Reactions of Amines with Silenes and Acylsilanes

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Primary and secondary amines add cleanly in the dark to the silicon−carbon double bonds of silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ to give the products $(Me_3Si)_2(R_2N)SiCH(OSiMe_3)R$. Secondary amines also add in the dark to acylsilanes of the family $R_3SiCOAr$ (R = alkyl, aryl) to give aminals $ArCH(NR_2)_2$ and silanols R_3SiOH, while primary amines form the imine $ArCH{=}NR$, corresponding to the acyl group of the acylsilane plus the related silanol. However, amines do not add in the dark to polysilylacylsilanes $(Me_3Si)_3SiCOR$. Mechanisms explaining the results are proposed.

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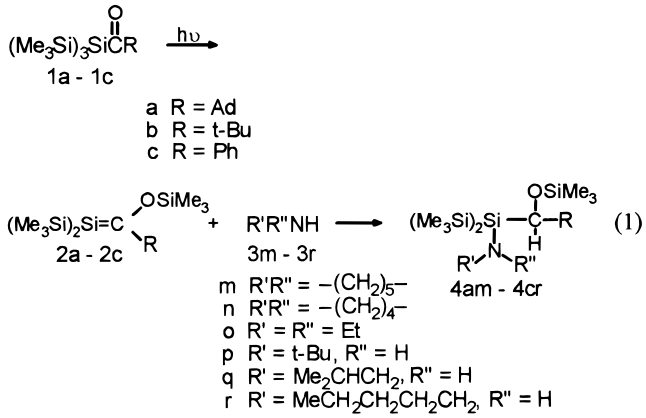
The reactions of silenes with a wide variety of reagents have been described by numerous workers and have been summarized in several recent reviews.[1] Noteworthy is the almost complete absence of publications on the reactions of silenes with amines. However, Wiberg has given data in a paper and review article about the reactions and relative reactivity of several amines with the silene $Me_2Si{=}C(SiMe_3)_2$,[2,3] where the silene was generated from a precursor at about 100 °C in the presence of the amine, which trapped it as the expected adduct involving Si−N bond formation. Leigh has recently mentioned the reaction of amines with silenes generated at relatively short UV wavelengths.[4] Silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ can be generated photochemically at room temperature or lower using long-wavelength radiation and thus provide an opportunity to ascertain the reactivity of amines toward addition to the Si=C double bond under much milder conditions.

It was found that there was no reaction between the parent acylsilanes $(Me_3Si)_3SiCOR$ (R = Ad, t-Bu, Ph), **1a**−**1c**, and various primary and secondary amines **3m**−**3r**, in the dark over several days. However when a mixture in benzene of the acylsilane and amine was photolyzed with radiation of 360 nm and longer wavelengths (conditions where the acylsilane is known to be converted to its isomeric silene as a result of a 1,3-silyl shift from silicon to oxygen), the adducts **4am**−**4cr** of the amine across the ends of the silicon−carbon double bond were formed in essentially quantitative yield, as confirmed by NMR spectroscopy and illustrated in eq 1.

It was also found that when silene, preformed by photolysis of the acylsilane, was treated with an amine in the dark, a rapid, clean and essentially quantitative addition occurred to give the expected adduct. These products were all viscous oils that failed to crystallize even in the cold. Purification was difficult due to their sensitivity to moisture and their very high boiling points (one compound was successfully distilled over a short path at a temperature in excess of 150 °C at less than 0.1 mmHg).



(1)

Thus it is clear that amines readily add across the ends of the silicon−carbon double bond in a dark reaction, almost certainly initiated by nucleophilic attack of the nitrogen lone pair on silicon, followed by migration of the hydrogen on nitrogen to the electron-rich carbon atom of the original double bond. This mechanism has been established for the addition of alcohols across the ends of the silicon−carbon double bond.[5] Rate studies reported by Wiberg[2,3] suggest that the rate of addition of amines is more rapid than that of the related alcohols. In our studies it was clear that when a mixture of acylsilane and amine was photolyzed, the rate of isomerization of acylsilane to silene was the rate-controlling step.

We also investigated the behavior of simpler acylsilanes such as $R_3SiCOAr$ (R = Me, Ph, etc.) with amines in the dark. This reaction had not been investigated previously except under photochemical conditions, where it had been observed that photolysis at 360 nm and longer wavelengths led to capture of the intermediary photochemically produced siloxycarbene

(1) Brook, A. G.; Brook, M. A. *Adv. Organometallic Chem.* **1996**, *39*, 71. Müller, T.; Ziche, W.; Auner, N. In *Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, UK, 1998; Vol. 2, p 857.

(2) Wiberg, N.; Preiner, G.; Wagner, G.; Köpf, H. *Z. Naturforsch.* **1984**, *42b*, 1062.

(3) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141.

(4) Leigh, W. J. *Pure Appl. Chem.* **1999**, *71*, *453*.

(5) Kira, M.; Maruyama, T.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 39.

