atom of the enamine remote from nitrogen, leads to the observed product shown, although it is not known whether this a concerted or a two-step process. For a silene that bears an electron-releasing group, Me_3SiO, on carbon, it has been calculated that the larger coefficient in the HOMO resides on silicon.[6] By analogy with the example cited, a heterodiene cyclization involving interaction with the orbital of higher coefficient in propenal or methyl vinyl ketone should lead to 1-sila-3-oxacyclohex-4-enes, the observed major products.

When β-substituents are present on the α,β-unsaturated carbonyl system, the coefficients of the atomic orbitals will be altered and steric interactions will be introduced. These factors singly, or in combination, could account for the observed change in regiochemistry, which leads to the formation of the 1-sila-2-oxacyclohex-3-enes as major products when the heterodiene bears a β-substituent, although the dramatic changes observed might not have been predicted. Alternatively, as mentioned earlier, the regiochemistries of these latter cyclizations may be dominated by the polarities of the reagents and the silaphilic character of oxygen.

Structure Identification of Compounds. The structures of the various types of compounds were established primarily from their NMR data. The ^{29}Si chemical shift of the ring silicon atoms was particularly informative. As established earlier,[1] the ring silicon atom in siloxetanes resonates far downfield in the region of 50–60 ppm, whereas silicon in a six-membered ring having a 1-sila-2-oxacyclohex-3-ene type structure absorbed further upfield in the range 5–7 ppm. Thus, silicon in rings containing silicon–oxygen bonds resonates downfield of TMS. It had also been shown previously[2] that the ring silicon atom in silacyclobutanes absorbed in the range −15 to −30 ppm, whereas silacyclohexenes absorbed further upfield in the range −45 to −50 ppm (except for mesitylsilene adducts, where the range was about −25 to −30 ppm). Thus, silicon in rings where the silicon atom is bonded to carbon resonates significantly upfield of TMS. Hence, it was possible to be fairly confident of the ring structure of the adducts on the basis of the position of the ring silicon atom absorption. The ring silicon atom of each of the compounds described in the present work falls in or very close to the absorption ranges previously observed. As confirmation of the reliability of these relationships, the major adduct of the adamantylsilene with methyl vinyl ketone, whose crystal structure showed it to be a 1-sila-3-oxacyclohex-4-ene, showed ring silicon absorption at −57 ppm, close to that which had been found for silicon in six-membered rings where carbon was attached to the ring silicon.[7]

Other relationships were also useful in determining the structures of the new compounds. Thus, the chemical shift of protons on ring carbon atoms attached to silicon consistently fell in the range of 1–2 ppm, whereas in cases with the reverse regiochemistry, where the ring carbon bearing the protons was attached to the ring carbon atom derived from the silene, the absorption consistently fell in the range 2–4 ppm. The ring carbon atoms themselves showed similar differences in chemical shift. Those attached to the ring silicon atom resonated in the ^{13}C spectra in the range 5–10 ppm, whereas carbon attached to the ring carbon atom bearing the trimethylsiloxy group resonated in the range 30–60 ppm, depending on whether or not a substituent was attached and whether the ring was six-membered or four-membered. In siloxetanes the ring carbon atom attached to the carbon atom of the original silene resonated in the range 85–110 ppm, depending on the attached substituents. While these relationships were not all available when this work was initiated, they became valuable and reliable criteria of structure as the work proceeded.

Crystal Structure. The overall conformation of the molecule (**13a**) is similar to that of the adducts of adamantylsilene with *tert*-butyl acrylate and ethyl cinnamate, as reported in the accompanying paper.[8] In **13a** the bulky adamantyl and trimethylsilyl groups have a pronounced steric effect on the molecule, and as a result some of the bond angles and distances have values that deviate from those expected on the basis of hybridization principles. This is clearly the case for angles C(1)–O(2)–Si(2) (142.3 (4)°), C(1)–Si(1)–Si(3) (117.96 (19)°), and C(1)–Si(1)–Si(3) (116.41 (18)°), which are significantly wider than expected, while the bond angles C(4)–Si(1)–C(1) (95.90 (26)°) and O(2)–C(1)–Si(1) (102.4 (4)°) are smaller than normal.

Steric hindrance may also be responsible for the apparent elongation of the bond C(1)–Si(1) (1.942 (6) Å). The other Si–C(sp^3) bond lengths in the molecule have an average value of 1.856 (8) Å, and the mean value (of a sample of 681 compounds) for a *C*(sp^3)–*Si*–X_3 bond length has been quoted[9] as 1.863 (24) Å.

The silaoxacyclohexene ring conformation is intermediate between sofa and half-chair. Atoms O(1), C(2), C(3), and C(4) lie in the best plane with C(1) −0.197 (6) Å and Si(1) 0.798 (2) Å out of the plane. In view of the magnitude of the interior ring angles already discussed and the wide angle O(1)–C(2)–C(3) (128.0 (5)°), a highly strained ring system is indicated.

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Experimental Section

Experiments were performed with oven-dried glassware under argon with use of inert-atmosphere and vacuum-line techniques. Reaction solvents were dried and double-distilled before use: diethyl ether and tetrahydrofuran were dried over sodium benzophenone ketyl; pentane and toluene were dried over lithium aluminum hydride. The liquid aldehydes and ketones were distilled under argon immediately before use. Photolysis experiments were carried out with use of two to three 100-W PAR 38 mercury spot lamps, whose output is mainly at 360 nm and longer wavelengths.

