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Attempted Stabilization of Silaethylenes with Aryl or Trifluoromethyl Groups

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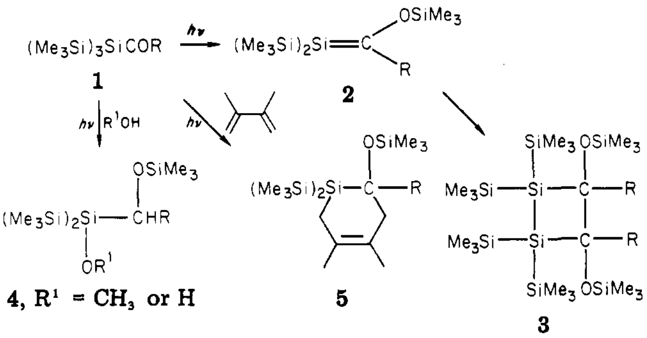
Photolysis of substituted benzoylsilanes $(Me_3Si)_3SiCOC_6H_4Y$ (Y = *p*-MeO, *o*-MeO, *p*-*t*-Bu, 3,5-Me$_2$) and of the related (trifluoroacetyl)silane yields silaethylenes, as demonstrated by their trapping with various reagents or by their head-to-head dimerization to yield 1,2-disilacyclobutanes. No evidence was found that the substituents significantly stabilize the silaethylenes through conjugative, electronic, or steric effects, relative to the protio analogues, and all the silaethylenes are less stable than the silaethylenes derived from alkoylsilanes containing a bulkyl alkyl group. The (*o*-methoxybenzoyl)silane shows some anomalous behavior attributable to the ortho substituent. Attempts to make highly hindered ortho-disubstituted acylsilanes by coupling of (tris(trimethylsilyl)silyl)lithium with various acid chlorides gave benzils instead.

Previous studies in our laboratory have shown that the photolysis of several alkoyltris(trimethylsilyl)silanes **1a** (R = Me_3C, Et_3C, 1-adamantyl, etc.) causes their rearrangement to isomeric silaethylenes **2a**, which were sufficiently stable and long-lived to be observable spectroscopically (IR, UV, NMR)[1-3] and in two cases (R = Et_3C, 1-adamantyl) to be isolable as crystalline solids at 25 °C.[3,4] When R = Me_3C, the silaethylene, in the absence of trapping agents, underwent head-to-head dimerization to give the 1,2-disilacyclobutane **3a**, having trans geometry of the groups attached to the asymmetric carbon atoms as shown from the crystal structure. In contrast, the photolysis of benzoyltris(trimethylsilyl)silane, **1b**, yielded a short-lived silaethylene, detectable by trapping experiments but not detectable spectroscopically, because it rapidly dimerized to the 1,2-disilacyclobutane **3b** in high yield. Apparently the arylsilaethylene **2b** was less stable than its alkyl analogues **2a**, despite the possible resonance stabilization through conjugation of the silicon–carbon double bond with the aromatic ring. We now report the extension of this study to a number of substituted aroylsilanes to see whether the electronic and/or steric effects provided by the substituents would increase the stability of the resulting arylsilaethylenes. In addition the behaviors of a pentafluorobenzoyl and a trifluoroacetylsilane were investigated to compare with those of the protio analogues described earlier.[1]

The (4-methoxybenzoyl)silane **1c** closely resembled the benzoyl compound **1b** in its behavior on irradiation. Photolysis in benzene gave a high yield of dimer **3c**, and immediate examination of the photolysis solution after the lamp was turned off gave no spectroscopic evidence for the presence of the intermediary silaethylene, indicating that the electronic effects of the *p*-methoxy group had done little to stabilize the silaethylene. Photolysis in methanol gave the methanol adduct **4c** of the expected silaethylene, as confirmed by its isolation, spectroscopic properties (Table III) and its synthesis from dimer **3c** by refluxing in THF containing methanol.

Scheme I



[a] a, R = alkyl (Me_3C, Et_3C, 1-adamantyl, etc.); **b**, R = C_6H_5; **c**, R = 4-$MeOC_6H_4$; **d**, R = 2-$MeOC_6H_4$; **e**, R = CF_3; **f**, R = C_6F_5; **g**, R = 4-*t*-BuC_6H_4; **h**, R = 3,5-$Me_2C_6H_3$.

The structure of the dimer **3c** was confirmed by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, as well as mass spectrometry. In particular, the ^{29}Si spectrum of this compound in C_6D_6 showed absorptions at −40.9 (ring Si), −11.9 and −13.2 (Me_3*Si*-Si), and 8.28 (Me_3*Si*-O) ppm, positions very similar to those observed previously for **3b**,[2] and the proton spectrum showed three 18 H signals at δ −0.28, −0.08 and 0.23 for the trimethylsilyl groups and a 6 H singlet at δ 3.67 for the methoxy groups.

The ^{13}C spectrum shows three Me_3Si signals at δ 3.4, 3.5, and 4.1, one methoxy signal at 54.8 ppm, and a ring carbon at 98.9 ppm. The mass spectrum is also specific to its structure. No $[M]^+$ is observed, but the ring cleaves leading to ions derived from the monomeric silaethylene, i.e., $[M/2]^+$ at *m*/*z* 382 (30%), $[M/2 - Me\cdot]^+$ at *m*/*z* 367 (100%), and $[(M/2) - Me - CH_2O]^+$ at *m*/*z* 337 (20%). Alternatively, the ring apparently also cleaves in the opposite sense yielding $[M^+ - Me_{12}Si_6]^+ \equiv [ArC(—OSiMe_3)=C(—OSiMe_3)Ar]^+$ at *m*/*z* 416 (25%) and $[M^+ - C_{22}H_{32}O_4Si_2]^+ \equiv [(Me_3Si)_2Si=Si(SiMe_3)_2]^+$ at *m*/*z* 348 (26%), and small ions. Further support for the proposed structure of the dimer comes from the methane-chemical ionization mass spectrum which exhibits $[MH]^+$ (*m*/*z* 765 (14%)) and $[MH-Me\cdot]^+$ (*m*/*z* 750 (10%)) ions. Exactly comparable behavior has been observed with the parent dimer **3b** (R = Ph)[5] and for other dimers (see below).

Thus the photochemistry of the *p*-methoxyphenyl compound closely parallels that of the unsubstituted phenyl

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[1] Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83.

[2] 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.

[3] Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R. *J. Chem. Soc. Chem. Commun.* **1981**, 191.

[4] Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y. M.; Wong-Ng, W. *J. Am. Chem. Soc.*, in press.

[5] Brook, A. G.; Harrison, A. G.; Kallury, R. K. M. R. *Org. Mass Spectrom.*, in press.

[6] (a) Fishman, E.; Chen, T. L. *Spectrochim. Acta, Part A* **1969**, *25A*, 1231. (b) Wood, G.; Srivastava, R. M.; Adlam, B. *Can. J. Chem.* **1973**, *51*, 1200.

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compound, and the lack of evidence for the presence of silaethylene in the photolysis solution indicates that the more electron-releasing *p*-methoxyphenyl group is not significantly more effective in stabilizing the intermediate silaethylene than the phenyl group had been found to be. It also seems clear, because of their similarities in behavior and spectroscopic properties, that dimers **3b** and **3c** (and others described below) are members of a family having closely related behavior. It is not known with certainty whether the aryl groups in **3b** and **3c** have the same trans disposition as was shown for **3a**. However, it is clear as a result of their recovery unchanged, after being heated in inert solvents to temperatures (60–80 °C) where they clearly react as if they formed the monomeric silaethylenes **2** (as shown by trapping with various added reagents), that the single isomer obtained in each case (but see one exception below) is strongly favored thermodynamically. Further discussion about the mechanism of formation of the dimers and their thermal stability will be deferred to a later paper.

