# Cycloaddition Reactions of Stable Silenes with Acylsilanes

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Silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (R = Ad, *t*-Bu, Mes) generally react with the simple aroylsilanes $R'_3SiCOAr$ (R′ = Ph, Me; Ar = Ph, $C_6H_4$-X-*p*) in a [2 + 4] manner to give relatively stable bicyclic adducts. Only the [2 + 2] adduct was formed when R = Mes, R′ = $Me_3Si$, and Ar = Ph. The $^1H$, $^{13}C$, and $^{29}Si$ NMR spectral data for a series of simple acylsilanes $Ph_3SiCOC_6H_4X$-*p* and $Me_3SiCOPh$ are given.

It has been well established in the recent past that silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (**2**) react with a wide variety of aldehydes and ketones $R'R''C{=}O$ (**3**) usually to give the [2 + 2] cycloadducts, the siloxetanes **4**.[1] However, in some cases the reaction occurred in a [2 + 4] manner to give the bicyclic adducts **5** (see Scheme I), where the four-π-electron component of the cycloaddition reaction usually was derived from the carbonyl group and two π electrons of an attached aromatic ring in the ketone $ArR''C{=}O$.[1]

In related work Wiberg reported that his silene $Me_2Si{=}C(SiMe_3)_2$ reacted with benzophenone to give the kinetic [2 + 4] or the thermodynamic [2 + 2] adduct, depending on the conditions,[2] and Auner reported that one of his silenes reacted with a number of aldehydes to give the [2 + 2] adducts.[3]

In the present studies the silene **2** was generated by the photolysis of the acylsilane $(Me_3Si)_3SiCOR$ (**1**) and thus was formed in the presence of a carbonyl group. It might have been anticipated from the above findings that the silene would react with its parent acylsilane, leading to bimolecular products such as **6**: however, such products have only been observed in one case, which involved reaction of a photochemically generated silene with its parent acyldisilane precursor.[4] Failure to react in this way could be due primarily to steric hindrance between a bulky silene and its bulky acylsilane precursor, or it could be due primarily to electronic factors influencing the reactivity of the carbonyl group of the acylsilane toward cycloaddition reactions with a silene. We have now investigated this situation to see whether silenes such as **2** will react with acylsilanes in general.

None of the silenes tested participated in cycloaddition reactions with their own acylsilane precursor (i.e. $(Me_3Si)_3SiCOR$) or with any other tris(trimethylsilyl)acylsilane introduced into their presence. However, when the nominal steric bulk of the added acylsilane was reduced, such that either a triphenylsilyl group or a trimethylsilyl group was attached to the carbonyl of the acylsilane **7** (i.e. $Ph_3SiCOAr$ or $Me_3SiCOAr$) instead of a tris(trimethylsilyl)silyl group, cycloaddition occurred readily in a [2 + 4] manner to give bicycloadducts **8**[17] of moderate stability (except when R = Mes, where the [2 + 2] adduct was formed), as shown in Scheme II.

Unlike the previous cases of [2 + 4] cycloaddition,[1] where conversions to the [2 + 2] adduct occurred spontaneously and cleanly, the [2 + 4] adducts in the present case did not isomerize to the [2 + 2] adducts. Attempts to cause isomerization by photolysis over 5 h, or by mild thermolysis at 70 °C, led to complex mixtures of products. In the case where the added acylsilane had an alkyl group attached to the carbonyl group, i.e. $Ph_3SiCOMe$, the only compound formed was the product of an ene reaction, a mode of reaction of silenes with simple ketones first described by Sommer et al.[5]

The formation of [2 + 4] rather than [2 + 2] cycloadducts as the end products of the reactions of the silenes with acylsilanes differs from the behavior of the same silenes with simple aldehydes or ketones. In the latter case it appears that the [2 + 4] adduct is the kinetic isomer and the [2 + 2] isomer is the thermodynamic isomer, as Wiberg also proposed.[3] In the reaction with acylsilanes the [2 + 4] adduct may be the thermodynamic product. It is striking that this pathway leads to loss of aromatic resonance stabilization energy in the products. Very similar results, namely [2 + 4] cycloadditions (except for the mesitylsilene), have been reported by us recently for the reactions of the same silenes with several imines.[6]

Whether this heterodiene [2 + 4] cycloaddition reaction occurs by a concerted process, thus following Woodward–Hoffman rules, or by a stepwise process is uncertain: some [2 + 4] cycloaddition reactions involving silenes are believed not to be concerted.[7-9] Evidence concerning the mechanisms of additions of various reagents, including carbonyl compounds, to silenes has been summarized by Raabe and Michl.[10] The [2 + 2] pathway followed by the mesitylsilene is most likely a stepwise reaction, and the results are in accord with the general observation that the mesitylsilene, which may be differently polarized because of conjugation and/or which may present unusual steric hindrance toward [2 + 4] additions,[11] frequently reacts