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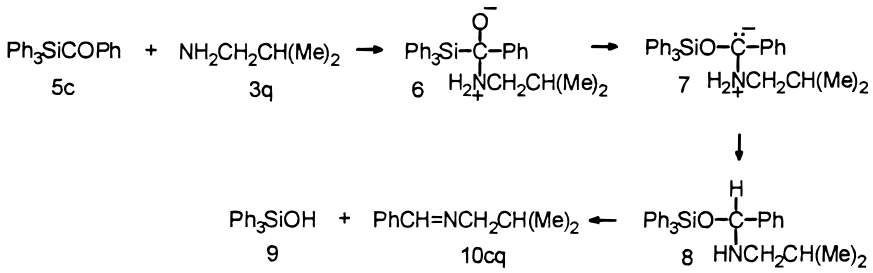
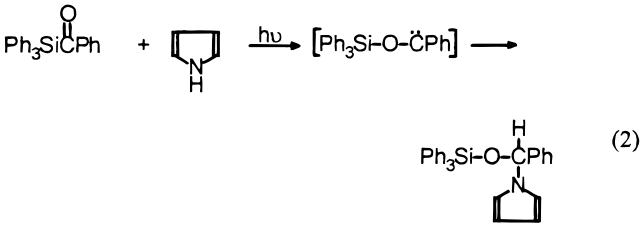
Scheme 1. Proposed Mechanism for Formation of Imine 10cq



by the weakly acidic NH bond of pyrrole (but not other amines), as shown in eq 2.[6] There was no reaction when these reagents were kept together in the dark for an extended period of time (several days).



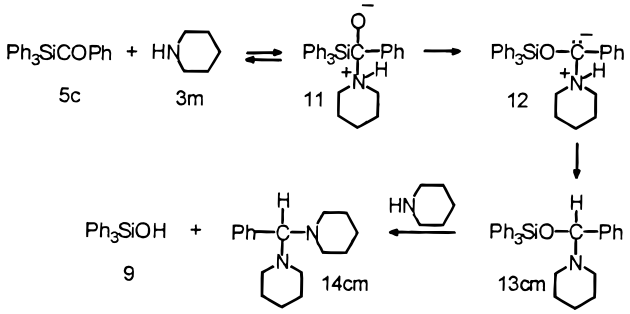
(2)

It was therefore surprising to find that other amines (*n*-butyl- and isobutylamine, piperidine, pyrrolidine) reacted *in the dark* within 3 to 24 h with a variety of simple acylsilanes. The reaction of benzoyltriphenylsilane **5c** with isobutylamine **3q** is typical of the behavior of primary amines. When an excess of amine was mixed with acylsilane in the dark, the yellow color disappeared in about 12 h. Removal of the excess amine and the solvent under reduced pressure led to the formation of much white solid, demonstrated to be triphenylsilanol **9** by melting point, and IR and NMR spectra, in a viscous colorless oil. Vacuum distillation of the oil showed that it was benzylidineisobutylamine **10cq**, on the basis of the identity of its ^{1}H and ^{13}C NMR spectra with published data.[7] This finding can be interpreted, as shown in Scheme 1, as the result of nucleophilic attack by the amine on the acylsilane carbonyl carbon giving adduct **6**, followed by a 1,2-silyl shift (Brook rearrangement) from carbon to oxygen yielding **7**, which after undergoing proton migration and loss of triphenylsilanol led to the formation of the known imine **10cq**.

Related products were obtained using *n*-butylamine (**3r**) with acylsilane **5c**, and with $Ph_3SiCOC_6H_4Cl$-*p* (**5d**) and $Ph_3SiCOC_6H_4OMe$-*p* (**5e**).

The reactions of acylsilanes with secondary amines such as piperidine or pyrrolidine (but not diethylamine, which reacted only very slowly, possibly due to steric hindrance) led to different products, namely, triphenylsilanol and the aminal of the acyl group of the original acylsilane. Using the reaction of benzoyltriphenylsilane, **5c**, with piperidine, **3m**, in benzene as a typical example, reaction of the acylsilane with an excess of amine over 36 h at room temperature in the dark gave rise to a colorless viscous oil after removal of excess amine and benzene under reduced pressure. The proton NMR

Scheme 2. Proposed Mechanism for the Formation of Aminal 14cm



spectra of this oil in deuteriobenzene indicated major signals attributable to the three expected piperidine ring C*H* resonances and to a deshielded CH group, in the ratio 4:8:8:1, in addition to aryl protons totaling 20 H. In addition some weaker signals were observed that also appeared to belong to a piperidine species: extensive pumping of the system at moderate temperatures failed to completely remove the source of these signals, suggesting that the piperidinyl species was either hydrogen bonded or part of a minor impurity (see below). When hexane or heptane was added to the viscous oil and the solution was cooled to about 0 °C, crystallization slowly occurred. The first fraction was shown by proton and carbon NMR spectra, IR spectrum, and mixed melting point to be primarily triphenylsilanol, **9**, the second fraction from further cooling was a mixture of triphenylsilanol and di(piperidyl)methylbenzene, and the third fraction was essentially pure di(piperidyl)methylbenzene, **14cm**, a known compound, identified by melting point and the virtual identity of its ^{1}H NMR and ^{13}C NMR spectra with published data.[8] The isolation of these two products in high yield indicated that they must be the major components in the original viscous oil. Scheme 2 indicates a probable mechanism for the reaction.

Initial nucleophilic attack by the amine **3m** on the carbonyl carbon of **5c** yields the adduct **11**. Instead of undergoing 1,3-proton rearrangement as might have been anticipated, a 1,2-silyl shift from carbon to oxygen occurs (Brook rearrangement), leading via the carbanion **12** to the initial product **13cm**. Further amine rapidly attacks **13cm** causing a nucleophilic displacement, leading to triphenylsilanol **9** and di(piperidyl)methylbenzene, **14cm** (even when only 1 equiv or less of amine is employed, **9** and **14cm** are formed, but in this case not all the acylsilane is consumed). A small amount of compound **13cm** is probably also present in the initial

(6) Duff, J. M.; Brook, A. G. *Can. J. Chem.* **1973**, *51*, 2869.
(7) Okuma, K.; Kimiya, Y.; Ohta, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2402.
(8) Katritzky, A. R.; Yannakopoulou, K.; Lang, H. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1867.