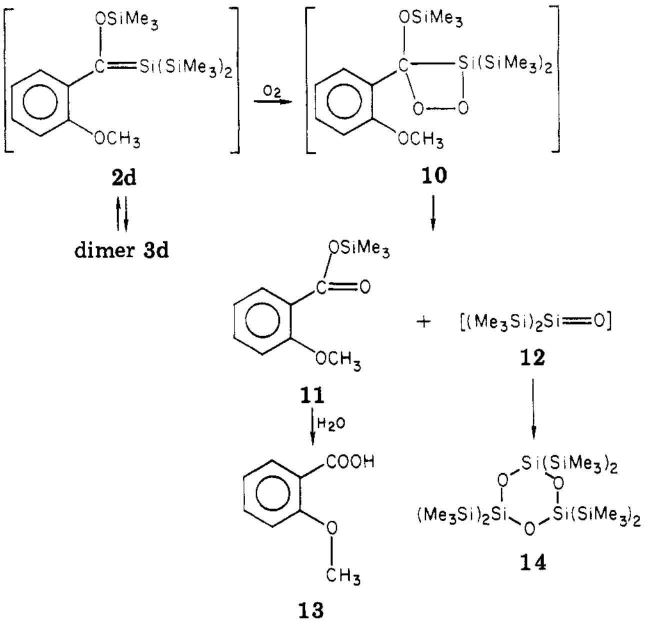
Initially it appeared that the photochemistry of the (*o*-methoxybenozyl)silane **1d** was significantly different from that of **1c** since under some conditions no dimer corresponding to **3c** was obtained. However, on closer examination, it was found that **1d** as isolated after recrystallization existed as a hemihydrate and the photochemistry of the hemihydrate was indeed different. However, the water could be removed by azeotropic distillation or prolonged pumping at steam bath temperature and semiquantitative measurements established there were two molecules of acylsilane per molecule of water. When the anhydrous acylsilane was photolyzed in methanol or excess water, products corresponding to **4d** (R′ = Me or H) were obtained in high yield and identified spectroscopically (see Table III), confirming the intermediacy of the silaethylene. Photolysis in 2,3-dimethylbutadiene led to the trapping of the silaethylene **2d** by the Diels–Alder reaction as a silacyclohexene (**5d**), as the phenyl analogue had been earlier observed to do,[1] and photolysis in inert solvents gave the expected 1,2-disilacyclobutane **3d** with spectroscopic properties closely related to those observed for the phenyl and *p*-methoxyphenyl compounds.

No spectroscopic evidence for the presence of the silaethylene in the photolysis solution was found when it was examined immediately after completion of the photolysis. Evidently the *o*-methoxyphenyl group, which could have affected the stability of the silaethylene through both electronic and steric interactions, plays no major role in altering the stability of **2d** relative to **2b** or **2c**: thus, like the latter silaethylenes, **2d** rapidly dimerizes.

However, unlike any other aroylsilaethylene dimer observed to date, **3d** is remarkably unstable toward various reagents. Thus mere dissolution of **3d** in methanol at room temperature over 48 h gave a near quantitative yield of the silaethylene–methanol adduct **4d** (R = Me) whereas the phenyl (**3b**) or *p*-methoxyphenyl (**3c**) dimers failed to react at room temperature and required at least 12-h reflux at 70–80 °C to yield the adduct. Thus it appears that the *o*-methoxy substituent destabilizes the silaethylene dimer **3d**, logically because of increased steric interactions, evidences of which are also found in the spectroscopic data (see below) and in the dimer's behavior in air.

Thus a solution of dimer **3d** exposed to air turned yellow and workup with sodium bicarbonate after 24 h yielded *o*-methoxybenzoic acid in good yield. A CI mass spectrum of the residue from the oxygenated solution after removal of the solvent revealed $[MH]^+$ ions corresponding to the trimethylsilyl ester **11** of *o*-methoxybenzoic acid (**13**) and the trimer **14** from bis(trimethylsilyl)silanone **12**, the formation of both of which could be explained through the intermediate **10** (Scheme II).

Scheme II



The ^{1}H NMR spectrum of the oxygenated solution also confirms the formation of **11** and **14**. Further, the chemical ionization spectrum of **14**, unambiguously synthesized from bis(trimethylsilyl)dichlorosilane,[7] was found to be identical with that of the product obtained from the air-exposed solution of dimer **3d**.

Dimer **3d** was characterized spectroscopically. Thus, the ^{1}H NMR spectrum consists of a complex aromatic region (δ 7.2–6.5 (8 H)), a broad singlet (δ 3.57 (6 H)) for the methoxy protons, and three 18 H signals (for 2 × Me_3Si and Me_3SiO) at δ 0.067, 0.38, and 0.68, the first two being broad. These bands are broad in contrast to those of **3c** and suggest that each *o*-methoxy group may be interacting sterically with one trimethylsilyl and a trimethylsiloxy group in the dimer. This fact is supported by the downfield shift of the methoxy carbon signal in the ^{13}C NMR of **3d** to 67.7 ppm. The ring carbon also undergoes a downfield shift (compared to **3c**) to 110.6 ppm because of the *o*-methoxy effect, and two signals are observed at 4.1 and 4.4 ppm (intensity ratio 1:2) in the silyl carbon region, indicating the overlapping of a trimethylsilyl carbon peak with the siloxy carbon signal. The EI mass spectrum of **3d** shows the same fragmentation pattern as the *p*-methoxy compound, with major high mass peaks at *m/z* 382 (10%), 367 (25%), 279 (45%), and 337 (3%) corresponding to the monomer and its cleavage products while ions at *m/z* 416 (5%) and 348 (5%) represent the alternate cleavage of the ring. The methane chemical ionization spectrum is more informative, giving $[MH]^+$ (*m/z* 765 (15%)) and $[MH - Me\cdot]^+$ (*m/z* 750 (8%)) ions in addition to the monomer and $[M/2 - Me\cdot]^+$ ions, the latter forming the base peak.

As indicated above, when the acylsilane **1d** as its hemihydrate was photolyzed in inert solvents, different results were obtained since dimer **3d**, a mixture of diols, or mixtures of all three were obtained depending on the temperature of the photolysis solution (from −10 to +25 °C) and the duration or intensity of the irradiation (see Table V). In general, lower temperatures (−10° to + 5 °C) favored formation of the dimer **3d** and slow photolysis at

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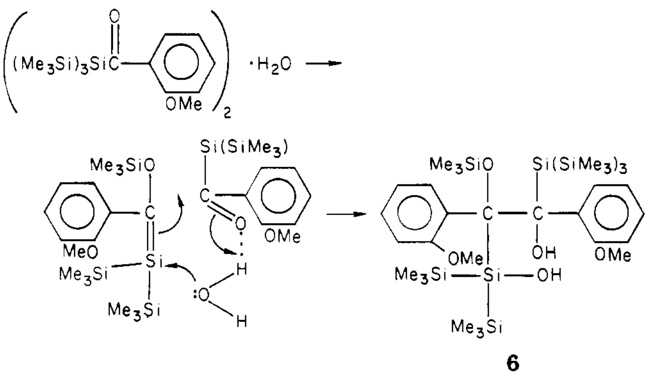
[7] Brook, A. G.; Abdesaken, F., unpublished observations.

Scheme III



room temperature led to formation of the diols **6**, although exact relationships were not established. The spectral details of the diols are consistent with their formulation as **6** (Scheme III), only one isomer of which survived workup and isolation, although the ^{1}H spectra of fresh photolysis solutions showed two very similar overlapping spectra in about 1:1 proportions.