All NMR spectra were obtained on either a Varian XL400 or a Gemini 200 spectrometer. The spectra were run in C_6D_6 unless otherwise specified. In the proton NMR spectra, multiplicities of the signals were designated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Where necessary, APT[10] and DEPT[11] pulse sequences were used in obtaining ^{13}C NMR spectra to allow unambiguous assignment of signals. All ^{29}Si NMR spectra were obtained with use of the DEPT sequence.

Melting points are uncorrected. In a few cases the products from reactions were not isolated or could not be separated from a mixture, and their structures were assigned purely on the basis of NMR data. In such cases the ^{1}H, ^{13}C, and ^{29}Si NMR spectra are provided as part of the supplementary material. In a few cases signals due to the presence of $(Me_3Si)_4$, a difficult to remove inert contaminant of the parent acylsilane, are present in the spectra. In the ^{29}Si spectra these occur at −9.7 and −135.2 ppm.

Most reactions were run in two ways. Cophotolysis of the relevant acylsilane with 1 equiv of the carbonyl coreagent in deuteriobenzene gave essentially the same results as were obtained if the acylsilane was prephotolyzed to the silene, and 1 equiv of the carbonyl coreagent was then added to the silene solution in the dark. Typical procedures are given below for a few cases.

Reaction of the Adamantylsilene 2a with Propenal. A solution of (1-adamantylcarbonyl)tris(trimethylsilyl)silane (0.3 mmol, 0.12 g) and 0.3 mmol (0.02 mL) of propenal in 0.5 mL of perdeuteriobenzene in a sealed NMR tube under argon was photolyzed with three 100-W PAR 38 lamps for about 24 h. Nuclear magnetic resonance spectra of the resulting colorless solution showed that two products, the 1-sila-3-oxacyclohex-4-ene **6a** and the 1-sila-2-oxacyclohex-3-ene **7a**, were formed in the ratio 5:1 as determined by ^{1}H NMR spectroscopy, together with a trace of an unidentified third compound. The compounds, isolated as a viscous oil, were not separated but were identified spectroscopically. Alternatively, a solution of 0.12 g (0.3 mmol) of (1-adamantylcarbonyl)tris(trimethylsilyl)silane in 0.5 mL of deuteriobenzene was photolyzed with use of three 100-W PAR 38 lamps for 3 days at 10 °C and then at −20 °C in a dry ice–carbon tetrachloride bath for another 24 h. To this pale yellow solution of the adamantylsilene was added 0.02 mL of propenal in the dark. The solution was left overnight, at which time of the NMR spectra of the solution showed the formation of the same two compounds in the same ratio. **6a** (major isomer): ^{1}H NMR δ 0.22, 0.26, 0.28 (each 9 H, s, Me$_3$Si), 1.12 (1 H, d × d, A part of ABMX system ring SiCH$_A$H$_B$—CH$_C$=CH$_D$—O–, J_{AB} = 17.1 Hz, J_{AC} = 8.0 Hz), H$_B$ hidden under Ad, 4.71 (1 H, d × d × d, H$_C$, J_{BC} = 2.2 Hz, J_{CD} = 6.9 Hz), 6.05 (1 H, d × d, H$_D$, J_{BD} = 2.9 Hz), 1.5–2.1 (Ad); ^{13}C NMR δ −0.12, 0.56 (Me$_3$Si), 2.15 (OSiMe$_3$), 2.89 (SiCH$_2$), 28.66 (Ad CH), 37.33, 38.31 (Ad CH$_2$), 41.39 (Ad quat C), 100.39 (ring C—*C*H=), 110.85 (ring C quat), 143.88 (ring =*C*H—O–); ^{29}Si NMR δ −14.46, −15.55 (Me$_3$Si), 9.09 (OSiMe$_3$), −56.37 (ring Si). **7a** (miner isomer): ^{1}H NMR δ 0.25, 0.26, 0.28 (Me$_3$Si, overlapping), H$_A$, H$_B$ of ring C—CH$_A$H$_B$—CH$_C$=CH$_D$—O– system (under Ad but probably 2.2, 2.3), 5.1 (1 H, m, H$_C$, J = 2.4, 6.1 Hz), 6.35 (1 H, m, H$_D$); ^{13}C NMR −0.40, 2.50 (Me$_3$Si), 3.52 (OSiMe$_3$), 31.00 (C—*C*H$_2$), 28.88 (Ad CH), 36.94, 39.99 (Ad CH$_2$), 40.82 (Ad quat C), 83.40 (ring C quat), 102.75 (ring Si—*C*H=), 143.40 (ring =*C*H—O); ^{29}Si NMR δ −16.04, −18.20 (Me$_3$Si), 7.51 (OSiMe$_3$), 8.96 (ring Si).