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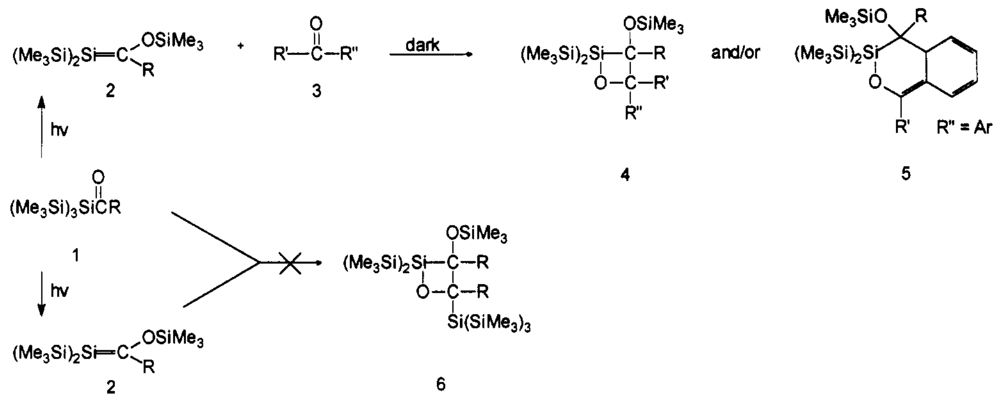
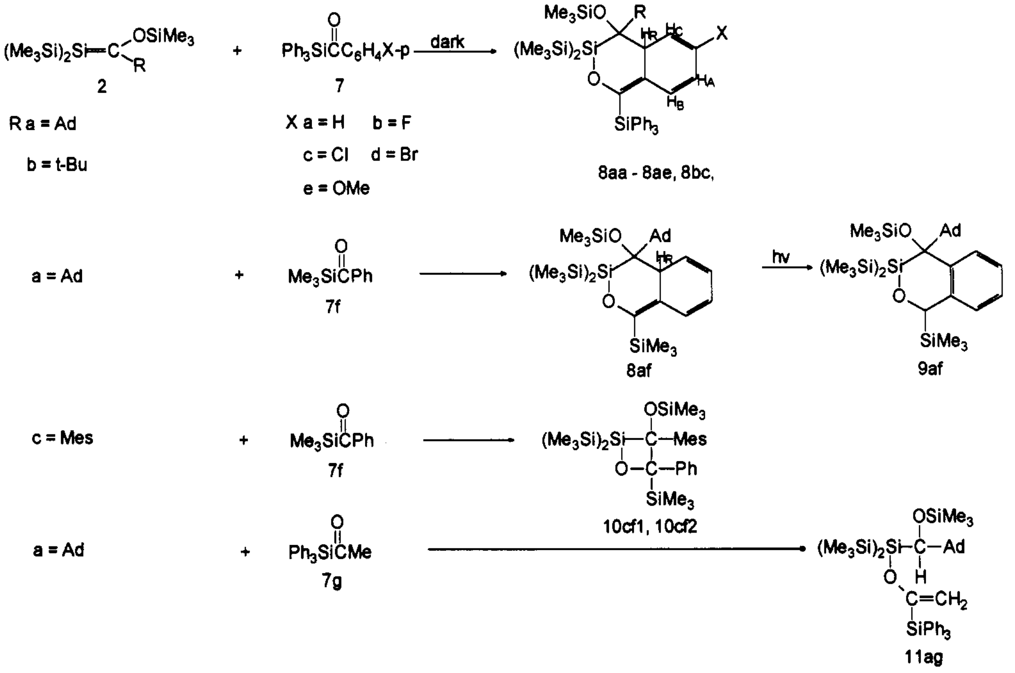
**Scheme I**



**Scheme II**



differently than the adamantyl- and other alkyl-substituted silenes.

It appears from the above results involving para-substituted acylsilanes that electronic effects do not play a major role in the cycloaddition reactions, since all the acylsilanes tested reacted at roughly comparable rates to give comparable amounts of product. When the tris(trimethylsilyl)silyl group replaced the triphenylsilyl or trimethylsilyl groups in the acylsilane, no cycloaddition reactions occurred. This suggests that steric effects play an important role in controlling these reactions.

## NMR Structure Determination and Decoupling Experiments

Previous NMR studies had established that the ring silicon atom in siloxetanes (the product of [2 + 2] reactions between silenes and carbonyl compounds) resonated in the range 40–65 ppm, whereas the ring silicon atom in six-membered rings containing a Si–O linkage (the products of [2 + 4] cycloaddition) resonated much further upfield (in the range −10 to +17.5 ppm).[1,7] Hence, it was evident using $^{29}$Si NMR spectroscopy that the products from reactions of the silenes **2** with the simple acylsilanes were [2 + 4] adducts since their chemical shifts were relatively far upfield (in the 15–18 ppm range). These findings were confirmed by the $^1$H NMR spectra, which showed the ring juncture $CH_R$ proton resonance in the range 4.8–5.1 ppm, as well as three (for para-substituted acylsilanes) vinylic C–H absorptions in the range from 5–6.7 ppm. Detailed proton decoupling experiments (described in the Experimental Section for the *p*-bromo acylsilane adduct) established the proton couplings involved in the observed multiplets for the ring hydrogen atoms, and the results were in accord with the proposed structures. A similar study had been done on closely related structures derived from other [2 + 4] additions.[1]

## Experimental Section

All NMR spectra were run on either a Varian XL400 spectrometer or a Varian XL200 NMR spectrometer in $C_6D_6$ with TMS as reference. Where appropriate, APT[12] or DEPT[13] NMR pulse sequences were employed for $^{13}$C NMR spectra. $^{29}$Si NMR spectra were run in the DEPT mode or were run with NOE suppressed. Mass spectra were obtained on a VG70-250S mass spectrometer operating in the electron impact (EI) mode for both low- and high-resolution mass spectra.