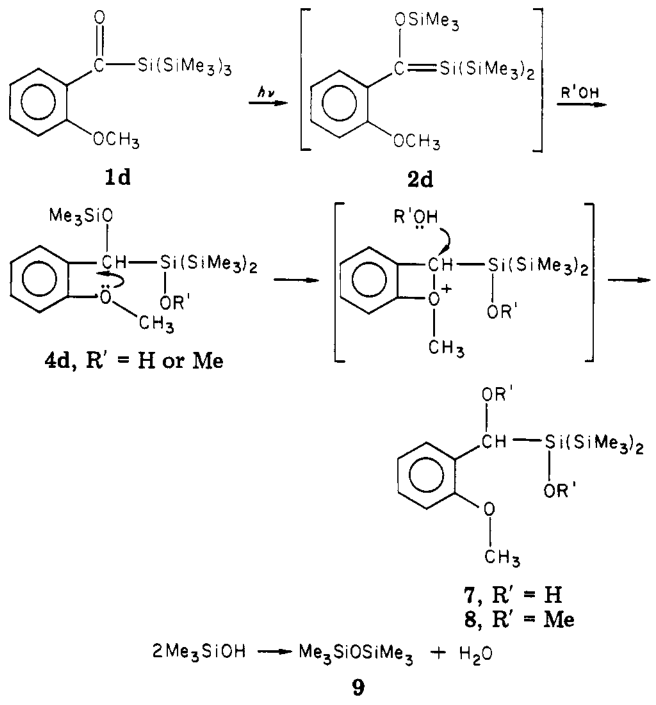
Neither column chromatography nor HPLC effectively separated the mixture, but on standing one isomer crystallised out as a very pale yellow solid which had spectral properties totally unlike those of dimer **3d**.

The ^{1}H spectrum of **6** showed four Me_3Si signals in the ratio 1:1:3:1 at δ 0.03, 0.13, 0.50, and 0.63 and two nonequivalent methoxy signals at 3.47 and 3.53 ppm. In the ^{13}C spectrum there was an intense Me_3Si signal at δ −3.6 ($(Me_3Si)_3Si$) with others of lesser but equivalent intensities at 0.9, 3.1, and 3.4 ppm. There were two methoxyl signals at 55.4 and 56.1 ppm, a signal at 95.7 ppm (C-OH), and a signal at 110.1 ppm assigned to the quaternary carbon Ar—*C*(—$OSiMe_3$)—Si by analogy with the positions observed for related carbons in **3d** and **4d** (R′ = Me or H). The ^{29}Si spectrum showed six nonequivalent silicon signals with the approximate intensity ratio of 1:1:3:1:1:1 at δ 16.9 (Me_3Si-O), 10.3 (Si-OH), −10.8 ($(Me_3\mathit{Si})_3Si$), −16.2, and −16.5 ($(Me_3\mathit{Si})_2Si$), and −66.7 ($(Me_3Si)_3\mathit{Si}$). This data is in good agreement with values observed in model compounds such as **4d** and **7**.

The EI mass spectrum showed the ions $[M]^+$, $[M - H_2O]^+$, $[M - H_2O - Me\cdot]^+$, $[M - H_2O - Me_3Si\cdot]^+$, and $[M - H_2O - (Me_3Si)_3Si\cdot]^+$ as is consistent with the proposed structure as is the CI mass spectrum with ions $[MH]^+$, $[MH - H_2O]^+$, and smaller fragments, confirming the assigned molecular weight. The IR spectrum showed broad hydroxyl absorption centered at 3300 cm^{-1}, although surprisingly the NMR bands at δ 5.12 and 4.37, each 1 H, believed to be due to the hydroxyl groups did not exchange readily with D_2O. 1,3- and 1,4-diols capable of intramolecular hydrogen bonding have been reported to undergo H-D exchange extremely slowly.[6] Moreover, the same behavior has been observed with the water adduct **4d** (R′ = OH) as well as the 1,2-diol **7**. Thus, in summary, all the data are consistent with the formulation **6**.

As noted above, there was evidence for two isomers of **6** in the photolysis solution, only one of which survived workup. The identity of the second isomer has not been established, but there was some evidence that in decomposing it yielded some of the isomer isolated. As formulated, **6** has two asymmetric centers and thus it could exist as two diastereoisomers, one of which may be significantly less stable. However, the duplicated NMR spectra could also have arisen from two different conformations, stabilized by hydrogen bonding, or from two different structural isomers, arising as a result of different sites of hydrogen bonding. Data to resolve this uncertainty are not available.

Scheme IV



While a detailed mechanism for the formation of **6** has not been established (note that photolysis of **1d** in excess water in THF does not give any **6**), it is evident that **6** must be derived from reaction of a molecule of silaethylene with a molecule of unphotolyzed acylsilane, with which water is known to be associated. A generalized mechanism is given in Scheme III.

The 1,2-diol **7** is an unusual byproduct formed during the photolysis of **1d** in water, and the related 1,2-dimethoxy compound **8** is obtained from photolysis in methanol. A reasonable explanation for the formation of these compounds is that they are derived from the precursors **4d** (R′ = H or Me) which with assistance from the spacially adjacent methoxyl group, lose the trimethylsiloxy group which is replaced by HO or MeO through attack of solvent on the benzylic carbon atom (see Scheme IV). This postulation is supported by the isolation of hexamethyldisiloxane, **9**, from these photolyses, which would arise from the trimethylsilanol formed on solvolysis.

In an effort to explore further the influence of electronic factors, in particular electron withdrawal, on the stability of silaethylenes, the (trifluoroacetyl)silane **1e** and the (pentafluorobenzoyl)silane **1f** were synthesized. Some difficulty was initially encountered in the synthesis of these species, but ultimately they were made by the coupling of the carefully purified acid chlorides with (tris(trimethylsilyl)silyl)lithium–tris(tetrahydrofuran)[8] in dry pentane at low temperatures. The properties of the acylsilanes are given in Table I, and other than the fact that the IR carbonyl stretching vibrations are shifted to higher frequencies (1650 cm^{-1}) than usual (1600–1620 cm^{-1}) because of the inductive effects of the fluorine atoms, the compounds had properties typical of acylsilanes. On photolysis in methanol, the expected methanol adducts **4e** and **4f**, respectively, were formed.

The trifluoroacetyl compound **1e** on photolysis in inert solvents gave rise to both possible diastereomeric 1,2-disilacyclobutane dimers **3e** and **3e′**, the predominant one probably being the trans isomer by analogy with the known trans structure of **3a** (R = Me_3C).[2] This is the only known

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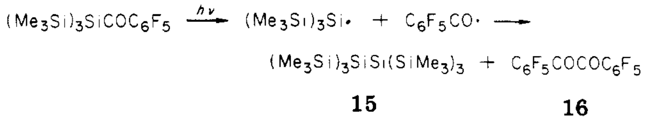
[8] Brook, A. G.; Gutekunst, G. *J. Organomet. Chem.* **1982**, *225*, 1.