Reaction of *tert*-Butylsilene with Propenal. The reaction yielded the 1-sila-3-oxacyclohex-4-ene **6b** and the 1-sila-2-oxacyclohex-3-ene **7b** in the ratio 6:1 together with a trace of a third unidentified compound. **6b** (major isomer): ^{1}H NMR δ 0.20, 0.23, 0.26 (each 9 H, s, Me$_3$Si), 1.07 (9 H, s, *t*-Bu), 1.12 (1 H, d × d, H$_A$ of ring Si—CH$_A$H$_B$—CH$_C$=CH$_D$—O– system, J_{AB} = 17.1 Hz, J_{AC} = 8.0 Hz), 1.60 (1 H, d × d × d, H$_B$, J_{BC} = 2.2, J_{BD} = 2.6 Hz), 4.69 (1 H, d × d × d, H$_C$, J_{CD} = 6.9 Hz), 6.04 (1 H, d × d, H$_D$); ^{13}C NMR δ −0.23, 0.42, (Me$_3$Si), 2.05 (OSiMe$_3$), 3.05 (SiCH$_2$), 26.40 (*Me*$_3$C), 39.83 (Me$_3$*C*), 100.32 (ring CH$_2$—*C*H=), 109.94 (ring quat C), 143.96 (ring =*C*H—O); ^{29}Si NMR δ −14.57, −15.59 (Me$_3$Si), 9.00 (OSiMe$_3$), −54.96 (ring Si). **7b** (minor isomer): ^{1}H NMR δ 0.22, 0.29, 0.32 (each 9 H, s, Me$_3$Si), 0.94 (9 H, *t*-Bu), 2.07 (1 H, d × d × d), H$_A$ of ABMX system, J_{AB} = 18.1, J_{AC} = 5.9, J_{AD} = 1.0 Hz), 2.27 (1 H, d × d × d, H$_B$, J_{BC} = 2.5, J_{BD} = 2.8 Hz), 5.08 (1 H, d × d × d, H$_C$, J_{CD} = 6.2 Hz), 6.35 (1 H, d × d × d, H$_D$); ^{13}C NMR δ −0.53, −0.31 (Me$_3$Si), 2.27 (OSiMe$_3$), 27.29 (*Me*$_3$C), 32.00 (ring C—*C*H$_2$), 39.55 (Me$_3$*C*), 83.00 (ring quat C), 102.90 (ring C—*C*H=), 144.50 (ring =*C*H—O–); ^{29}Si NMR δ −16.22, −18.17 (Me$_3$Si), 7.51 (OSiMe$_3$), 9.44 (ring Si). Traces of a second minor product were observed.

Reaction of Adamantylsilene with Crotonaldehyde. Two products were observed from the reaction, the 1-sila-2-oxacyclohex-3-ene **8a** and the siloxetane **9a**, in the ratio 4:1. **8a** was separated from the mixture by chromatography on alumina with use of hexane. **8a** (major isomer): mp 93–94 °C; MS (*m*/*e*) calcd for M$^+$ 480,2731, found 480.2720; ^{1}H NMR δ 0.28, 0.29, 0.37 (each 9 H, s, Me$_3$Si), 1.15 (3 H, d, $J_{H_A\text{-}Me}$ = 7.1 Hz, Me of ring CH$_A$*Me*—CH$_B$=CH$_C$—O system), 1.6–2.0 (m, Ad), 2.49 (1 H, d × d × q, H$_A$, J_{AB} = 6.1 Hz, J_{AC} = 0.9 Hz), 4.27 (1 H, d × d, H$_B$, J_{BC} = 6.3 Hz), 6.21 (1 H, d × d, H$_C$; ^{13}C NMR δ 0.06, 1.62 (Me$_3$Si), 3.29 (OSiMe$_3$), 22.53 (Me), 29.07 (Ad CH), 37.11, 40.01 (Ad, CH$_2$), 40.54 (Ad quat C), 38.13 (ring *C*H$_A$), 89.53 (ring quat C), 111.39 (ring =*C*H$_B$—C), 141.95 (ring =*C*H$_C$—O); ^{29}Si NMR δ −16.58, −15.56 (Me$_3$Si), 5.68 (OSiMe$_3$), 6.46 (ring Si). Anal. Calcd for $C_{24}H_{48}Si_4O_2$: C, 59.93; H, 10.06. Found: C, 59.70; H, 10.18. **9a** (minor isomer): ^{1}H NMR δ 0.31, 0.34, 0.36 (each 9 H, s, Me$_3$Si), 1.10 (3 H, d, Me), 4.02 (1 H, d × d, J = 1.9, 6.2 Hz, H$_A$ of ring -CH$_A$—CH$_C$=CH$_B$—Me), 5.45 (1 H, m, H$_B$), 5.79 (1 H, m, H$_C$), 1.6–2.0 (Ad); ^{13}C NMR δ −0.22, 0.27 (Me$_3$Si), 3.44 (OSiMe$_3$), 17.30 (Me), 28.71 (Ad CH), 37.23, 40.26 (Ad CH$_2$), 40.49 (Ad quat C), 95.54 (ring CH sp^3), 103.05 (ring quat C), 125.10, 132.23 (=CH); ^{29}Si NMR δ −18.14, −18.39 (Me$_3$Si), 8.53 (OSiMe$_3$), 60.28 (ring Si).