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viscous oil, supported by the weak signals in the NMR spectra mentioned above and the finding that a molecular ion corresponding to **13cm** is a weak peak in the mass spectrum of the viscous oil, which also shows molecular ions and fragmentations of **9**, **14cm,** and of hexaphenyldisiloxane, $Ph_3SiOSiPh_3$, formed from triphenylsilanol under the conditions of the mass spectroscopy.

Similar behavior was observed in the reactions of other benzoylsilanes $R_3SiCOPh$ (R_3Si = Me_3Si, **5f**, and α-NpPhMeSi, **5g**) with the amine piperidine **3m**, each of which gave the piperidyl aminal **14cm** together with the appropriate silanol. In the reaction of $Me_3SiCOPh$ with piperidine, the aminal was observed in the initial oil, but the expected trimethylsilanol, being volatile, was removed by the pumping used in workup. Pyrrolidine (**3n**) gave the analogous known aminals **14cn**, characterized by their NMR spectra.[8] With the acylsilanes $Ph_3SiCOC_6H_4Cl$-*p* (**5d**) and $Ph_3SiCOC_6H_4OMe$-*p* (**5e**) the corresponding aminals *p*-$XC_6H_4CH(NC_5H_{10})_2$ **14dm** and **14em** and *p*-$XC_6H_4CH(NC_4H_8)_2$ **14dn** and **14en** were formed and characterized. All of the aminals were very sensitive to moisture, readily hydrolyzing to give the amine and the aldehyde R′CHO, causing problems in their purification and analyses.

Attempts to duplicate these additions in the dark using alcohols instead of amines failed as expected, and only recovered starting material was obtained. However, as has been reported, when these reagents were photolyzed, the mixed acetals derived by reaction of the intermediary siloxycarbene with the alcohol OH bond were obtained.[6] These results support the proposal that the reactions of the acylsilanes with the amines involve a nucleophilic attack on the carbonyl group as the first step of the reaction. Alcohols evidently are too weakly nucleophilic to undergo the reaction.

In summary, amines readily add across the ends of silicon−carbon double bonds of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$. Also, amines have been shown to react with simple acylsilanes R_3SiCOR' in the dark to yield imines or aminals together with silanols.

Experimental Section

Nomenclature. New compounds are characterized by a numeral and two letters, the latter relating to the acylsilane (**a**−**g**) and the amine (**m**−**r**) employed as reagents.

General Procedures. All experiments were performed in oven-dried glassware under nitrogen using standard inert-atmosphere and vacuum line techniques. Benzene was dried over lithium aluminum hydride prior to distillation. All amines were distilled prior to use.

NMR spectra were run on Varian Unity 400 or 500 machines in C_6D_6 unless otherwise noted. ^1H signals are reported relative to residual proton resonances in deuterated solvents, ^{13}C signals were referenced to δ C 128.00, and ^{29}Si signals were referenced to external TMS. Where necessary $^{13}C-^1H$ coupled spectra were obtained: the multiplicities observed are noted in the ^{13}C spectral data by s, d, t.

Melting points are uncorrected.

General Experimental Procedure. Photolyses of polysilylacylsilanes were run under dry nitrogen and employed a small excess of amine relative to acylsilane. Irradiations at 360 nm and longer wavelengths used three 100 W PAR 38 clear mercury spot lamps (BLAK-Ray ANSI code H44GS) to illuminate NMR tubes positioned in the intense central beam about 12 in. from the lamps and cooled by a double-walled jacket containing running water. At the end of the experiment the excess amine and solvent were removed by pumping under reduced pressure. A typical experiment involving a polysilylacylsilane follows.

Photolysis of Adamantoyltris(trimethylsilyl)silane (1a) with Piperidine (3m). A solution of 0.041 g (0.01 mmol) of the acylsilane (**1**) and 0.01 mL (0.01 mmol) of piperidine in 0.4 mL of C_6D_6 was irradiated under nitrogen for 16 h. Removal of the piperidine and C_6D_6 gave the adduct **4am**, as a colorless oil. Attempts to crystallize the material from a variety of solvents failed, and attempted chromatography on silica gel caused decomposition. ^1H NMR (C_6D_6): δ 0.27, 0.37, 0.38 (each 9 H, s, $SiMe_3$), 1.44 (6 H, s br, $(CH_2)_3$, 1.60−1.79, 1.95−2.03 (15 H, m, br, Ad), 2.88 (4 H, br, CH_2NCH_2), 3.75 (1 H, s, CHOSi). ^{13}C NMR (C_6D_6): δ 2.02, 2.06 (SiMe), 2.54 ($OSiMe_3$), 25.28, 27.68 ($(CH_2)_3$), 29.18 (CH Ad), 37.38 (CH_2 Ad), 38.13 (C quat Ad), 40.80 (CH_2 Ad), 51.43 (CH_2NCH_2), 80.79 (CHOSi). ^{29}Si NMR (C_6D_6): δ −19.00, −17.96 ($SiMe_3$), −12.55 ($Si(SiMe_3)_2$), 13.55 ($OSiMe_3$). MS (EI): *m*/*z* (rel int) 480 ($M - Me)^+$ (3), 422 ($M - Me_3Si)^+$ (33), 339 ($422 - C_5H_{10}N + H)^+$ (12), 274 $((Me_3Si)(Me_3SiO)Si(C_5H_{10}N))^+$ (14), 259 $((Me_3Si)_2SiH(C_5H_{10}N)^+$ (38), 258 $((Me_3Si)_2Si(C_5H_{10}N)^+$ (100), 237 $((Me_3Si)CH(C_{10}H_{15}))^+$ (11), 207 (20), 191 $((Me_3Si)(Me_3SiO)SiH)^+$ (16), 135 $(C_{10}H_{15})^+$ (16), 73 $(Me_3Si)^+$ (57). HRMS for $(M - Me)^+ = C_{24}H_{50}NOSi_4$: calcd 480.2967; found 480.2968. Anal. Calcd for $C_{15}H_{53}NOSi_4$: C, 60.53; H, 10.76; N, 2.87. Found: C, 60.50; H, 10.30; N, 1.83.