Table I. Physical and Spectroscopic Data of Acylsilanes $(Me_3Si)_3SiCOR$ (1c-f)

R	mp, °C	yield, %	spectroscopic data[f]
o-$MeOC_6H_4$	114	80[a]	UV λ_{max} (log ϵ) 223 (4.35), 247-252 (4.07), 275 (infl), 366 (236), 380 (258), 396 (250), 410 nm (202) IR ν 1610 (>C=O) cm^{-1} ^1H NMR (CCl_4) δ 0.17 (s, 27 H), 3.72 (s, 3 H), 6.67-7.33 (m, 4 H) ^{13}C NMR (C_6D_6) 1.36, 54.89, 240.05 ppm ^{29}Si NMR (C_6D_6) −11.15, −70.57 ppm EI MS, *m/z* (%I) 382 (M^+, 2%), 367 (53.5), 279 (49), 73 (100) CH_4 CI MS, *m/z* (%I) 383 (MH^+) (100), 368 (10)
p-$MeOC_6H_4$	*b*	71[c]	UV λ (log ϵ) 222-226 (4.25), 272-274 (4.41), 286 (infl), 290 (infl), 348 (161), 374 (190), 390 (118), 410 (110), 430 nm (72) IR ν 1605 (>C=O) cm^{-1} ^1H NMR (CCl_4) δ 0.23 (s, 27 H), 3.86 (s, 3 H), 7.00-6.80, 7.78-7.62 (d, 4 H) ^{13}C NMR (C_6D_6) 1.90, 55.13, 230.34 ppm ^{29}Si NMR (C_6D_6) −11.45, −72.90 ppm EI MS, *m/z* (%I) 382 (M^+, 5%), 367 (100), 279 (25), 73 (48) CH_4 CI MS, *m/z* (%I) 383 (MH^+, 100), 368 (15)
CF_3	89-90 °C	90[d]	UV λ (log ϵ) 217 (4.5), 273 (4.05), 359 (70), 372 (116), 386 (112), 404 nm (54) IR ν 1658 (C=O) cm^{-1} ^1H NMR (CCl_4) δ 0.28 (s, 27 H) ^{13}C NMR (C_6D_6) 1.09, 125.98 (q, J = 296 Hz), 225.45 ppm (q, J = 36 Hz) ^{29}Si NMR (C_6D_6) −9.89, −70.17 ppm EI MS, *m/z* (%I) 344 (M^+, 0.1) 329 (1), 275 (20), 247 (38), 73 (100) CH_4 CI MS, *m/z* (%I) 345 (MH^+, 10%), 330 (10), 275 (100), 247 (40)
C_6F_5	bp 112 °C (0.1 mm)	*e*	UV λ (log ϵ) 230 (4.33), 272 (4.13), 352 (152), 368 (203), 382 (209), 400 nm (170) IR ν 1650 (C=O) cm^{-1} ^1H NMR (C_6D_6) δ 0.20 (s, 27 H) ^{29}Si NMR (C_6D_6) −10.25, −62.85 ppm EI MS, *m/z* (%I) 442 (M^+, 1), 427 (14), 339 (10), 73 (100)
4-*t*-BuC_6H_4	59-60	60	IR (CCl_4) ν 1613 (C=O) cm^{-1} ^1H NMR (CCl_4) δ 0.35 (s, 27 H), 1.45 (s, 9 H) 7.3-7.8 (m, A_2B_2, 4 H) EI MS, *m/z* 408 (M^+), 393 (M − Me^+) 319, 305
3,5-$Me_2C_6H_3$	52.5-53.5	50	IR (CCl_4) ν 1607 (C=O) cm^{-1} ^1H NMR (CCl_4) 0.32 (s, 27 H), 2.38 (s, 6 H), 7.10 (b s, 1 H), 7.28 (b s, 2 H) EI MS, *m/z* 380 $(M)^+$, 365 $(M - Me)^+$, 349, 307

[a] Anal. Calcd for $C_{17}H_{34}O_2Si_4$: C, 53.36; H, 8.99. Found: C, 53.64; H, 9.28. [b] Liquid decomposes above 100 °C under vacuum without distilling. [c] Anal. Calcd for $C_{17}H_{34}O_2Si_4$: C, 53.36; H, 8.99. Found: C, 53.01; H, 8.94. [d] Anal. Calcd for $C_{11}H_{27}F_3OSi_4$: C, 38.37; H, 7.85. Found: C, 38.47; H, 8.14. [e] Anal. Calcd for $C_{16}H_{27}F_5OSi_4$: C, 43.44; H, 6.11. Found: C, 43.60; H, 6.28. [f] The NMR spectral data are reported in δ (ppm) relative to Me_4Si. Absorption intensities for λ greater than 300 nm are reported as ε.

Scheme V

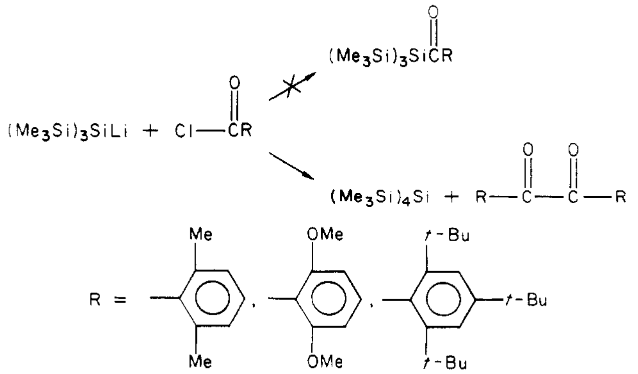


$$(Me_3Si)_3SiCOC_6F_5 \xrightarrow{h\nu} (Me_3Si)_3Si\cdot + C_6F_5CO\cdot \longrightarrow \underset{15}{(Me_3Si)_3SiSi(SiMe_3)_3} + \underset{16}{C_6F_5COCOC_6F_5}$$

case to date where both possible 1,2-disilacyclobutanes have been observed. Both compounds were shown unambiguously to be 1,2-disilacyclobutanes since the mass spectra of each showed abundant ions at *m/z* 348 corresponding to the fragment ion $(Me_3Si)_2Si{=}Si(SiMe_3)_2$, not possible from a 1,3-disilacyclobutane.

Unlike any other polysilylacylsilane prepared to date, photolysis of the (pentafluorobenzoyl)silane **1f** in inert solvent failed to give any dimeric species. Norrish type I cleavage evidently occurred instead and substantial quantities of hexakis(trimethylsilyl)disilane (**15**) were isolated together with material having infrared and mass spectra similar to that of decafluorobenzil (**16**).[9] No spectroscopic evidence for silaethylenes could be observed from the photolysis solutions from either **1e** or **1f**.

Attempts were made to study several other acylsilanes. The (4-*tert*-butylbenzoyl)silane **1g** and the (3,5-dimethylbenzoyl)silane **1h** were readily synthesized, and on photolysis gave the usual 1,2-disilacyclobutane dimers **3g** and **3h**, with no spectroscopic evidence found for a stable intermediary silaethylene. Attempts to prepare the more sterically crowded (2,6-dimethylbenzoyl)-, (2,6-dimethoxybenzoyl)- or (2,4,6-tri-*tert*-butylbenzoyl)silanes by coupling of the respective acid chlorides with (tris(trimethylsilyl)silyl)lithium at −70 °C failed to yield any of the expected products.



Instead, what is presumed to be radical coupling following a one-electron transfer occurred, since benzils were formed in good yield, accompanied by much tetrakis(trimethylsilyl)silane. This alternative pathway presumably occurs because severe steric interactions prevent formation of the acylsilanes.

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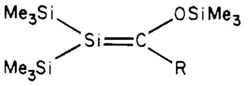
(9) Dua, S. S.; Jukes, A. E.; Gilman, H. *Organomet. Chem. Synth.* **1970**, *1*, 87.