Reaction of *tert*-Butylsilene with Crotonaldehyde. A solution of 0.125 g (0.04 mmol) of pivaloyltris(trimethylsilyl)silane in 0.5 mL of deuteriobenzene and 0.034 mL of freshly distilled crotonaldehyde in a sealed NMR tube under argon was photolyzed with two 100-W PAR 38 lamps for 2 days. The NMR spectra showed the presence of a major compound, the 1-sila-2-oxacyclohex-3-ene **8b** and traces of other identified species. The same compound **8b** was formed when preformed silene, derived by photolysis of 0.12 g of the acylsilane, was photolyzed in 0.5 mL of deuteriobenzene for 48 h, followed by 24 h at −60 °C, was treated in the dark with an excess (0.05 mL) of crotonaldehyde. **8b**: ^{1}H NMR δ 0.24, 0.25, 0.35 (each 9 H, s, Me$_3$Si), 1.01 (9 H, s, *t*-Bu), 1.07 (3 H, d, Me of ring -CH$_A$Me—CH$_B$=CH$_C$—O–, $J_{Me\text{-}H_A}$ = 7.0 Hz), 2.43 (1 H, d × d × q, H$_A$, J_{AB} = 5.7, J_{AC} = 1.1 Hz), 4.27 (1 H, d × d, H$_B$, J_{BC} = 6.3 Hz), 6.21 (1, d × d, H$_C$); ^{13}C NMR δ −0.07, 1.53 (Me$_3$Si), 3.15 (OSiMe$_3$), 22.07 (ring CH—*Me*), 28.57 (Me of *t*-Bu), 38.22 (Me$_3$*C*), 38.89 (ring *C*H$_A$Me), 88.50 (ring C quat), 111.22 (ring =*C*H$_B$), 141.91 (ring *C*H$_C$); ^{29}Si NMR δ −15.56, −16.67 (Me$_3$Si), 5.65 (OSiMe$_3$), 6.99 (ring Si).

Reaction of Adamantylsilene with Cinnamaldehyde. Two products were observed, the 1-sila-2-oxacyclohex-3-ene **10a** and the siloxetane **11a** in a ratio of about 4:1. The major product was separated on silica gel with use of a 20:1:1 mixture of hexane–chloroform–ethyl acetate as eluant. **10a** (major product): mp 131–132 °C; MS (*m*/*e*) calcd for M$^+$ 542.2888, found 542.2921; ^{1}H NMR δ 0.33, 0.389, 0.392 (each 9 H, s, Me$_3$Si), 1.3–2.0 (Ad), 3.91 (1 H, d, H$_A$ of ring CH$_A$Ph—CH$_B$=CH$_C$—O– system, J_{AB} = 6.8 Hz), 4.63 (1 H, d × d, H$_B$, J_{BC} = 6.2 Hz), 6.36 (1 H, d, H$_C$), 6.9–7.5 (Ph); ^{13}C NMR δ 1.44, 1.73 (Me$_3$Si), 4.30 (OSiMe$_3$), 28.93 (Ad CH), 37.04, 39.49 (Ad CH$_2$), 41.81 (Ad quat C), 50.44 (ring *C*H—Ph), 93.72 (ring quat C), 111.00 (ring =*C*H—C), 142.24 (ring =*C*H—O), 126.73, 126.77, 131.40 (CH of Ph), 144.03 (ipso C of Ph); ^{29}Si NMR δ −14.22, −16.91 (Me$_3$Si), 6.37 (OSiMe$_3$), 15.82 (ring Si). Anal. Calcd for $C_{29}H_{50}Si_4O_2$: C, 64.13; H, 9.28. Found: C, 63.35; H, 9.41. **11a** (minor product): ^{1}H NMR δ 0.23, 0.30, 0.35

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(each 9 H, s, Me$_3$Si), 1.3–2.0 (Ad), 5.7–6.1 (3 H, m, ring *C*H—C*H*=C*H*Ph); ^{13}C NMR δ −0.13, 0.27 (Me$_3$Si), 3.47 (OSiMe$_3$), 28.63 (Ad CH), 37.14, 40.44 (Ad CH$_2$), 39.90 (Ad quat C), 86.2 (ring CH), 104.1 (ring quat C), 95.24, 112.55 (=CH); ^{29}Si NMR δ −17.91, −17.99 (Me$_3$Si), 8.95 (OSiMe$_3$), 61.55 (ring Si).

Reaction of *tert*-Butylsilene with Cinnamaldehyde. Two products were observed, the 1-sila-2-oxacyclohex-3-ene **10b** and the siloxetane **11b** in a ratio of about 4:1. **10b** (major product): viscous liquid, purified by chromatography on silica gel with use of hexane; MS (*m*/*e*) calcd for M$^+$ (C$_{23}$H$_{44}$Si$_4$O$_2$) 464.2418, found 464.2416; ^{1}H NMR δ 0.34, 0.39, 0.40 (each 9 H, s, Me$_3$Si), 0.92 (9 H, s, *t*-Bu), 3.87 (1 H, d, H$_\mathrm{A}$ of ring CH$_\mathrm{A}$Ph—CH$_\mathrm{B}$=CH$_\mathrm{C}$—O– system, J_{AB} = 6.7 Hz), 4.66 (1 H, d × d, H$_\mathrm{B}$, J_{BC} = 6.2 Hz), 6.41 (1 H, d, H$_\mathrm{C}$), 6.9–7.5 (Ph), ^{13}C NMR δ 1.36, 1.51 (Me$_3$Si), 4.15 (OSiMe$_3$), 28.56 (*Me*$_3$C), 39.35 (Me$_3$*C*), 51.64 (ring *C*H—Ph), 92.55 (ring quat C), 110.81 (ring =*C*H—C), 142.30 (ring =CH—O), 126.76, 128.58, 131.78 (CH of Ph), 143.90 (ipso C of Ph); ^{29}Si NMR δ −14.29, −17.14 (Me$_3$Si), 6.22 (OSiMe$_3$), 15.72 (ring Si). **11b** (minor product): ^{1}H NMR δ 0.32, 0.36, 0.38 (each 9 H, s, Me$_3$Si), 1.13 (Me$_3$C), 5.7–6.8 (3 H, m, ring C*H*—C*H*=C*H*Ph); ^{13}C NMR −0.16, 0.17 (Me$_3$Si), 3.39 (OSiMe$_3$), 28.77 (*Me*$_3$C), 37.39 (Me$_3$*C*), 88.2 (ring CH), 102.35 (ring quat C), 95.24, 111.25 (=CH); ^{29}Si NMR δ −17.76, −17.98 (Me$_3$Si), 8.49 (OSiMe$_3$), 59.99 (ring Si).