When a solution of 0.035 g (0.09 mmol) of the acylsilane **1a** and 0.01 mL (0.01 mmol) of piperidine in 0.4 mL of C_6D_6 was stored in the dark at room temperature under nitrogen for 96 h, only starting materials were observed by ^1H, ^{13}C, and ^{29}Si NMR spectra.

Addition of Piperidine (3m) to the Adamantylsilene (2a) in the Dark. A solution of 0.043 g (0.1 mmol) of acylsilane **1a** in 0.4 mL of C_6D_6 was irradiated under nitrogen for 16 h to yield the equilibrium mixture of **1a** (minor) and its silene isomer **2a** (major), as shown by NMR spectroscopy. To this solution was added 0.02 mL (0.2 mmol) of piperidine, and the solution was stored in the dark for 12 h at room temperature. NMR spectroscopy showed that all the silene had been converted to the amine adduct **4am**, which had NMR spectra as described above.

Photolysis of Adamantoyltris(trimethylsilyl)silane (1a) with Pyrrolidine (3n). The adduct **4an** was isolated as a colorless oil following the procedure given above in the Experimental Section. ^1H NMR (C_6D_6): δ 0.24 (9 H, s, $SiMe_3$), 0.36 (18 H, s, 2 $SiMe_3$, accidental overlap), 1.58 (4 H, br, $(CH_2)_2$), 1.60−2.01 (15 H, br, CH, CH_2 Ad), 2.98 (4 H, br m, CH_2NCH_2), 3.79 (1 H, s, CHOSi). ^{13}C NMR (C_6D_6): δ 1.83, 1.90 ($SiMe_3$), 2.12 ($OSiMe_3$), 27.19 ($(CH_2)_2$), 29.14 (CH Ad), 37.41 (CH_2 Ad), 38.21 (quat C Ad), 40.73 (CH_2 Ad), 51.00 (CH_2NCH_2), 80.34 (CHOSi). ^{29}Si NMR (C_6D_6): δ −21.25−18.44, −17.71 ($SiMe_3$ and $Si(SiMe_3)_2$), 13.53 ($OSiMe_3$).

Photolysis of Adamantoyltris(trimethylsilyl)silane (1a) with Diethylamine (3o). Photolysis of 0.05 g (0.12 mmol) of acylsilane and 0.04 mL of diethylamine in 0.4 mL of C_6D_6 followed by removal of the solvent under reduced pressure gave the colorless oil **4ao**. ^1H NMR: δ 0.26, 0.37, 0.39 (each 9 H, s, Me_3Si), 1.01 (6 H, t, J = 7.3 Hz, Me), 1.6−2.02 (15 H, m, Ad), 2.89 (4 H, m, CH_2N), 3.76 (1 H, s, CHOSi). ^{13}C NMR: δ 2.01, 2.09 (Me_3Si), 2.49 (Me_3SiO), 15.32 (Me), 29.19, 37.36, 39.48, 40.99 (Ad), 44.51 (CH_2N), 81.47 (CHOSi). ^{29}Si NMR δ −19.73, −18.36 (Me_3Si), −11.31 ($Si(SiMe_3)_2$), 13.18 (Me_3SiO).

Photolysis of Pivaloyltris(trimethylsilyl)silane (1b) with Piperidine (3m). Following the procedure described above the adduct **4bm** was formed as a colorless oil. ^1H NMR (C_6D_6): δ 0.24, 0.34, 0.35 (each 9 H, s, $SiMe_3$), 1.06 (9 H, s, CMe_3), 1.42 (6 H, br, $(CH_2)_3$), 2.85 (4 H, br, CH_2NCH_2), 3.81 (1 H, s, CHOSi). ^{13}C NMR (C_6D_6): δ 2.00, 2.04 ($SiMe_3$), 2.35 ($OSiMe_3$), 25.30, 27.73 ($(CH_2)_3$), 29.08 (CMe_3), 35.93 (CMe_3), 51.47 (CH_2NCH_2), 79.67 (CHOSi). ^{29}Si NMR (C_6D_6): δ −19.11,

−18.10 ($SiMe_3$), −11.38 ($Si(SiMe_3)_2$), 13.60 ($OSiMe_3$). MS (EI): *m/z* (rel int) 402 $(M - Me)^+$ (1), 344 $(M - Me_3Si)^+$ (1), 274 $((Me_3SiO)(Me_3Si)Si(C_5H_{10}N))^+$ (28), 258 $((Me_3Si)_2SiNC_5H_{10})^+$ (100), 191 (14), 175 $(258 - C_5H_9N)^+$ (15), 159 $(C_4H_9CHOSiMe_3)^+$ (5), 73 $(Me_3Si)^+$ (65). HRMS (EI) calcd for $(M - Me)^+ = C_{18}H_{44}NOSi_4$: 402.2500; found, 402.2519; calcd for $C_{16}H_{38}NOSi_3$ $(M - Me_3Si)^+$, 344.2261; found, 344.2247. Anal. Calcd for $C_{19}H_{47}NOSi_4$: C, 54.60; H, 11.34; N, 3.35. Found: C, 53.18; H, 11.34; N, 2.53.