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Solutions in sealed NMR tubes were photolyzed inside a water-cooled Dewar flask maintained at 10 °C, using three external 100-W Par38 mercury spot lamps (BLAK RAY long-wavelength ultraviolet lamps, Ultraviolet Products Inc.) having wavelengths $\lambda > 360$ nm. The preparations of the para-substituted benzoylacylsilanes[14] and of $Me_3SiCOPh$[15] have been described earlier. Yields given are based either on moles of isolated material relative to moles of parent acylsilane or, where products were not isolated, on the proton NMR intensities of a $Me_3Si$ signal of the product relative to one-third of the $Me_3Si$ signal of unconsumed acylsilane.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

**Typical Procedure.** Adamantoyltris(trimethylsilyl)silane (**1a**; 0.1 g, 0.24 mmol) was placed in an NMR tube, which was evacuated in a Schlenk tube and then flushed with argon as 0.5 mL of $C_6D_6$ was added. The solution was photolyzed for 17–24 h to yield the adamantylsilene **2a** containing a small amount of **1a**. An equimolar amount of the appropriate simple acylsilane **7** was added in the dark under argon at room temperature. The progress of the reaction was monitored by $^1H$ NMR spectroscopy, and in many cases the reaction appeared to be complete shortly after the reagents were mixed. The cycloadducts **8aa**–**8ae**, **8bc**, etc. were isolated and purified by passing the crude reaction mixtures through a column of silica gel which had been treated with trimethylchlorosilane, using hexane as eluent. Many of the compounds were difficult to purify by recrystallization.

**Reaction of the Silene 1a with Benzoyltriphenylsilane (7a) To Give 8aa.** Following the above procedure benzoyltriphenylsilane (**7a**; 0.09 g, 0.24 mmol) was added to the adamantylsilene **2a** prepared from photolysis of 0.1 g (0.24 mmol) of acylsilane **1a** in 0.5 mL of $C_6D_6$. The reaction was complete within 1 h, and workup gave 46% of **8aa**, which could not be purified further by crystallization or chromatography due to decomposition in solution. **8aa**: $^1H$ NMR $\delta$ 0.15, 0.29, 0.30 (each 9H, s, $Me_3Si$), 1.66–2.19 (15H, s, Ad), 4.87 (1H, br m, $H_R$), 5.36 (1H, m, $H_A$), 5.75 (1H, m, $H_X$), 6.39 (1H, d × d, $H_C$), 6.50 (1H, d, $H_B$), 7.15–7.87 (15H, m, Ph); $^{13}C$ NMR $\delta$ 1.05, 1.29, 4.81 ($Me_3Si$), 29.40 (CH Ad), 37.35, 39.76 ($CH_2$ Ad), 43.38 (quat C Ad), 49.64 (ring $CH_R$), 84.32 (ring *C*–$OSiMe_3$), 120.07, 121.80, 128.06, 129.32 (CH $sp^2$), 128.11, 129.97, 136.89 (CH $sp^2$ Ph), 130.29, 134.84, 155.90 (quat C $sp^2$); $^{29}Si$ NMR $\delta$ −19.70 ($Ph_3Si$), −17.35, −15.91 ($Me_3$-Si–Si), 4.18 ($OSiMe_3$), 14.86 (ring Si); HR-MS *m/e* calcd for $C_{45}H_{62}O_2Si_5$ ($M^+$) 774.3596, found 774.3626.

***p*-Fluorophenyl Adduct 8ab.** After a less than 1-h reaction, workup gave the bicyclic adduct **8ab** in 51% yield: mp 91–93 °C dec; $^1H$ NMR $\delta$ 0.12, 0.24, 0.26 (each 9H, s, $Me_3Si$), 1.6–2.2 (15H, m, Ad), 5.13–5.22 (2H, overlapping m, $CH_R + H_A$), 5.85 (1H, distorted d × t?, $H_B$), 6.45 (1H, d × m?, $H_C$), 7.15–7.30, 7.6–7.9 (15H, m, Ph); $^{13}C$ NMR $\delta$ 0.98, 1.06, 4.80 ($Me_3Si$), 29.29 (CH Ad), 37.22, 39.85 ($CH_2$ Ad), 43.63 (quat C Ad), 48.66 (ring $CH_R$), 83.98 (ring *C*–$OSiMe_3$), 103.76, 103.94, 114.76, 115.13, 128.22, 129.93, 131.45, 136.77 (CH $sp^2$), 129.06, 134.32, 155.04, 158.13 (quat C $sp^2$); $^{29}Si$ NMR $\delta$ −19.48 ($Ph_3Si$), −16.80, −15.52 ($Me_3Si$), 4.82 ($OSiMe_3$), 17.47 (ring Si); HR-MS *m/e* calcd for $C_{45}H_{61}FO_2Si_5$ 792.3502, found 792.3537; MS *m/e* (%) 777 (9, $M^+ - Me$), 719 (77, $M^+ - Me_3Si$), 584 (9, 719 − Ad), 259 (98, $Ph_3Si$). Anal. Calcd for $C_{45}H_{61}FO_2Si_5$: C, 68.18; H, 7.70. Found: C, 68.67; H, 7.50.