Reaction of Mesitylsilene with Cinnamaldehyde. Two diastereomers of the siloxetane **11c** were formed in a ratio of 1.4:1 in an overall yield of 94%. **11c** (major diastereomer): ^{1}H NMR δ 0.42, 0.51, 0.93 (each 9 H, s, Me$_3$Si), 2.53, 2.72, 2.80 (each 3 H, s, Me of mesityl, restricted rotation), 6.2–7.9 (10 H, m, H$_\mathrm{A}$, H$_\mathrm{B}$, H$_\mathrm{C}$, and aryl H of ring CH$_\mathrm{A}$—CH$_\mathrm{B}$=CH$_\mathrm{C}$Ph system); ^{13}C NMR δ −1.25, −0.40 (Me$_3$Si), 2.25 (OSiMe$_3$), 20.79, 21.79, 24.01 (Me of mesityl), 89.78 (ring quat C), 90.06 (ring CH$_\mathrm{A}$), 115.22 (2 C), 126.89, 128.96, 129.53, 129.76, 131.47 (CH sp^2), 134.41, 136.97, 137.63, 137.66, 138.01 (quat C sp^2); ^{29}Si NMR δ −16.60, −18.33 (Me$_3$Si), 11.97 (OSiMe$_3$), 55.71 (ring Si). **11c** (minor diastereomer): ^{1}H NMR δ 0.49, 0.63, 0.96 (each 9 H, s, Me$_3$Si), 2.46, 2.60, 2.67 (each 3 H, s, Me of mesityl, restricted rotation), 6.3–7.9 (10 H, m, H$_\mathrm{A}$, H$_\mathrm{B}$, H$_\mathrm{C}$, and aryl H); ^{13}C NMR δ −0.26, −0.13 (Me$_3$Si), 2.77 (OSiMe$_3$), 20.91, 21.22, 23.34 (Me of mesityl), 91.19 (ring quat C), 95.35 ring CH$_\mathrm{A}$ sp^3), 111.20, 112.64, 126.75, 128.90, 129.13, 129.18, 131.02 (CH sp^2), 135.64, 137.50, 137.59, 138.33, 138.85 (quat C sp^2); ^{29}Si NMR δ −16.84, −17.87 (Me$_3$Si), 9.44 (OSiMe$_3$), 53.87 (ring Si).

Reaction of Mesitylsilene with β-Phenylcinnamaldehyde. The product was a 50:50 mixture of two diastereomers of siloxetane **12c**. Since these were not separated, the NMR data report the combined data for both species. **12c** (both diastereomers): ^{1}H NMR δ 0.41, 0.53, 0.68, 0.71, 0.97, 1.00 (each 9 H, s, Me$_3$Si), 2.39, 2.56, 2.69, 2.72, 2.78, 2.85 (each 3 H, Me of mesityl, restricted rotation), 6.22, 6.39 (each 1 H, d, H$_\mathrm{A}$ ring CH$_\mathrm{A}$—CH$_\mathrm{B}$=CPh$_2$ system, J = 7.0, J = 6.5 Hz, respectively), 6.93, 7.24 (possibly =CH$_\mathrm{B}$– in aryl region), 6.9–8.2 (Ar); ^{13}C NMR δ −1.22, −0.66, −0.25, −0.22 (Me$_3$Si), 2.48, 2.58 (OSiMe$_3$), 20.68, 20.97, 21.14, 21.65, 22.73, 23.09 (Me of mesityl), 86.21, 93.11 (ring CH sp^3), 89.13, 91.28 (ring quat C), 127.63, 127.82, 127.88, 127.96, 128.27, 128.35, 128.46, 129.13, 129.41, 130.75, 130.88, 130.91, 131.19 (CH sp^2), 135.10, 136.03, 136.84, 137.58, 137.73, 138.08, 138.61, 138.71, 139.38, 140,70, 143.24, 143.44, 143.48, 144.14 (quat C sp^2); ^{29}Si NMR δ −16.69, −17.05, −17.56, −18.30 (Me$_3$Si), 9.62, 12.16 (OSiMe$_3$), 52.24, 52.32 (ring Si).