Table II. Physical and Spectroscopic Data of the Disilacyclobutanes (3c–f)

R	mp, °C	yield, %	spectroscopic data[a]
4-$MeOC_6H_4$	178–180	60 [b]	IR (Nujol) 2840 (OCH_3), 1520 (C–Ar), 1250 (Si–C), 1020 (Si–O), 850 (Si-C–H) ^1H NMR (CCl_4) –0.28, –0.08, 0.23 (s, 18 H each), 3.67 (s, 6 H), 6.53–6.67, 7.13–7.42 (d, 8 H) ^{13}C NMR 3.40, 3.48, 4.06, 54.85, 98.92 (plus aromatic carbons) ^{29}Si NMR 8.29, –11.95, –13.17, –40.91 EI MS 416 (25), 382 (30), 367 (100), 348 (26), 337 (20) CI MS 765 (MH^+, 14), 750 (10), 382 (35), 367 (100)
2-$MeOC_6H_4$	94–95	62 [c]	IR (Nujol) 2850 (CH_3O), 1485 (C–Ar), 1255 (Si–C), 1060–1010 (Si–O), 840 (Si–C–H) ^1H NMR 0.067, 0.38, 0.68 (s, 18 H each), 3.57 (b, 6 H), 6.51–7.23 (m, 8 H) ^{13}C NMR 4.09, 4.44, 67.73, 110.58 (plus aromatic carbons) EI MS, 416 (5), 382 (10), 367 (25), 348 (5), 279 (45), 73 (100) CI MS, 765 (MH^+, 15), 750 (8), 382 (35), 367 (100)
CF_3	212–213	60 [d]	IR (Nujol) 1250 (Si–C), 1155, 1120 (Si–O), 840 (Si–C–H) ^1H NMR 0.28, 0.35, 0.37 (s, 18 H each) ^{13}C NMR 2.34, 2.47, 3.21, 79.75 (q, J = 30 Hz), 134.23 (q, J = 284 Hz) ^{29}Si NMR 13.7, –8.97, –9.95, –48.58 EI MS 367 (5), 348 (24), 294 (10), 275 (8), 73 (100) CI MS 689 (MH^+, 5), 619 (10), 275 (28), 73 (100)
CF_3	205–206	22 [e]	IR (Nujol) 1245 (Si–C), 1135, 1125 (Si–O), 835 (Si–C–H) ^1H NMR 0.357 (s, 36 H), 0.433 (s, 18 H) ^{13}C NMR 2.60, 3.10, 3.56, 76.76 (q, J = 28 Hz), 129.82 (q, J = 283 Hz) ^{29}Si NMR 16.27, –11.12, –11.84, –40.22 EI and CI MS very similar to above isomer
4-*t*-Bu-C_6H_4	43–44		IR (CCl_4) 1237, 833 ^1H NMR (CCl_4) 0.0 (s, 18 H), 0.52 (s, 18 H), 0.79 (s, 18 H)
3,5-$Me_2C_6H_3$	142–143		IR (CCl_4) 1592, 1234, 1080, 833 ^1H NMR (CCl_4) –0.25 (s, 18 H), 0.16 (s, 18 H), 0.48 (s, 18 H), 2.35 (s, 12 H), 6.86 (b s, 2 H), 7.28 (b s, 4 H) EI MS 380 $(M/2)^+$, 365 $(M/2 - Me)^+$, 307 $(M/2 - Me_3Si)^+$

[a] Unless otherwise noted, all NMR spectral data were obtained in C_6D_6 and chemical shifts are in δ (ppm) relative to Me_4Si; IR in cm^{-1}; MS as m/z (%I). [b] Anal. Calcd for $C_{34}H_{68}O_4Si_8$: C, 53.36; H, 8.90. Found: C, 53.17; H, 8.81. [c] No C and H analysis obtained because compound decomposes at room temperature. [d] Anal. Calcd for $C_{22}H_{54}F_6O_2Si_8$: C, 38.37; H, 7.85. Found: C, 38.33; H, 8.00. [e] Anal. Calcd for $C_{22}H_{54}F_6O_2Si_8$: C, 38.37; H, 7.85. Found: C, 38.39; H, 8.11.

Conclusions



Of the silaethylenes in the family synthesized to date, those where R is a large bulky alkyl group are by far the most stable, two silaethylenes (where R = CEt_3 or 1-adamantyl) having been isolated as solids and several others having survived in solution at room temperature for a week or longer as observed spectroscopically.[4]

It has not been possible to observe the phenylsilaethylene (R = Ph) spectroscopically since it evidently is not nearly as stable as the alkyl species above, despite the potential for conjugative interaction of the silicon–carbon double bond with the aromatic π system. The present attempts to increase the stability by putting electron-releasing substituents, or bulky substituents on the aromatic ring, or by withdrawing electron density using a trifluoromethyl group as R failed to significantly stabilize the silaethylenes relative to their protio analogues, since all rapidly dimerized to the head-to-head 1,2-disilacyclobutane dimers. Within the general framework of this family of silaethylenes, it appears that conjugation and additional electronic effects are much less important than steric bulk in stabilizing these reactive species.

Experimental Section

General Data. A 100-W PAR 38 clear mercury spot lamp (Blak-Ray, ANSI code H44GS) was used for all photolysis experiments. Irradiations were carried out under dry argon in Pyrex Schlenk tubes, cooled in baths of running water (temperature 5–8 °C) and positioned in the intense central beam about 6 in. from the lamp.

Benzene, pentane, and tetrahydrofuran were distilled from metallic sodium immediately prior to use, while methanol was distilled from potassium hydroxide.

The IR spectra were recorded on a Pye Unicam SP3-200 infrared spectrophotometer in carbon tetrachloride or Nujol. The ^1H, ^{13}C, and ^{29}Si NMR spectra were measured on Varian T60, Varian CFT 20, and Bruker WP-80 NMR spectrometers, respectively, in deuteriobenzene unless otherwise stated. The EI mass spectra were recorded on an AEI MS-9 mass spectrometer with source temperatures ranging from 50 to 80 °C, while the methane chemical ionization spectra were obtained on a Du Pont 21-490 mass spectrometer (gas pressure ~0.3 torr) at approximately the same source temperature.

Satisfactory (0.3%) analyses (C, H) were obtained for all stable new compounds and were performed by Galbraith Labs. Inc., Knoxville, TN.

Preparation of (*o*-Methoxybenzoyl)tris(trimethylsilyl)silane (1d) and Its *p*-Methoxy Analogue 1c. (Tris(trimethylsilyl)silyl)lithium (0.033 mol), prepared from tetrakis(trimethylsilyl)silane according to the method of Gilman,[10] was added dropwise into a solution of the appropriate benzoyl chloride (0.04 mol) in 100 mL of THF at –70 °C over a period of 2 h. The mixture was stirred at this temperature for a further period of 3 h. Most of the solvent was removed on a rotary evaporator, and the residue was stirred with water (200 mL) at room temperature for 1 h. The mixture was extracted with ether (3 × 100 mL), and the combined ether layers were dried over anhydrous sodium sulfate and then were evaporated on a rotary evaporator. The residue was chromatographed on silica gel with pentane to give the pure acylsilane.

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(10) Gilman, H.; Lichtenwalter, G. D. *J. Am. Chem. Soc.* **1958**, *80*, 608.