**Preparation of the *p*-Chloro Adduct 8ac.** The reaction with (*p*- chlorobenzoyl)acylsilane occurred over less than 1 h to give a single product, isolated in 56% yield: mp 152–154 °C dec; $^1H$ NMR $\delta$ 0.14 (9H, s, $Me_3Si$), 0.25 (18H, s, $Me_3Si + OSiMe_3$), 1.59–2.13 (15H, m, Ad), 4.97 (1H, d × d?, $H_R$), 5.23 (1H, apparent d × t, $J_{AB} = 10.0$, $J_{AC} = 1.8$ Hz, $H_A$), 6.43 (1H, d × d, $J_{RB} = 1.6$ Hz, $H_B$), 6.48 (1H, d?, $H_C$), 7.15–7.26, 7.73–7.81 (15H, m, Ph); $^{13}C$ NMR $\delta$ 0.94, 1.11, 4.77 ($Me_3Si$), 29.31 (CH Ad), 37.18, 39.74 ($CH_2$ Ad), 43.26 (quat C Ad), 50.70 (ring $CH_R$), 84.31 (ring *C*–$OSiMe_3$), 121.34, 124.71, 129.95, 130.41, 136.79 (each CH $sp^2$), 126.90, 127.22, 134.28, 158.57 (each quat C $sp^2$); $^{29}Si$ NMR $\delta$ −19.67 ($Ph_3Si$), −16.71, −15.69 ($Me_3Si$), 5.17 ($OSiMe_3$), 16.49 (ring Si); HR-MS *m/e* calcd for $M^+$ 808.3206, found 808.3257; MS *m/e* (%) 793 (4, $M^+ - Me$), 735 (40, $M^+ - Me_3Si$), 259 (60, $Ph_3Si$), 135 (100, Ad). Anal. Calcd for $C_{45}H_{61}ClO_2Si_5$: C, 66.83; H, 7.54. Found: C, 66.63, H, 7.15.

**Preparation of 8bc from Silene 2b and Acylsilane 7c.** A solution of the *tert*-butylacylsilane **1b** (0.1 g, 0.3 mmol) in 0.5 mL of $C_6D_6$ was photolyzed for 17 h, to yield a mixture of the silene **2b** and its head-to-head dimer. To this mixture was added 0.12 g (0.30 mmol) of the *p*-chloroacylsilane **7c** in the dark, and this solution was kept in the refrigerator for 7 days, by which time conversion to the [2 + 4] adduct **8bc** was complete. Workup gave crystalline product in 48% yield, mp 151–153 °C dec. **8bc**: $^1H$ NMR $\delta$ 0.06, 0.20, 0.22 (each 9H, s, $Me_3Si$), 1.27 (9H, s, $Me_3C$), 4.97 (1H, m, $H_R$), 5.18 (1H, d × t?, apparent $J = 1.7$, 9.9 Hz, $H_A$), 6.35–6.41 (2H, m, $H_B$ and $H_C$), 7.17–7.20, 7.72–7.77 (15H, m, Ph); $^{13}C$ NMR $\delta$ 0.70, 0.74, 4.52 ($Me_3Si$), 30.08 (*Me*$_3$C), 41.01 ($Me_3$*C*), 50.97 (ring $CH_R$), 83.61 (ring *C*–$OSiMe_3$), 120.98, 124.47, 128.25 (3C), 129.94 (6C), 136.73 (6C) (CH $sp^2$), 127.30, 128.26, 134.28 (3C), 158.36 (quat C $sp^2$); $^{29}Si$ NMR $\delta$ −19.79 ($Ph_3Si$), −16.68, −16.25 ($Me_3Si$), 4.90 ($OSiMe_3$), 18.22 (ring Si); HR-MS *m/e* calcd for $M^+$ 730.2737, found 730.2768; MS *m/e* (%) 730 (2, $M^+$), 715 (2, $M^+ - Me$), 657 (27), 259 (60, $Ph_3Si$). Anal. Calcd for $C_{39}H_{55}ClO_2Si_5$: C, 64.06; H, 7.53. Found: C, 64.02; H, 7.61.