Reaction of Adamantylsilene with Methyl Vinyl Ketone. Two different products, the 1-sila-3-oxacyclohex-4-ene **13a** and the 1-sila-2-oxacyclohex-3-ene **14a**, from [2 + 4] cycloaddition, were observed in the ratio 3.8:1. Chromatography of the mixture on a silica gel column with use of 4:1 hexane–ethyl acetate led to the isolation of pure **13a**, mp 146–147 °C, after recrystallization from ethyl acetate. Anal. Calcd for C$_{24}$H$_{48}$O$_2$Si: C, 59.93; H, 10.06. Found: 59.68; H, 10.20. MS (*m*/*e*): calcd 480.2731, found 480.2739. Figure 1 shows the ORTEP diagram for the crystal structure of this material, confirming its identity. ^{1}H NMR: δ 0.24 (18 H, s, two overlapping Me$_3$Si groups), 0.27 (Me$_3$Si), 1.145 (1 H, d × d, H$_\mathrm{A}$ of ABX system ring Si—CH$_\mathrm{A}$H$_\mathrm{B}$—CH$_\mathrm{C}$=CMe—O–, J_{AB} = 15.1 Hz, J_{AC} = 8.5 Hz), H$_\mathrm{B}$ underneath Ad group, 4.62 (1 H, d × d, H$_\mathrm{C}$, J_{BC} = 0.9 Hz), 1.70 (3 H, s, Me), 1.6–2.1 (Ad + H$_\mathrm{B}$). ^{13}C NMR: δ −0.27, 0.37 (Me$_3$Si), 2.24 (OSiMe$_3$), 3.45 (SiCH$_2$), 21.69 (CH$_3$), 28.72 (Ad CH), 37.35, 38.47 (Ad CH$_2$), 39.60 (Ad quat C), 95.32 (ring =CH–), 111.24 (ring quat C), 150.13 (ring =C—O). ^{29}Si NMR: δ −14.57, −15.68 (Me$_3$Si), 8.16 (OSiMe$_3$), −57.99 (ring Si). **14a**: ^{1}H NMR δ 0.23, 0.28, 0.34 (each 9 H, s, Me$_3$Si), 2.14 (1 H, d × d, H$_\mathrm{A}$ of ABX system ring C—CH$_\mathrm{A}$H$_\mathrm{B}$—H$_\mathrm{C}$=CMe—O—Si (ring), J_{AB} = 18.8 Hz, J_{AC} = 7.2 Hz), 2.34 (1 H, d × d, H$_\mathrm{B}$, J_{BC} = 2.3 Hz), 5.15 (1 H, m, H$_\mathrm{C}$), 1.70 (3 H, s, Me); ^{13}C NMR δ −0.40, −0.07 (Me$_3$Si), 2.69 (OSiMe$_3$), 22.65 (Me), 30.09 (ring C—*C*H$_2$—C), 28.93 (Ad CH), 39.61, 41.44 (Ad CH$_2$), 40.8 (Ad quat C), 82.80 (ring quat C), 97.92 (ring =CH—), 151.35 (ring =CH—O—); ^{29}Si NMR δ −16.28, −18.09 (Me$_3$Si), 7.11 (OSiMe$_3$), 8.15 (ring Si).

Reaction of *tert*-Butylsilene with Methyl Vinyl Ketone. The reaction yielded two structural isomers, the 1-sila-3-oxacyclohex-4-ene **13b** and the 1-sila-2-oxacyclohex-3-ene **14b**, in the ratio 4:1, both resulting from [2 + 4] cycloaddition. **13b** (major isomer): ^{1}H NMR δ 0.21, 0.22, 0.24 (each 9 H, s, Me$_3$Si), 1.08 (9 H, s, *t*-Bu), 1.68 (3 H, m, Me), 1.14 (1 H, d × d, H$_\mathrm{A}$ of ABX system ring Si—CH$_\mathrm{A}$H$_\mathrm{B}$—CH$_\mathrm{C}$=CMe—O–, J_{AB} = 16.8, J_{AC} = 8.6 Hz), 1.64 (1 H, m, $J_{\mathrm{H_B-Me}}$ = 2.4 Hz), 4.61 (1 H, m, $J_{\mathrm{H_C-Me}}$ = 1.1 Hz); ^{13}C NMR δ −0.10, 0.29 (Me$_3$Si), 2.16 (OSiMe$_3$), 3.66 (Si—CH$_2$), 21.76 (Me), 26.52 (*Me*$_3$C), 39.89 (Me$_3$*C*), 95.26 (ring =CH–), 110.29 (ring quat C), 150.27 (ring =C—O); ^{29}Si NMR δ −14.70, −15.70 (Me$_3$Si), 8.03 (OSiMe$_3$), −56.51 (ring Si). **14b** (minor isomer): ^{1}H NMR δ 0.22, 0.23, 0.32 (each 9 H, s, Me$_3$Si), 0.96 (9 H, s, *t*-Bu), 1.76 (3 H, m, Me), 2.12 (1 H, d × d × m, H$_\mathrm{A}$ of ring Si—CH$_\mathrm{A}$H$_\mathrm{B}$CH$_\mathrm{C}$=CMe—O– system, J_{AB} = 17.9 Hz, J_{AC} = 5.9 Hz, $J_{\mathrm{H_A-Me}}$(?) = 1.2 Hz), 2.31 (1 H, d × d × q?, H$_\mathrm{B}$, J_{BC} = 2.3 Hz, $J_{\mathrm{H_B-Me}}$ = 2.3 Hz), 4.25 (1 H, d × d × q?, $J_{\mathrm{H_C-Me}}$ = 1.0 Hz); ^{13}C NMR δ −0.53, −0.19 (Me$_3$Si), 2.61 (OSiMe$_3$), 22.62 (Me), 27.40 (*Me*$_3$C), 31.62 (C—*C*H$_2$–), 37.55 (Me$_3$*C*), 98.09 (ring =CH—C), 112.55 (ring quat C), 151.28 (ring =C—O–); ^{29}Si NMR δ −16.47, −18.03 (Me$_3$Si), 8.64 (OSiMe$_3$), 7.08 (ring Si).