Table III. Spectroscopic Data for $RC(-OSiMe_3)H-Si(-OR')(SiMe_3)_2$ (4c–f)

R	R′	yield	spectral data[a]
p-$MeOC_6H_4$	CH_3	80	IR (neat) 2830 (CH_3O), 1510 (C-Ar), 1060-1040 (Si-O-C) ^1H NMR (CCl_4) −0.02, 0.05, 0.25 (s, 9 H each), 3.35, 3.72 (s, 3 H each), 4.81 (s, 1 H), 6.7-7.0 (q, 4 H) EI MS 414 (M^+, 16), 399 (22), 341 (24), 310 (28), 309 (36), 209 (13), 73 (100)
o-$MeOC_6H_4$	CH_3	85	IR (neat) 2840 (CH_3O), 1490, 1465, 1440 (C-Ar), 1055, 1030 (Si-O-C) ^1H NMR (CCl_4) −0.13, 0.03, 0.23 (s, 9 H each), 3.50 (s, 3 H), 3.85 (s, 3 H), 5.82 (s, 1 H) 6.80-7.15 (m, 4 H) ^{13}C NMR 2.43, 2.79, 54.70, 65.15, 109.90 (plus aromatic carbons) ^{29}Si NMR 18.87, 10.16, −18.48, −18.63 EI MS 414 (M^+, 10), 399 (20), 341 (100), 310 (29), 209 (17), 73 (37)
o-$MeOC_6H_4$	H	78	IR (neat) 3550-3400 (b, OH), 2840 (OCH_3), 1490, 1465 (C-Ar), 1050-1030 (Si-O-C) ^1H NMR 0.267 (s, 9 H), 0.37 (s, 18 H), 3.23 (b, 1 H), 3.50 (s, 3 H), 5.40 (s, 1 H), 6.53-6.73 (m, 1 H), 6.93-7.20 (m, 2 H), 7.56-7.78 (m, 1 H) ^{13}C NMR −1.33, 1.85, 54.81, 110.06 (plus aromatic carbons) EI MS 400 (M^+, 10), 385 (20), 327 (40), 209 (25), 191 (20), 73 (100)
CF_3	CH_3	85	^1H NMR 0.20 (b s, 18 H), 0.10 (s, 9 H), 3.37 (s, 3 H), 4.20 (q, 1 H) ^{13}C NMR −0.66, −0.43, 0.06, 54.33, 67.03 (q, J = 33 Hz), 127.5 (q, J = 279 Hz)
C_6F_5	CH_3	35	^1H NMR (CCl_4) 0.40 (s, 9 H), 0.50 (d, 18 H), 3.85 (s, 3 H), 5.33 (s, 1 H)

[a] Unless otherwise stated, all NMR spectra are measured in C_6D_6 and chemical shifts are in ppm with respect to Me_4Si; IR in cm^{-1}; MS in m/z (%I).

The *o*-methoxy compound **1d** was recrystallized from pentane to yield light yellow needles of the hemihydrate, mp 80–81 °C (with methanol, a different species, mp 114–115 °C, was obtained). The *p*-methoxy analogue **1c** is a yellow oily anhydrous liquid which decomposed on heating and could not be distilled even under vacuum.

Preparation of (Trifluoroacetyl)tris(trimethylsilyl)silane (1e) and the Pentafluoro Analogue (1f). A solution of the solid salt $(Me_3Si)_3SiLi\cdot 3THF$ (0.03 mol) in pentane (300 mL) was dropped into a solution of the appropriate thrice-degassed acid chloride (0.031 mol) in pentane (200 mL) maintained at −30 to −40 °C over a period of 5 h with constant stirring which was continued for a further 2 h after the completion of the addition. The lithium chloride precipitate was filtered off and the solution concentrated. In the case of **1e**, the residue was sublimed under vacuum to yield colorless crystals, mp 89–90 °C, while with **1f**, the residue was distilled under vacuum to give a pale yellow oily liquid, bp 112 °C (0.1 mm).

An almost quantitative yield of the acylsilanes **1c** and **1d** were also obtained by this method.

For the physical, analytical and spectral data of the acylsilanes **1c–f**, see Table I.

Preparation of the Anhydrous Acylsilane 1d. The hydrated compound was refluxed with benzene for 24 h, and then the solvent was removed by azetropic distillation to leave a thick oily residue. Alternatively, the hydrated species was heated under vacuum at 100 °C for 6 h, and quantitative measurements indicated a weight loss of 2.31% on the basis of the initial weight of the acylsilane (a hemihydrate requires 2.35% of water content). The anhydrous acylsilane displays a single peak at 1610 cm^{-1} in the IR while the hemihydrate shows a doublet at 1600 and 1590 cm^{-1}.

Photolysis of 1d in Benzene To Yield the Dimer 3d. The (*o*-methoxyacyl)silane **1d** (1 g, 2.62 mmol) in 3 mL of benzene was irradiated at 0–5 °C for 5 h with four lamps. Dimer **3d** crystallized out of the solution and was recrystallized from benzene–THF to give colorless crystals, mp 94–95 °C, in nearly quantitative yield.

Photolysis of 1d in Benzene to the Diol 6. The hydrated acylsilane **1d** (1 g, 2.62 mmol) in 2 mL of benzene was irradiated at 20–25 °C for 10 h with one lamp. Longer photolysis did not produce any change in the ^1H NMR of the solution which indicated the presence of about 35% of the starting material. The mixture was chromatographed on silica gel with pentane to yield a mixture of isomeric diols (combined yield ~50%) in the first fraction. The pentane solution of the mixture was allowed to stand for 24 h when a yellow crystalline solid slowly formed. This material on recrystallization from ether containing a trace of methanol gave a light yellow solid, mp 137–138 °C (yield 40%). The ^1H NMR spectrum of a solution of the diol mixture which had been allowed to stand for several days suggested that one of the forms of **6** was converted in part to the other isomer (mp 137–138 °C).

For a summary of the variation in products with time and light intensity, see Table V.

Photolysis of the *p*-Methoxy Silane 1c in Benzene. The acylsilane **1c** (2 g, 5.2 mmol) in 5 mL of benzene was photolyzed at room temperature (20 °C) with one lamp for 3 h at which time no >C=O absorption was observed in the IR. The mixture was concentrated in vacuo, and the residue was recrystallized from pentane–acetone to afford colorless crystals of **3c**, mp 177–178 °C dec.

Photolysis of the Trifluoro Silane 1e in Benzene. Acylsilane **1e** was irradiated under the same conditions as above. The residue upon recrystallization from acetone deposited colorless crystals of **3e**, mp 212 °C. The mother liquor, treated with a few drops of methanol and left overnight, deposited a second isomeric dimer of **3e**, mp 205–206 °C.

Photolysis of the Pentafluoro Compound 1f in Benzene. The acylsilane **1f** (1 g) was irradiated in benzene (3 mL) at 5 °C with one lamp for 3 h. The solution was concentrated in vacuo, and the residue was sublimed in vacuo at 100 °C to yield white crystals, mp 370–371 °C, whose spectral data [^1H NMR (C_6D_6) δ 0.32 (s), ^{29}Si NMR (C_6D_6) −9.42 and −129.36 ppm, and EI MS, m/z 494 (M^+, 20%)] and elemental analysis are consistent with those for hexakis(trimethylsilyl)disilane (**15**), reported[11] by an alternate route (mp 372–374 °C). (Anal. Calcd for $C_{18}H_{54}Si_8$: C, 43.72; H, 10.93. Found: C, 43.91; H, 10.90.)

The sublimation residue showed peaks in the IR at $\nu_{C=O}$ 1723 and 1708 cm^{-1} with a base peak in the EI MS at m/z 195, values corresponding to decafluorobenzil.[9,12]

Photolysis of the Acylsilanes 1c–f in Methanol. The acylsilanes (0.5 g) were irradiated for 1 h in a mixture of benzene (3 mL) and methanol (1 mL) with one lamp. The solvents were removed in vacuo, and the residue was chromatographed on silica gel with pentane to yield the corresponding methanol adducts **4c–f** in the first fraction. The adducts **4c** and **4d** were also obtained by refluxig the dimers **3c** and **3d** with THF–methanol

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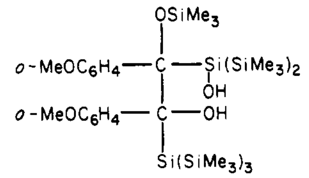
[11] Gilman, H.; Harrell, R. L., Jr. *J. Organomet. Chem.* **1967**, *9*, 67.