**Isolation of the *p*-Bromo Adduct 8ad.** After being allowed to react for about 1 h, the *p*-bromo compound **8ad** was isolated in 50% yield: mp 165 −167 °C dec; $^1H$ NMR $\delta$ 0.11, 0.24, 0.25 (each 9H, s, $Me_3Si$), 1.55–2.15 (15H, m, Ad), 4.80 (1H, looks like two overlapping triplets, $J_{RC} = 4.2$, $J_{RA} = 1.7$, $J_{RB} = 1.4$ Hz, $H_R$), 5.33 (1H, looks like d × t?, $J_{AB} = 10.0$, $J_{AC} = 1.4$ Hz, $H_A$), 6.35 (1H, d × d, $H_B$), 6.70 (1H, d × d, $H_C$), 7.15–7.22, 7.72–7.79 (15H, m, Ph); $^{13}C$ NMR $\delta$ 0.93, 1.15, 4.47 ($Me_3Si$), 29.32 (CH Ad), 37.19, 39.74 ($CH_2$ Ad), 43.18 (quat C Ad), 51.78 (ring $CH_R$), 84.37 (ring *C*–$OSiMe_3$), 123.18, 128.29, 128.71, 129.96, 130.31, 136.80 (CH $sp^2$), 115.70, 127.61, 134.26, 158.85 (quat C $sp^2$); $^{29}Si$ NMR $\delta$ −19.76 ($Ph_3Si$), −16.73, −15.73 ($Me_3Si$), 5.27 ($OSiMe_3$), 16.15 (ring Si); HR-MS *m/e* calcd for $M^+$ 852.2701, found 852.2642; MS *m/e* (%), 854 (2, $M^+$), 839 (3, $M^+ - Me$), 781 (25, $M^+ - Me_3Si$), 259 (65, $Ph_3Si$), 135 (100, Ad). Anal. Calcd for $C_{45}H_{61}BrO_2Si_5$: C, 63.41; H, 7.23. Found: C, 63.85; H, 7.43.

**Properties of the *p*-Methoxy Adduct 8ae.** After less than 1 h of reaction the *p*-methoxy compound **8ae** was isolated in 40% yield: mp 105–108 °C dec; $^1H$ NMR $\delta$ 0.16, 0.31, 0.33 (each 9H, s, $Me_3Si$), 1.65–2.20 (15H, m, Ad), 3.31 (3H, s, MeO), 5.11 (1H, m, $H_R$), 5.26 (1H, m, $H_A$), 5.43 (1H, d × t?, $J_{AB} = 10.1$, $J_{RB?} = 1.8$ Hz, $H_B$), 6.50 (1H, d × d, $J_{AC?} = 1.3$ Hz, $H_C$), 7.15–7.20, 7.75–7.81 (15H, m, Ph); $^{13}C$ NMR $\delta$ 1.06, 1.19, 4.97 ($Me_3Si$), 29.37 (CH Ad), 37.33, 40.09 ($CH_2$ Ad), 43.70 (quat C Ad), 48.52 (ring $CH_R$), 53.71 (MeO), 85.04 (ring *C*–$OSiMe_3$), 96.18, 119.43, 128.13, 129.65, 129.79, 136.83 (CH $sp^2$), 130.17, 134.64, 151.62, 156.19 (quat C $sp^2$); $^{29}Si$ NMR $\delta$ −19.77 ($Ph_3Si$), −17.43, −15.72 ($Me_3Si$), 3.64 ($OSiMe_3$), 15.69 (ring Si); HR-MS *m/e* calcd for $C_{46}H_{64}O_3Si_5$ 804.3698, found 804.3701. Anal. Calcd for $C_{46}H_{64}O_3Si_5$: C, 68.65; H, 7.96. Found: 68.77; H, 8.30.

**Attempted Reaction of Silene 2a with $Ph_3SiCOC_6H_4NO_2$-*p*.** When the (*p*-nitroacyl)silane was added to prepared silene **2a** in $C_6D_6$, the NMR spectra indicated that a complex mixture of products had formed. This reaction was not investigated further.

**Proton Decoupling Experiment To Identify Proton Couplings in Adduct 8ad.** The proton spectra of the adduct from (*p*-bromobenzoyl)triphenylsilane, **8ad**, showed the best resolved multiplets of vinylic protons of all the compounds studied, and these results were used in a proton decoupling experiment to identify the couplings present. Irradiation at 4.89 ppm ($H_R$) caused the apparent doublet of triplets at 5.35 ppm ($H_A$) (with measurable couplings of 10.0 Hz and a second coupling of about 1.7 Hz) to be reduced to a doublet of doublets, with $J_{AC} = 1.4$ Hz and $J_{AB} = 10.0$ Hz (thus $J_{RA} = 1.7$ Hz), the doublet of doublets for $H_B$ at 6.35 ppm (with *J*'s of 10.0 and 1.4 Hz) to become a doublet with $J_{AB} = 10.0$ Hz (thus $J_{RB} = 1.4$ Hz), and the doublet of doublets at 6.70 ppm ($H_C$) (with *J*'s of 4.2 and 1.4 Hz) to

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become a doublet with $J_{AC}$ = 1.4 Hz (thus $J_{RC}$ = 4.2 Hz). Therefore, $H_R$ is coupled to each of the three vinylic protons.

Irradiation at 5.35 ppm ($H_A$) caused the complex multiplet of $H_R$ at 4.89 ppm to become less complex, so that $J_{RC}$ = 4.2 Hz and $J_{RB}$ = 1.4 Hz could be measured. The original doublet of doublets of $H_B$ at 6.35 ppm collapsed to a doublet with $J_{RB}$ = 1.4 Hz, thus identifying $J_{AB}$ = 10.0 Hz, while the original doublet of doublets of $H_C$ at 6.70 ppm became a doublet with $J_{RC}$ = 4.2 Hz, thus identifying $J_{AC}$ = 1.4 Hz.