When a solution of 0.060 g (0.18 mmol) of acylsilane **1b** and 0.018 mL (0.18 mmol) of piperidine in 0.4 mL of C_6D_6 was stored under nitrogen in the dark for 2 weeks at room temperature, only starting materials were observed by ^1H, ^{13}C, and ^{29}Si NMR spectra. When a similar solution was refluxed for 16 h, only starting materials were observed by NMR spectroscopy; after 48 h reflux the acylsilane had decomposed.

Photolysis of Pivaloyltris(trimethylsilyl)silane (1b) with Diethylamine (3o). A solution of 0.090 g (0.27 mmol) of acylsilane and 0.055 mL (0.54 mmol) of diethylamine in 0.4 mL of C_6D_6 was irradiated under nitrogen for 27 h. The mixture was allowed to stand for 36 h. Removal of the diethylamine and C_6D_6 gave the adduct **4bo** as a colorless oil. ^1H NMR: δ 0.23, 0.34, 0.35 (each 9 H, s, $SiMe_3$), 0.99 (6 H, t, $J = 7.3$ Hz, NCH_2CH_3), 1.07 (9 H, s, CMe_3), 2.87, 2.88 (4 H, 2q, $J = 7.3$ Hz, NCH_2CH_3), 3.83 (1 H, s, CHOSi). ^{13}C NMR: δ 1.97, 2.03 ($SiMe_3$), 2.26 ($OSiMe_3$), 15.24 (NCH_2CH_3), 29.27 (CMe_3), 36.31 (CMe_3), 44.43 (NCH_2CH_3), 80.28 (CHOSi). ^{29}Si NMR: δ −19.78, −18.47 ($SiMe_3$), −10.03 ($Si(SiMe_3)_2$), 13.20 ($OSiMe_3$).

Photolysis of Pivaloyltris(trimethylsilyl)silane (1b) with *tert*-Butylamine (3p). A solution of the acylsilane and *tert*-butylamine in C_6D_6 was irradiated under nitrogen for 18 h and then was stored at room temperature for 3 days. Removal of the volatiles under reduced pressure gave the amine adduct **4bp** of the silene as a colorless oil. ^1H NMR (C_6D_6): δ 0.26, 0.31, 0.34 (each 9 H, s, Me_3Si), 0.99 (1 H, br s, NH), 1.01 (9 H, s, Me_3CCH), 1.19 (9 H, s, Me_3CNH), 3.71 (1 H, s, CHOSi). ^{13}C NMR (C_6D_6): δ 1.73, 1.83 ($SiMe_3$), 2.03 ($OSiMe_3$), 28.78 (Me_3CCH), 34.03 (Me_3CNH), 36.06 (Me_3CCH), 50.31 (Me_3CNH), 84.38 (CHOSi). ^{29}Si NMR (C_6D_6): δ −24.01, −20.06 ($SiMe_3$), −16.73 ($Si(SiMe_3)_2$), 13.23 ($OSiMe_3$). MS (EI): *m/z* (rel int) 390 $(M - Me)^+$ (1), 348 $(M - C_4H_9)^+$ (3), 332 $(M^+ - Me_3Si)$ (4), 276 $(332 - C_4H_8)^+$ (8), 262 $(332 - C_4H_8N)^+$ (40), 246 $((Me_3Si)NHC_4H_9)^+$ (82), 206 $(262 - C_4H_8)^+$ (43), 190 $(Me_3Si)_2SiNH_2)^+$ (82), 175 $(Me_3Si)_2SiH)^+$ (8), 159 $(Me_3C-CHOSiMe_3)^+$ (20), 73 $(Me_3Si)^+$ (100), 57 $(C_4H_9)^+$ (81).

Photolysis of Pivaloyltris(trimethylsilyl)silane (1b) with Isobutylamine (3q) in C_6D_6. A solution of 0.81 g (0.0024 mol) of **1b** and 0.3 mL (0.0029 mol) of **3q** in 9 mL of benzene was photolyzed in 5 mm NMR tubes for 23 h. Removal of the solvent and excess amine gave a colorless oil, which was distilled through a short path apparatus at >150 °C/0.1 mm to give $(Me_3Si)_2(Me_2CHCH_2NH)SiCH(OSiMe_3)CMe_3$ (**4bq**). ^1H NMR (C_6D_6): δ 0.22, 0.31, 0.32 (each 9 H, s, Me_3Si), 0.89, 0.90 (6 H, each a doublet, $J = 6.6$ Hz, 2 Me), 1.03 (9 H, s, Me_3C), 1.61 (1 H, approximate septet, CH), 2.71 (2 H, m, $J = 6.4$ Hz, CH_2), 3.76 (1 H, s, CHO). ^{13}C NMR: δ 1.46, 1.64, 1.82 (Me_3Si), 20.70, 20.80 (Me_2), 29.22 (Me_3C), 32.91 (Me_2CH), 36.05 (Me_3C), 54.74 (CH_2N), 81.01 (CHO). ^{29}Si NMR: δ 13.82 (Me_3SiO), −17.33, −18.70, −19.18 (Me_3Si and $(Me_3Si)_2Si$). MS (EI): *m/z* (rel int.) 405 M^+ (<1), 390 $(M - Me)^+$ (1), 332 $(M - Me_3Si)^+$ (1), 320 (4), 262 $((Me_3Si)(Me_3SiO)SiNHCH_2CHMe_2)^+$ (49), 246 $(Me_3Si)_2SiNHCH_2CHMe_2)^+$ (93), 207 (13), 191 (34), 175 $(246 - C_4H_9N)^+$ (30), 159 $(Me_3CCHOSiMe_3)^+$ (9), 73 $(Me_3Si)^+$ (100). HRMS calcd for $(M - Me)^+ = C_{17}H_{44}NOSi_4$: 390.2500; found, 390.2489.