[12] Chambers, R. D.; Clark, M. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2469.

Table IV. Physical and Spectroscopic Data of the Diols 6



mp, °C	yield, %	spectroscopic data
		A. Stable Isomer
137–138 dec	38[a]	IR ν 3350, 1550, 1240, 1090, 1040, 835, 685 cm^{-1} ^{1}H NMR (C_6D_6) δ 0.03, 0.13, 0.65 (s, 9 H each), 0.50 (s, 27 H), 3.47 (s, 3 H), 3.50 (s, 3 H), 4.37 (s, 1 H), 5.13 (s, 1 H), 6.23–7.73 (m, 8 H) ^{13}C NMR (C_6D_6) −3.57, 0.88, 3.08, 3.36, 55.43, 56.07, 95.73, 110.12 ppm (plus 12 aromatic carbon peaks) ^{29}Si NMR (C_6D_6) 16.89, 10.34, −10.84, −16.18, −16.49, −66.73 ppm EI MS, m/z (%I) 782 (M$^+$, 0.1), 764 (3), 749 (3), 691 (20), 517 (33), 382 (10), 367 (20), 232 (15), 191 (13), 73 (100) CH_4 CI MS m/z (%I) 783 (MH$^+$, 5), 765 (15)
		B. Unstable Isomer
		^{1}H NMR (C_6D_6) δ 0.097, 0.24, 0.58 (s, 9 H each), 0.55 (s, 27 H), 3.50 (s, 3 H), 3.53 (s, 3 H), 5.19 (s, 1 H), 5.33 (s, 1 H), 6.50–7.73 (m, 8 H) ^{13}C NMR (C_6D_6) 1.81, 2.27, 2.99, 3.46, 54.46, 55.74, 88.15, 111.42 ppm (plus aromatic protons) ^{29}Si NMR (C_6D_6) 14.03, 9.67, −11.00, −16.65, −18.46, −66.15 ppm

[a] Anal. Calcd for $C_{34}H_{70}O_5Si_8$: C, 51.95; H, 8.95. Found: C, 51.63; H, 8.74.

Table V. Irradiation of 1d under Various Conditions[a]

exptl conditns	products
(1) one lamp, −10 °C, 8 h	acylsilane (1d) + dimer (3d) (2:1)
(2) two lamps, −10 °C, 6 h	1d + 3d (1:1)
(3) one lamp, 5 °C, 8 h	3d + isomers 6 (1:1) plus small amounts of 1d
(4) one lamp, 20–25 °C, 10 h	isomers 6 + 1d (2:1)
(5) four lamps, 5 °C, 5 h	mostly 3d with traces of 6 isomers
(6) four lamps, 20–25 °C, 3 h	several decomposition products
(7) one lamp, 20–25 °C, 8 h photolysis in a sealed tube	isomers 6 + 3d (2:1) plus some 1d

[a] Product estimated on the basis of integration of relevant peaks in ^{1}H NMR spectrum under each condition.

for 24 and 1 h, respectively. The spectral data of these products **4c–f** are presented in Table III.

From the chromatograph of the residue from the photolysis of **1d** in methanol, besides **4d**, a second fraction was isolated as a colorless oil with pentane as eluent. The following spectral characteristics are consistent with structure **8** for this product: ^{1}H NMR (CCl_4) δ 0.18 (s, 9 H), 0.33 (s, 9 H), 2.63 (s, 1 H), 3.87 (s, 3 H), 3.90 (s, 3 H), 4.11 (s, 3 H), 6.90–7.50 (m, 4 H), EI MS, m/z (%I) 356 (M$^+$, 8%), 341 (43), 325 (9), 310 (7), 283 (100), 252 (19), 236 (19), 221 (9), 163 (14), 73 (10).

Photolysis of 1d in Water. The acylsilane (0.5 g) was dissolved in THF (5% water content, 1 mL) and irradiated with one lamp for 30 min. The residue was chromatographed over silica gel with pentane, and the first fraction was found to be the water adduct (**4d**, R′ = H) (for spectral details, see Table III). The second fraction with pentane–benzene (3:1) was found to be the diol **7** (yield ~40%) on the basis of the following spectral data: IR (neat) ν_{OH} 3650 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.57, 0.62 (s, 9 H each), 2.62 (s, 1 H), 3.34 (s, 3 H), 3.41 (s, 1 H), 5.30 (s, 1 H), 6.47–7.64 (m, 4 H); ^{29}Si NMR (C_6D_6) δ 6.8 ($(Me_3Si)_2\mathit{Si}OH$), −18.45 (2 × Me_3Si); EI MS, m/z 328 (M$^+$, 6%), 313 (8), 295 (11), 255 (100%), 240 (15), 237 (29), 191 (52), 175 (57), 137 (22), 135 (48), 73 (63).

Photolysis of 1d with 2,3-Dimethylbutadiene: 5d. A mixture of **1d** (1 g) and 2,3-dimethyl-1,3-butadiene (1 mL) in THF (5 mL) was irradiated for 3 h at 20–25 °C with one lamp. The mixture was concentrated under vacuum and the residue chromatographed on silica gel with pentane to afford a white crystalline solid **5d** which was recrystallized from pentane: mp 136–137 °C; yield 40%; ^{1}H NMR (C_6D_6) δ −0.07, 0.07, 0.43 (s, 9 H each), 1.57–1.67 (b, 2 H), 1.97 (s, 6 H), 2.85–2.90 (b s, 2 H), 3.50 (s, 3 H), 6.43–7.40 (m, 4 H); EI MS, 464 (M$^+$, 5%), 449 (8), 391 (100), 382 (20), 367 (13), 73 (50). (Anal. Calcd for $C_{23}H_{44}O_2Si_4$: C, 59.28; H, 9.54. Found: C, 58.93; H, 9.72.

Decomposition of the Dimer 3d in Benzene in Air. A solution of the dimer **3d** (0.1 g) in deuteriobenzene (1 mL) was allowed to stand at room temperature for 24 h in the air. The dimer signals in the silyl proton region gradually diminished, and two new signals gradually increasing in intensity appeared. The mixture was extracted with ether and shaken with 5% $NaHCO_3$ solution. The aqueous layer on acidification deposited a solid (0.025 g, 68% yield), mp 100–101 °C. Mixed melting point and an IR spectrum established its identity as *o*-methoxybenzoic acid. The ether layer on evaporation yielded an oil whose CI mass spectrum indicated it to be a cyclotrisiloxane by comparison with an authentic sample: ^{1}H NMR (C_6D_6, the air-exposed mixture) due to 11 δ 0.26 (s, 9 H, Me_3SiO), 3.46 (s, 3 H, MeO), 6.5–7.6 (m, 4 H); due to 14, δ 0.43 (s, 18 H, $(Me_3Si)_2Si$); CH_4 CI MS of the mixture, corresponding to 2-MeO—$C_6H_4C(=O)$—$OSiMe_3$, m/z 225 (MH$^+$, 100%), 135 (10), 107 (18), 90 (10), 73 (10); corresponding to $[(Me_3Si)_2Si—O—]_3$, m/z 571 (MH$^+$, 3%), 498 (7), 483 (10), 425 (70), 410 (100), 394 (35).