Irradiation at $H_B$ (6.35 ppm) caused the signal at 4.89 ppm to collapse to a clean doublet of doublets with $J_{RC}$ = 4.2 ppm and $J_{RA}$ = 1.7 ppm. The doublet of doublets at 6.70 ppm ($H_C$) was unchanged, indicating that there was no 1,4-coupling between $H_B$ and $H_C$. Irradiating $H_C$ at 6.70 ppm effected the expected changes in the other multiplets. On the basis of these studies, the coupling constants in **8d** are $J_{AB}$ = 10.0, $J_{RC}$ = 4.2, $J_{RA}$ = 1.7, and $J_{RB}$ = $J_{AC}$ = 1.4 Hz.

The spectra of the other members of the family of compounds with structure 8 were more severely overlapped, and while $J_{AB}$ and $J_{RC}$ could usually be measured, the other couplings were often not identifiable.

**Attempted Reaction of Silene 2 with Its Precursor Acylsilane.** Separate 100-mg samples of the adamantylacylsilane **1a**, the *tert*-butylacylsilane **1b**, and the mesitylacylsilane **1c** were placed in NMR tubes which were evacuated and then flushed with argon. Deuteriobenzene (0.3 mL) was added to each tube under argon, and these solutions were then photolyzed for 12 h, at which time each tube was found to contain a mixture of the original acylsilane and the silene derived therefrom, using NMR spectroscopy. After the mixture stood for 24 h at room temperature, it was found that the acylsilanes had not reacted with the silenes present but that the silenes were partially converted back to the parent acylsilanes as expected. Heating of the samples at 70 °C for 24 h caused no observable reaction between the acylsilanes and silenes, except that the silenes had been converted back to their parent acylsilanes.[16]

**Attempted Reaction between Silenes and Tris(trimethylsilyl)acylsilanes.** Two 100-mg samples of the (adamantylacyl)silane **1a** in 0.3 mL of $C_6D_6$ in NMR tubes were photolyzed for 18 h, at which time the solutions contained about 85% silene and 15% residual acylsilane. To one sample was added an equimolar amount of the (*tert*-butylacyl)silane **1b** and to the second an equimolar amount of the (mesitylacyl)silane **1c**. After the mixtures stood in the dark at room temperature, NMR spectroscopy indicated that no reaction had occurred. Heating the samples to 70 °C for 24 h caused the adamantylsilene **2a** to revert back to its parent acylsilane **1a**, shown to be present with the other acylsilane added, but there was no evidence that reaction had occurred between silene **2a** and the added acylsilane. The samples were then photolyzed for 24 h, at which time NMR spectroscopy indicated the presence of two different silenes.

**Reaction of the Adamantylsilene 2a with Benzoyltrimethylsilane To Give 8af and 9af.** (Adamantylacyl)silane **1a** (0.10 g, 0.24 mmol) and 0.3 mL of $C_6D_6$ in an NMR tube under argon were photolyzed for 17 h. To this solution containing mainly silene **2a** was added 0.043 g (0.24 mmol) of benzoyltrimethylsilane. After this mixture stood in the dark for 3 h, NMR spectroscopy indicated that the [2 + 4] cycloadduct **8af** was present in 89% yield ($^1$H NMR). Further photolysis for 72 h led to the conversion of **8af** to **9af**, present in 85% yield. **8af**: $^1$H NMR $\delta$ 0.24, 0.25, 0.29, 0.37 (each 9H, s, $Me_3Si$), 1.61–1.95 (15H, m, Ad), 3.79 (1H, m, $CH_R$), 5.75–5.92 (2H, br m, vinyl CH), 6.39–6.46 (1H, d × d, vinyl CH); $^{13}$C NMR $\delta$ 0.14, 0.55, 2.14, 4.16 ($Me_3Si$), 29.43 (CH Ad), 37.57, 40.14 ($CH_2$ Ad), 41.53 (quat C Ad), 48.76 (ring $CH_R$), 86.33 (ring *C*-$OSiMe_3$), 120.77, 124.06, 128.24, 129.13 (CH sp$^2$), 125.77, 163.63 (quat C sp$^2$); $^{29}$Si NMR $\delta$ −17.88, −15.95 ($Me_3Si$–Si), −6.23 ($Me_3Si$–C), 4.48, 5.92 ($OSiMe_3$ and ring Si). HR-MS *m/e* calcd for $C_{30}H_{56}O_2Si_5$ ($M^+$) 588.3126, found 588.3126. **9af**: $^1$H NMR $\delta$ 0.20, 0.25, 0.33, 0.38 (each 9H, s, $Me_3Si$), 1.5–2.1 (15H, m, Ad), 4.23 (1H, s, ring $CH_R$), 6.6–7.9 (4H, br m, Ar); $^{13}$C NMR $\delta$ 0.07, 0.32, 0.74, 4.41 ($Me_3Si$), 29.47 (CH Ad), 37.22, 40.92 ($CH_2$ Ad), 41.12 (quat C Ad), 46.70 (ring $CH_R$), 85.94 (ring *C*-$OSiMe_3$), 117.99, 124.87, 128.45, 128.84 (CH sp$^2$), 126.07, 163.52 (quat C sp$^2$); $^{29}$Si NMR $\delta$ −18.69, −14.79 ($Me_3Si$), −6.04 ($Me_3Si$–C), 6.27, 7.33 ($OSiMe_3$ and ring Si).