Photolysis of Benzoyltris(trimethylsilyl)silane (1c) with Piperidine (3m). Following the general procedure the adduct **4cm** was isolated as a yellow oil. ^1H NMR (C_6D_6): δ 0.06, 0.23, 0.28 (each 9 H, s, $SiMe_3$), 1.30−1.55 (6 H, m, $(CH_2)_3$, 2.88 (4 H, m, CH_2NCH_2), 4.89 (1 H, s, CHOSi), 7.00−7.28 (5 H, m, Ph). ^{13}C NMR (C_6D_6): δ 0.70, 0.83 ($SiMe_3$), 1.00 ($OSiMe_3$), 25.32 (CH_2, C3), 28.21 ($(CH_2)_2$ C2,C4), 51.53 (CH_2NCH_2), 72.54 (CHOSi), 125.84, 126.26, 127.71, 145.9 Ph). ^{29}Si NMR (C_6D_6): δ −19.34, −19.04 ($SiMe_3$), −8.96 ($Si(SiMe_3)_2$), 18.39 ($OSiMe_3$). MS (EI): *m/z* (rel int) 437 M^+ (1), 436 $(M - H)^+$ (2), 281 (23), 258 $((Me_3Si)_2SiNC_5H_{10})^+$ (100), 207 (38), 191 $(Me_3SiO)(Me_3Si)SiH)^+$ (4), 179 $(PhCHOSiMe_3)^+$ 23, 105 $(PhCO)^+$ (30), 73 $(Me_3Si)^+$ (62). HRMS calcd for $(M - H)^+ = C_{21}H_{42}NOSi_4$: 436.2344; found, 436.2364.

Reactions of Simple Acylsilanes with Amines in the Dark. Addition of Piperidine (3m) to Benzoyltriphenylsilane (5c), a Typical Experiment. A solution of 0.86 g (2.3 mmol) of benzoyltriphenylsilane (**5c**) and 1.5 mL (15.1 mmol) of piperidine (**3m**) in 10 mL of benzene was stored at room temperature under nitrogen in the dark for 36 h. Removal of piperidine and benzene under reduced pressure gave an almost colorless viscous liquid containing **14cm** and triphenylsilanol (**9**). ^1H NMR (C_6D_6): δ 1.26 (4 H, m, C4 CH_2), 1.49 (8 H, m, C3, C5 CH_2), 2.43 (8 H, br s, C2−N−C6 CH_2), 3.58 (1 H, s, CH), 7.13−7.23 (8 H, m, Ph), 7.68−7.70 (12 H, m, Ph). ^{13}C NMR (C_6D_6): δ 25.68 (t, C4), 26.56 (t, C3, C5), 50.55 (t, C2, C6), 90.26 (d, CH), 127.43, 128.05, 128.95, 129.98, 135.50, 136.64 (Ph). ^{29}Si NMR (C_6D_6): δ −14.98 (triphenylsilanol). ^1H NMR ($CDCl_3$): δ 1.29 (4 H, m) 1.41−1.57 (8 H, m), 2.24 (8 H, br s), 3.49 (1 H, s) 7.1−7.4 (5 H, m) (lit.[8] in $CDCl_3$: 1.37, 1.4−1.6, 2.33, 3.56, 7.1−7.4). ^{13}C NMR ($CDCl_3$): δ 25.32, 26.24, 50.15, 89.73, 126.90, 127.21, 128.60, 136.32 (lit.[8] for **14cm** in $CDCl_3$: 25.2, 26.2, 50.0, 89.7, 126.9, 127.1, 128.5, 136.1). In addition to the above NMR signals, the proton spectra had signals at 1.14, 2.28, intensity ratio 3:2, which we attribute to the C3, C4, C5 and C2, C6 protons of the intermediary **13cm** and the OH group of triphenylsilanol, species which pumping failed to remove from the viscous oil. The corresponding ^{13}C signals occurred at 24.66 and 26.62 ppm. MS (EI) for the oil: *m/z* (rel int) 534 $Ph_3SiOSiPh_3^+$ (1), 457 $Ph_3SiOSiPh_2^+$ (5), 449 $Ph_3SiOCHPh(C_5H_{10}N)^+$ = **13cm** (3), 379 (8), 372 $(449 - Ph)^+$ (18), 365 $(449 - C_5H_{10}N)^+$ (22), 276 Ph_3SiOH^+ (47), 259 Ph_3Si^+ (51), 258 $PhCH(C_5H_{10}N)_2^+$ (7), 199 Ph_2SiOH^+ (100), 182 Ph_2Si^+ (38), 174 $(PhCHC_5H_{10}N)^+$ (65), 91 (41), 84 $C_5H_{10}N^+$ (6), 77 Ph^+ (65). HRMS calcd for **13cm**, $C_{30}H_{31}NOSi$: 449.2175; found, 449.2179.