Preparation of (4-*tert*-Butylbenzoyl)- (1g) and (3,5-Dimethylbenzoyl)tris(trimethylsilyl)silane (1h). Acylsilanes **1g** and **1h** were prepared following the general procedure used for **1c** and **1d** by slow addition of the appropriate acid chloride to a solution of $(Me_3Si)_3SiLi$ in THF at about −70 °C. Normal workup gave the products with properties listed in Table I.

Attempted Preparation of (2,4,6-Tri-*tert*-butyl)benzoyl)- and (2,6-Dimethylbenzoyl)tris(trimethylsilyl)silanes. The acid chloride of 2,4,6-tri-*tert*-butyl)benzoic acid, prepared by the method of Barclay,[13] was prepared by treatment with thionyl chloride in ether, to which was added 1 equiv of pyridine. The purified acid chloride was added in one portion to 1 equiv of $(Me_3Si)_3SiLi$ in THF at −70 °C, and the deep brown solution was stirred for 16 h at −10 °C, yielding a yellow solution. Workup gave a mixture of compounds (TLC) including tetrakis(trimethylsilyl)silane, and the yellow fraction in the mixture was isolated to give 88% of 2,2′,4,4′,6,6′-hexa-*tert*-butylbenzil, recrystallized from ethanol: mp 208–208.5 °C; IR (Nujol) 1700 cm^{-1} (C=O); NMR (CCl_4-CH_2Cl_2) δ 1.22 (s, 9 H), 1.30 (s, 9 H), 1.35

(s, 9 H), 7.30 (br s, 2 H); MS, *m/z* 273 ($M^+/2$, 100%), 57 (t-Bu^+, 30%). Anal. Calcd for $C_{38}H_{58}O_2$: C, 83.46; H, 10.69. Found: C, 83.51; H, 10.79.

A similar coupling of 2,6-dimethylbenzoyl chloride with $(Me_3Si)_3SiLi$ at −78 °C gave no acylsilane but 25% of a yellow solid assigned the structure 2,2′,6,6′-tetramethylbenzil, mp 150–151 °C, from hexane, was isolated: IR (CCl_4) 1694 cm^{-1} (CO); ^1H NMR (CCl_4–CH_2Cl_2) δ 2.24 (s, 12 H), 6.9–7.3 (b m, 6 H); *m/z* 133 ($M^+/2$, 105 $(M - CO)^+$. Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: 80.59; H, 6.81.

Acknowledgment. This research was supported by the National Science and Engineering Research Council of Canada.

Registry No. 1c, 81671-44-5; **1d**, 81671-45-6; **1e**, 81671-46-7; **1f**, 81671-47-8; **1g**, 81740-72-9; **1h**, 72189-49-2; **3c**, 81740-73-0; **3d**, 81740-74-1; **3e**, 81740-75-2; **3e′**, 81753-06-2; **3g**, 81753-07-3; **3h**, 72231-87-9; **4c** (R^1 = Me), 81753-08-4; **4d** (R^1 = Me), 81740-76-3; **4d** (R^1 = H), 81740-77-4; **4e** (R^1 = Me), 81740-78-5; **4f** (R^1 = Me), 81753-09-5; **5d**, 81740-79-6; (*R**,*S**)-**6**, 81740-80-9; (*R**,*R**)-**6**, 81740-81-0; **7**, 81740-82-1; **8**, 81740-83-2; **11**, 25436-32-2; **14**, 81740-84-3; **15**, 5181-43-1; **16**, 19555-07-8; (tris(trimethylsilyl)silyl)lithium, 4110-02-5; benzoyl chloride, 98-88-4; trifluoroacetyl chloride, 354-32-5; perfluorobenzoyl chloride, 2251-50-5; 2,3-dimethylbutadiene, 513-81-5; 4-(1,1-dimethylethyl)benzoyl chloride, 1710-98-1; 3,5-dimethylbenzoyl chloride, 6613-44-1; 2,4,6-tris(1,1-dimethylethyl)benzoyl chloride, 20208-55-3; 2,2′,4,4′,6,6′-hexakis(1,1-dimethylethyl)benzil, 19873-22-4; 2,6-dimethylbenzoyl chloride, 21900-37-8; 2,2′,6,6′-tetramethylbenzil, 1225-22-5.

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^{13}C and ^{29}Si Chemical Shifts and Coupling Constants Involving Tris(trimethylsilyl)silyl Systems

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^{13}C and ^{29}Si NMR data have been compiled for a variety of tris(trimethylsilyl)acylsilanes and related compounds and are compared with data for simple acylsilanes. In addition, data for the isomeric silaethylenes, obtained from the tris(trimethylsilyl)acylsilanes by photolysis, have been obtained. The chemical shifts for sp^2-hybridized silicon in these compounds lies in the range of 41–54 ppm. Several one-bond coupling constants and one two-bond coupling constant involving sp^2- and sp^3-hybridized silicon and carbon have been observed. As expected, the size of coupling constants involving sp^2-hybridized silicon are significantly larger than those involving sp^3-hybridized silicon.

In the course of investigations leading to our recently reported synthesis and isolation of a stable solid silaethylene[1] by photolysis of an isomeric acylsilane, we have synthesized a wide variety of organosilicon compounds containing the tris(trimethylsilyl)silyl [$(Me_3Si)_3Si$–] group.[2,3] During the characterization of these species by both ^{13}C and ^{29}Si NMR spectroscopy, not only was the chemical shift of sp^2-hybridized silicon observed for the first time, but also it was found possible to measure the magnitudes of several coupling constants involving both sp^2- and sp^3-hybridized silicon and carbon atoms not hitherto observed.

Table I provides data for a series of tris(trimethylsilyl)acylsilanes, [$(Me_3Si)_3SiCOR$], and a few related compounds, all of which have sp^3-hybridized silicon adjacent to a carbonyl group. There are two chemical shifts of particular interest, that of the carbonyl carbon and that of the silicon attached thereto.

It is evident from Table I that silicon adjacent to a carbonyl group has a strong deshielding effect on the ^{13}C carbonyl–carbon chemical shift, since all the acylsilanes described absorb in the range of 230–247 ppm whereas ketones closely related in structures to the simpler acylsilanes have the carbonyl–carbon resonance in the range of 198–209 ppm. The deshielding by silicon of 30–40 ppm relative to carbon analogues (e.g., Me_3CCOPh) is virtually the same for a given carbonyl system whether the group is Me_3Si, Ph_3Si, or $(Me_3Si)_3Si$: e.g., $\delta(^{13}C)$ $Me_3SiCOPh$, 233.7, $Ph_3SiCOPh$, 230.6, $(Me_3Si)_3SiCOPh$, 233.8. In addition to the large effect caused by silicon, a smaller effect on the carbonyl–carbon chemical shift is observed which depends on whether the other group attached to the carbonyl group is alkyl or aryl. Thus alkylacylsilanes (R_3SiCOR', R′ = alkyl) are more deshielded (244–247 ppm) than their aryl counterparts R_3SiCOR' (R′ = aryl) (230–240 ppm). This latter effect is one normally also observed with simple ketones (MeCOMe, 205, MeCOPh, 197 ppm).

The observed strong deshielding of the carbonyl carbon atoms in acylsilanes, also observed previously in acylphosphines,[7] undoubtedly involves electronegativity effects, at least in part, but also may be another manifestation of the strong interaction of silicon (or the Si–C σ bond) with an attached carbonyl group (either the π system or the lone pair on oxygen), also previously observed in the abnormally low-frequency carbonyl stretching vibrations of acylsilanes (1607–1645 cm^{-1})[7] compared to structurally related ketones (1675–1712 cm^{-1}) and the long wavelength carbonyl ultraviolet absorptions of acylsilanes (380–424 nm) compared to ketones (280–329 nm). The IR and UV results have

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