Reaction of Mesitylsilene with Methyl Vinyl Ketone. Cophotolysis of 140 mg (3.5 mmol) of the mesitylacylsilane **1c** with 25 mg (3.5 mmol) of methyl vinyl ketone in 0.5 mL of deuteriobenzene sealed under argon yielded a complex mixture of four compounds in the approximate ratio 43:26:20:11. These were the 1-sila-3-oxacyclohex-4-ene **13c**, one of the diastereomers of siloxetane **15c**, the 1-sila-2-oxacyclohex-3-ene **14c**, and the second (minor) siloxetane diastereomer **15c**, respectively. Because of the complexity of the NMR spectra it was not possible to assign all peaks unambiguously, although the stronger ^{13}C and ^{29}Si peaks associated with **13c** were assigned with confidence. **13c**: ^{1}H NMR δ −0.18, 0.08, 0.29 (Me$_3$Si), 1.52–2.53 (Me of ring C—*Me* and mesityl, not assignable), 5.4–6.4 (vinyl H), 6.5–6.9 (Ar H); ^{13}C NMR δ −0.43, 0.56 (Me$_3$Si), 2.27 (OSiMe$_3$), 3.75 (SiCH$_2$), 22.79, 24.70, 26.23 (Me of mesityl), 96.99 (ring =CH), 112.75 (quat ring C sp^3), 150.16 (ring =*C*Me—O–); ^{29}Si NMR δ −13.86, −14.79 (Me$_3$Si), 13.24 (OSiMe$_3$), −39.01 (ring Si). Assignable peaks of **15c** (major diastereomer): ^{1}H NMR δ 0.10, 0.23, 0.37 (Me$_3$Si); ^{13}C NMR δ −0.34, −0.30 (Me$_3$Si), 2.89 (OSiMe$_3$), 93.78, 113.37 (ring *C* quat); ^{29}Si NMR δ −17.04, −17.32 (Me$_3$Si), 11.21 (OSiMe$_3$), 44.98 (ring Si). **14c**: ^{1}H NMR δ −0.11, −0.09, 0.09 (Me$_3$Si); ^{13}C NMR δ −0.52, 0.91 (Me$_3$Si), 2.27 (OSiMe$_3$), 38.15 (ring C—*C*H$_2$), 103.14 (ring =CH), 106.98 (ring quat C sp^3), 153.34 (ring =*C*Me—O–); ^{29}Si NMR δ −13.45, 16.62 (Me$_3$Si), 9.05, 20.45 (OSiMe$_3$ and ring Si). **15c** (minor diastereomer): ^{1}H, δ −0.07, 0.27, 0.38 (Me$_3$Si); ^{13}C NMR δ −0.23, −0.11 (Me$_3$Si), 2.70 (OSiMe$_3$); ^{29}Si NMR δ −16.89, −17.16 (Me$_3$Si), 9.17 (OSiMe$_3$), 45.98 (ring Si).

Reaction of Adamantylsilene with Benzalacetophenone. The silene reacted in a [2 + 4] manner to give the 1-sila-2-oxacyclohex-3-ene **16a** in >95% yield, with a small amount of unidentified byproduct. Recrystallization from benzene gave a colorless solid: mp 180–181 °C; MS (*m*/*e*) calcd 618.3201, found 618.3186. ^{1}H NMR δ 0.33, 0.36, 0.37 (each 9 H, s, Me$_3$Si), 1.6–2.0 (Ad), 4.16 (1 H, d, H$_\mathrm{A}$ of ring C—CH$_\mathrm{A}$Ph—CH$_\mathrm{B}$=CPh—O– system, J_{AB} = 7.2 Hz), 5.55 (1 H, d, H$_\mathrm{B}$), 6.9–7.75 (Ph); ^{13}C NMR δ 1.72, 1.76 (Me$_3$Si), 4.27 (OSiMe$_3$), 28.96 (Ad CH), 37.09, 39.70 (Ad CH$_2$), 41.71 (Ad quat C), 51.09 (ring *C*H—Ph), 93.21 (ring quat C, 106.81 (ring =*C*H—C–), 124.84, 126.87, 127.81, 128.39, 128.78, 131.40 (Ar CH), 138.05, 144.02 (Ar quat C), 149.11 (ring =*C*Ph—O–); ^{29}Si NMR δ −13.96, −16.45 (Me$_3$Si), 6.45 (OSiMe$_3$), 17.36 (ring Si). Anal. Calcd for C$_{35}$H$_{54}$Si$_4$O$_2$: C, 67.90; H, 8.79 Found: C, 67.64; H, 8.96.