When the above oil was dissolved in about 3 mL of hexane, crystals of triphenylsilanol were slowly deposited, 0.29 g (44%), mp 154−155 °C, IR identical to an authentic sample. After removal of a second crop of crystals containing some triphenylsilanol (total 68%) and some solvent, cooling to about 0 °C gave crystals of di(piperidinyl)methylbenzene (**14cm**), 0.31 g (51%), mp 77.5−79.5 °C, lit. 77−79 °C, whose NMR spectra in $CDCl_3$ were virtually identical to the reported values.[8]

Addition of Pyrrolidine (3n) to Benzoyltriphenylsilane (5c). To 0.8 g (2.2 mmol) of benzoyltriphenylsilane in 4 mL of benzene was added 1 mL (12 mmol) of pyrrolidine in the dark. After about 3 h the solution was colorless. After pumping under reduced pressure a viscous oil was obtained. After addition of 1 mL of hexane and storage at 0 °C crystals of triphenylsilanol precipitated. The supernatant was evaporated to dryness, yielding a viscous slightly yellow oil that contained mainly bis(pyrrolidinyl)methylbenzene, **14cn**, on the basis of the identity of its NMR spectra with literature results.[8] ^1H NMR ($CDCl_3$): δ 1.65 (8 H br s), 3.91 (1 H, s), 7.23−7.40 (Ar). ^{13}C NMR ($CDCl_3$): δ 23.02 (CH_2), 49.35 (CH_2N), 84.34 (CH), 127.08, 127.22, 128.92, 136.89 (Ph). In addition there were weak signals attributable to the pyrrolidine intermediate **13cn**, analogous to **13cm**.

Addition of Benzoyltriphenylsilane (5c) with Isobutylamine (3q). A yellow solution of 0.68 g (0.0019 mol) of **5c** and 1 mL of freshly distilled isobutylamine in 10 mL of benzene was left in the dark for 22 h, although it had become colorless after 6 h. On pumping under reduced pressure, a white solid was formed together with a viscous oil. The solid,

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shown to be triphenylsilanol **9** by melting point, 154−155 °C, and NMR spectra, was washed with hexane, removing the viscous oil. Distillation of the oil obtained after removal of the hexane through a short path apparatus gave a colorless oil, benzilideneisobutylamine **10cq**, identified by NMR spectra.[7] ^{1}H NMR ($CDCl_3$): δ 0.93 (6 H, d, J = 6.6 Hz, Me_2), 1.99 (1 H, approximate sept, J = 6.6 Hz, CH), 3.40 (2 H, dxd, J = 1.3, 6.6 Hz, CH_2), 7.3−7.7(5 H, m, Ph), 8.20 (1 H, s CH=N). ^{13}C NMR ($CDCl_3$): δ 20.68 (Me_2), 29.62 (CH) 69.81 (CH_2), 128.69, 130.00, 130.55, 136.60 (Ph), 160.82 (Ph*C*H=N).

Addition of Benzoyltriphenylsilane (5c) with *n*-Butylamine (3r). A solution of 0.66 g (0.0018 mol) of **5c** and 1 mL of freshly distilled *n*-butylamine in 10 mL of benzene was left in the dark for 22 h. On pumping under reduced pressure, a white solid was formed together with a viscous oil. The solid, shown to be triphenylsilanol by melting point and NMR spectra, was washed with hexane, removing the viscous oil. Distillation of the oil obtained after removal of the hexane through a short path apparatus gave a colorless oil, benzilidenebutylamine **10cr**, identified by NMR spectra.[7] ^{1}H NMR ($CDCl_3$): δ 0.93 (3 H, t, J = 7.4 Hz CH_3), 1.36 (2 H, m, CH_2), 1.67 (2 H, m, CH_2), 3.58 (2 H, m, CH_2N), 7.23−7.73 (5 H, m, Ph), 8.24 (1 H, s, CH=N). ^{13}C NMR (C_6D_6): δ 13.90 (Me), 20.60 (CH_2), 33.13 (CH_2), 61.26 (CH_2N), 128.69, 129.92, 130.57, 136.89 (Ph), 160.82 (Ph*C*H=N).

Addition of Piperidine (3m) to *p*-Chlorobenzoyltriphenylsilane (5d). The adduct **14dm** was prepared as described above. ^{1}H NMR: δ 1.28 (2 H, m, C4), 1.48 (4 H, m, C3, C5), 2.32 (4 H, br s, C2, C6), 3.46 (1 H, s CHOSi), 6.96 (m, Ar), 7.08−7.20 (m, aryl), 7.66−7.75 (m, Ar). ^{13}C NMR: δ 25.63 (C4), 26.48 (C3, C5), 50.40 (C2, C6), 89.31 (CHOSi), 127.96, 128.05, 129.98, 130.11, 133.04, 134.81, 135.49, 136.62 (Ar). ^{29}Si NMR: δ −15.00. MS (EI): *m*/*z* (rel int) 483 $Ph_3SiOCH(C_5H_{10}N)C_6H_4Cl^+$ (9), 457 (483 − Ph)$^+$ (11), 399 (483 − $C_5H_{10}N)^+$ (28), 372 (483 − $C_6H_4Cl)^+$ (16), 276 Ph_3SiOH^+ (54), 259 Ph_3Si^+ (54), 208 $(ClC_6H_4CH(C_5H_{10}N)_2^+$ (93), 207 (208 − H)$^+$ (20), 199 Ph_2SiOH^+ (28), 198 Ph_2SiO^+ (100), 125 $ClC_6H_4CH_2^+$ (39), 84 $C_5H_{10}N^+$ (11), 77 Ph^+ (25).