**Reaction of Mesitylsilene 2c with Benzoyltrimethylsilane To Give 10cf1 and 10cf2.** The (mesitylacyl)silane **1c** (0.13 g, 0.34 mmol) in 0.25 mL of $C_6D_6$ was photolyzed under argon for 24 h, forming the silene **2c** in 95% yield ($^1$H NMR). To this solution was added 0.06 g (0.34 mmol) of benzoyltrimethylsilane. After 4 h in the dark at room temperature NMR spectroscopy indicated the presence in 95% yield ($^1$H NMR) of the pair of diastereomeric siloxetanes **10cf1**, **10cf2** in a ratio of 3:2. **10cf1** (major diastereomer): $^1$H NMR $\delta$ −0.18, −0.07, 0.26, 0.40 (each 9H, s, $Me_3Si$), 1.95, 1.99, 2.47 (each 3H, s, Me Mes), 6.6–7.6 (with **10cf2**, br m, Ar); $^{13}$C NMR $\delta$ 0.41, 0.64, 2.07, 3.48 ($Me_3Si$), 20.75, 22.85, 25.11 (Me Mes), 99.03, 99.82 (quat ring C sp$^3$), 126.15, 127.52 (2C), 128.46 (2C), 129.69, 130.37 (CH sp$^2$), 136.63, 137.00, 137.75, 139.94, 144.41 (quat C sp$^2$); $^{29}$Si NMR $\delta$ −16.06, −15.86 ($(Me_3\textit{Si})_2Si$), 4.26 ($Me_3Si$–C), 8.79 ($OSiMe_3$), 50.89 (ring Si). **10cf2** (minor diastereomer): $^1$H NMR $\delta$ −0.29, 0.02, 0.15, 0.16 (each 9H, s, $Me_3Si$), 1.99, 2.08, 2.54 (each 3H, s, Me Mes), 6.5–7.7 (with **10cf1**, m, Ar); $^{13}$C NMR $\delta$ 0.17, 0.30, 1.37, 2.95 ($Me_3Si$), 20.68, 21.96, 24.99 (Me Mes), 96.23, 101.36 (ring quat C sp$^3$), 125.40, 127.18 (2C), 127.56 (2C), 129.78, 129.89 (CH sp$^2$), 137.10, 137.42, 138.27, 138.33, 144.88 (quat C sp$^2$); $^{29}$Si NMR $\delta$ −16.62, −16.50 ($(Me_3\textit{Si})_2Si$), 3.59 ($Me_3Si$–C), 7.50 ($OSiMe_3$), 54.15 (ring Si).

**Formation of the Ene Product 11ag from Silene 2a and Acetyltriphenylsilane (7g).** To a solution of the adamantylsilene **2a** (prepared by photolysis over 17 h of 0.1 g (0.24 mmol) of acylsilane **1a** in 0.5 mL of $C_6D_6$) was added 0.07 g (0.24 mmol) of $Ph_3SiCOMe$ in the dark. After about 1 h, the product was isolated after recrystallization from hexane in 62% yield; mp 153–154 °C. **11ag**: $^1$H NMR $\delta$ 0.20 (9H, s, $Me_3Si$), 0.32 (18H, s, two $Me_3Si$, accidental overlap), 1.65–1.95 (15H, m, Ad), 4.08 (1H, s, CH–$OSiMe_3$), 4.93 (1H, d, *J* = 1.7 Hz, CH sp$^2$), 5.15 (1H, d, CH sp$^2$), 7.18–7.37, 7.76–7.83 (15H, m, Ph); $^{13}$C NMR $\delta$ 0.99, 1.29, 2.38 ($Me_3Si$), 29.08 (CH Ad), 37.36, 40.35 ($CH_2$ Ad), 38.85 (quat C Ad), 79.80 (CH–$OSiMe_3$), 108.22 (=$CH_2$), 128.05, 129.92, 136.88 (CH sp$^2$, Ph), 133.82 (ipso C Ph), 165.30 (quat C–O sp$^2$); $^{29}$Si NMR $\delta$ −17.22 ($Me_3Si$ and $Ph_3Si$, accidental overlap), −17.08 ($Me_3Si$), −3.63 (central Si), 15.49 ($OSiMe_3$); HR-MS *m/e* calcd for $C_{39}H_{57}O_2Si_5$ ($M^+$ − Me) 697.3204, found 697.3244; MS *m/e* (%) 697 (2, $M^+$ − 15), 639 (28, $M^+$ − $Me_3Si$), 259 (100, $Ph_3Si$), 237 (66, $CHAd(OSiMe_3)^+$). Anal. Calcd for $C_{40}H_{60}O_2Si_5$: C, 67.41; H, 8.42. Found: C, 67.61; H, 8.37.