Reaction of Mesitylsilene with Benzalacetophenone. To a clean dry NMR tube were added 0.23 g (5.9 mmol) of mesityltris(trimethylsilyl)silane and 0.12 g (5.8 mmol) of benzalacetophenone. The tube was placed in a Schlenk tube, which was

Table I. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters

empirical formula	$C_{24}H_{48}O_2Si_4$
M_r	481.0
cryst size, mm	0.40 × 0.15 × 0.35
cryst class	triclinic
space group	$P\bar{1}$
a, Å	10.424 (3)
b, Å	16.674 (4)
c, Å	9.924 (3)
α, deg	93.65 (3)
β, deg	114.11 (3)
γ, deg	105.88 (2)
V, Å^3	1483.7 (7)
Z	2
D_{calc}, g cm^{-3}	1.08
μ(Mo Kα), cm^{-1}	2.10
F(000)	528
ω-scan width, deg	0.7 + 0.35 tan θ
range θ collected, deg	1–25 ($\pm h, \pm k, l$)
total no. of reflns	5217
no. of obsd data [$I > 3\sigma(I)$]	3312
weighting g	0.001
R	0.081
R_w	0.086
goodness of fit	2.94
largest Δ/σ	0.003
no. of parms refined	272
max density in ΔF map, e/Å^3	0.57[a]

[a] Largest residual electron density peaks were less than 1.6 Å from Si atoms and were not chemically significant.

Table II. Important Bond Distances (Å) and Angles (deg) for 13a

	Bond Distances		
Si(1)–Si(3)	2.3582 (27)	O(1)–C(1)	1.444 (6)
Si(1)–Si(4)	2.3498 (26)	Si(1)–C(1)	1.942 (6)
Si(2)–O(1)	1.637 (5)	av Si–C_{methyl}	1.856 (8)
	Bond Angles		
Si(4)–Si(1)–Si(3)	112.83 (10)	O(2)–C(1)–Si(1)	102.4 (4)
C(1)–Si(1)–Si(3)	117.96 (19)	C(1)–O(2)–Si(2)	142.3 (4)
C(1)–Si(1)–Si(4)	116.41 (18)	C(4)–Si(1)–C(1)	95.9 (26)

evacuated, and then argon was allowed into the system, followed by the addition of 0.3 mL of C_6D_6. The tube was sealed under argon and was photolyzed for 3 h at 10 °C. NMR spectroscopy showed that 1-sila-2-oxacyclohex-3-ene **16c** was formed essentially quantitatively. **16c**: ^{1}H NMR δ 0.35, 0.52, 1.28 (each 9 H, s, Me_3Si), 2.72, 3.27, 3.55 (each 3 H, s, Me of mesityl, restricted rotation), 5.67 (1 H, d, H_A of ring system C—CH_APh—CH_B═CPh—O–, J_{AB} = 7.5 Hz), 6.60 (1 H, d, H_B), 7.4–8.3 (Ar); ^{13}C NMR δ 0.59, 0.62 (Me_3Si), 1.94 ($OSiMe_3$), 20.42, 25.34, 26.24 (Me of mesityl), 51.95 (ring *C*H—Ph), 84.83 (ring quat C), 109.16 (ring ═CH), 151.55 (ring ═CPh—O–), 124.73 (2 C), 126.09, 127.90, 128.05 (2 C), 128.23 (2 C), 130.13 (2 C), 132.00, 132.78 (Ar CH), 132.62, 135.91, 137.09, 139.91, 144.24, 145.94 (Ar quat C); ^{29}Si NMR δ −13.35, −14.53 (Me_3Si), 11.21 ($OSiMe_3$), 17.48 (ring Si).

X-ray Structural Determination. Compound **13a** proved to be stable to air exposure. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The ω–2θ scan technique was applied with variable scan speeds. The intensities of three standard reflections measured ever 2 h showed a mean decrease of 38%, and a correction was applied to the data with the assumption of linear decay. An empirical absorption correction was applied.[12]

The structure was solved by direct methods. C, O, and Si atoms were refined anisotropically by full-matrix least squares to minimize $\sum w(F_o - F_c)^2$, where $w^{-1} = \sigma^2(F) + gF^2$. Hydrogen atoms were positioned on geometric grounds (C–H = 0.95 Å) and overall hydrogen atom thermal parameters refined to a value of 0.125 (1) Å^2. Crystal data, data collection, and least-squares parameters are listed in Table I. All calculations were performed with use of SDP,[13] SHELX76,[14] and SHELXS86[15] on a PDP11/23 and an Apollo computer. Some important bond angles and distances are given in Table II. An ORTEP[16] diagram of the structure of **13a** is presented in Figure 1.

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Supplementary Material Available: Tables of atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, torsion angles, and least-squares planes for **13a** and ^{1}H, ^{13}C, and ^{29}Si NMR spectra of compounds **6a** and **7a**, **6b** and **7b**, **8b**, **10a** and **11a**, **10b** and **11b**, **12**, **13b** and **14b**, **14c** and **15c**, and **16c** (37 pages); a listing of observed and calculated structure factors for **13a** (12 pages). Ordering information is given on any current masthead page.

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