**NMR Spectra of Simple Acylsilanes.** The preparations of all of the (para-substituted benzoyl)triphenylsilanes,[14] benzoyltrimethylsilane,[15] and acetyltriphenylsilane[15] have been described previously, but details of their NMR spectra have not been reported; these are given below.

**$Ph_3SiCOPh$ (7a)**: $^1$H NMR $\delta$ 6.85–7.14, 7.65–8.00 (20H, m, Ph); $^{13}$C NMR $\delta$ 128.45 (6CH), 128.62 (2CH), 128.81 (2CH), 130.29 (3CH *p*), 132.85 (3CH *p*), 133.12 (3C quat), 136.77 (6CH), 142.95 (C quat), 229.74 (C=O); $^{29}$Si NMR $\delta$ −28.47.

**$Ph_3SiCOC_6H_4F$-*p* (7b)**: $^1$H NMR $\delta$ 6.46 (2H, apparent t (overlapping d × d, $J_{AB}$ = 8.7 Hz, $J_{AF}$ = 8.7 Hz, $H_A$ (*o* to F)), 7.09–7.16, 7.68–7.79 (15H, m, Ph), 7.82 (2H, d × d, $J_{BF}$ = 5.5 Hz); $^{13}$C NMR $\delta$ 115.69 (2 CH, d, *J* = 21.9 Hz, *o* to CF), 128.53 (6CH), 130.46 (3CH *p*), 131.39 (d, *J* = 9.2 Hz, *m* to CF), 132.91 (3 quat C), 136.72 (6CH), 139.39, 168.18 (C quat), 227.66 (C=O); $^{29}$Si NMR $\delta$ −28.42.

**$Ph_3SiCOC_6H_4Cl$-*p* (7c)**: $^1$H NMR $\delta$ 6.81 (2H, d, *J* = 8.6 Hz, part $A_2B_2$), 7.05–7.20, 7.64–7.71 (15H Ph + 2H, $A_2B_2$); $^{13}$C NMR $\delta$ 128.53 (6CH), 128.99 (2CH), 130.11 (2CH), 130.48 (3CH *p*), 132.72 (3C quat), 136.68 (6CH), 139.36, 140.89 (C quat), 228.36 (C=O); $^{29}$Si NMR $\delta$ −28.28.

**$Ph_3SiCOC_6H_4Br$-*p* (7d)**: $^1$H NMR $\delta$ 6.97 (2H, d, *J* = 8.6 Hz, part $A_2B_2$), 7.63 (2H, d), 7.06–7.16, 7.66–7.72 (15H, m); $^{13}$C NMR

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[16] Brook, A. G.; Nyburg, S. C.; Reynolds, W. F.; Poon, Y. C.; Chang, Y.-M.; Lee, J.-S.; Picard, J.-P. *J. Am. Chem. Soc.* **1979**, *101*, 6750.

[17] The products of silene **2x** with acylsilane **7y** are named as **8xy** in this paper, the first letter defining the parent silene and the second letter defining the added acylsilane.

δ 128.58 (6CH), 130.22 (2CH), 130.52 (3CH *p*), 132.03 (2CH), 132.77 (3C quat), 136.74 (6CH), 141.23, 141.27 (quat C), 228.66 (C=O); $^{29}$Si NMR δ −28.30.

**$Ph_3SiCOC_6H_4OMe$-*p* (7e)**: $^1$H NMR δ 3.03 (3H, s, MeO), 6.46 (2H, d, *J* = 9.0 Hz, part $A_2B_2$), 7.06–7.21, 7.73–7.80 (15 H, m, Ph), 8.03 (2H, d); $^{13}$C NMR δ 54.89 (OMe), 114.03 (2CH), 128.49 (6CH), 130.29 (3CH *p*), 131.34 (2CH), 133.64 (3C quat), 136.88 (6CH), 136.95, 163.71 (quat C), 226.56 (C=O); $^{29}$Si NMR δ −29.01.

**$Ph_3SiCOC_6H_4NO_2$-*p***: $^1$H NMR δ 7.05–7.15 (19H, m); $^{13}$C NMR δ 127.77 (2CH), 128.63 (6CH), 128.83 (2CH), 130.71 (3CH *p*), 132.03 (3C quat), 136.61 (6CH), 145.31, 150.00 (quat C), 229.71 (C=O); $^{29}$Si NMR δ −27.45.

**$Me_3SiCOPh$ (7f)**: $^1$H NMR δ 0.20 (9H, s, $Me_3Si$), 7.15–7.18, 7.84–7.87 (5H, m, Ph); $^{13}$C NMR δ −1.40 ($Me_3Si$), 127.69 (2CH), 128.85 (2CH), 132.58 (CH *p*), 141.83 (C ipso), 233.68 (C=O); $^{29}$Si NMR δ −8.10.

**$Ph_3SiCOMe$ (7g)**: $^1$H NMR δ 2.13 (3H, s, Me), 7.06–7.20, 7.60–7.65 (15H, m, Ph); $^{13}$C NMR δ 37.80 (Me), 128.48, 130.41, 136.48 (CH sp$^2$, Ph), 132.02 (quat C, Ph), 239.82 (C=O); $^{29}$Si NMR δ −30.47 ($Ph_3Si$).

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