Addition of Pyrrolidine (3n) to *p*-Chlorobenzoyltriphenylsilane (5d). The adduct **14dn** was prepared as described above, the reagents having stood for 3 h in the dark. ^{1}H NMR (C_6D_6): δ 1.48 (8 H, m, CH_2 of C3,C4), 2.39 (8 H, m, CH_2 of C2, C5), 3.73 (1 H, s, CH), 7.01 (2 H, d J = 8.3 Hz, part of A_2B_2, 7.08−7.18, 7.72−7.76 (17 H m, Ar). ^{13}C NMR (C_6D_6): δ 23.40 (t, C3, C4), 49.62 (t, C2, C5), 84.73 (d, CH), 128.09, 129.96, 130.64, 135.07, 135.60, 137.19 (Ar including Ph_3SiOH). ^{29}Si NMR (C_6D_6): δ −16.31 (Ph_3SiOH).

Addition of Isobutylamine (3q) to *p*-Chlorobenzoyltriphenylsilane (5d). The imine *p*-ClC_6H_4CH=NCH_2CHMe_2 (**10dq**) plus triphenylsilanol (**9**) were present in the oil isolated, as described above. ^{1}H NMR (C_6D_6): δ 0.82 (6 H, d, J = 6.6 Hz, Me_2CH), 1.92 (1 H, sept J = 6.6 Hz, Me_2CH), 2.87 (1 H, br, OH of Ph_3SiOH), 3.13 (2 H, d, J = 6.6 Hz, CH_2), 6.99 (2 H, d J = 8 Hz, CH of aryl A_2B_2), 7.03−7.16 (9H, m, Ar), 7.39 (2 H, d J = 8 Hz, CH of aryl A_2B_2), 7.56−7.68 (16 H, m, Ar = CH=N). ^{13}C NMR (C_6D_6): δ 20.65 (q, Me_2C), 29.60 (d, CH), 69.50 (t, CH_2), 128.97, 129.77, 135.90, 136.88 (ClC_6H_4), and 128.09, 130.11, 135.44, 136.13 (Ph_3SiOH), 159.81 (Ph*C*H=N). ^{29}Si NMR (C_6D_6): δ −13.71 (Ph_3SiOH).

Addition of Piperidine (3m) to *p*-Methoxybenzoyltriphenylsilane (5e). The adduct **14em** was prepared using the general procedure. ^{1}H NMR ($CDCl_3$) of the viscous oil containing triphenylsilanol and the bis(piperidinyl)methyl-*p*-methoxybenzene: δ 1.30−1.39 (4 H, m, CH_2 of C4), 1.45−1.55 (8 H, m, C3, C5), 2.35 (8 H, br s, C2, C6), 3.55 (3 H, s, MeO), 3.81 (1 H, s, CH), 6.87 (2 H, d J = 8.7 Hz, part of A_2B_2), 7.15 (2 H, d, J = 8.7 Hz), lit.[8] 1.3−1.4 (4 H), 1.45−1.55 (8H), 2.31 (8 H) 3.51 (1 H), 3.77 (3 H), 6.85 (d, J = 8.7 Hz), 7.11 (2 H, d, J = 8.7 Hz). (Other signals due to the analogue of **13cm** were observed at 1.5 (6 H), 2.63 (6H), and 4.66 (2H br) 7.36−7.43, 7.66−7.86 (m, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ 25.35 (t, C4), 26.25 (t, C3, C5), 50.19 (t, C2, C6), 55.05 (q, MeO), 89.19 (d, CH), 112.66, 128.66, 129.55, 158.63, lit.[8] 25.3, 26.2, 50.0, 54.9, 89.1, 112.5, 128.4, 129.4, 158.4. Other signals due to the analogue of **13**: 26.66, 46.71 127.63, 134.99, 136.59 ppm. ^{29}Si NMR: δ −16.64. MS (EI) *m*/*z* (rel int) 402 (M − Ph)$^+$ (11), 276 $(Ph_3SiOH)^+$ (19), 259 Ph_3Si^+ (13), 204 (M − $Ph_3SiO)^+$ (94), 199 Ph_3Si^+ (100), 121 $(MeOC_6H_4CH_2)^+$ (29), 84 $C_5H_{10}N^+$ (57), 77 Ph^+ (26).

Addition of Piperidine (3m) to Benzoyl-1-naphthylphenylmethylsilane (5f). A solution of 0.050 g (0.14 mmol) of benzoyl-1-naphthylphenylmethylsilane and 0.11 mL (1.14 mmol) of piperidine in 0.4 mL of C_6D_6 was stored at room temperature under nitrogen in the dark for 60 h. Removal of piperidine and C_6D_6 at reduced pressure gave the aminal adduct **14cm** and naphthylphenylmethylsilanol. ^{1}H NMR (C_6D_6): δ 0.76 (3 H, s, MeSi), 1.29 (4 H, m, CH_2 of C4), 1.51 (8 H, m, C3, C5), 2.44 (8 H, br s, C2, C6), 3.60 (1 H, s, CH), 7.12−7.31, 7.63−7.74, 7.91−7.93, 8.44−8.46 (17 H, m, Ar). ^{13}C NMR (C_6D_6): δ 0.50 (q, MeSi), 25.62 (t, C4), 26.51 (t, C3, C5), 50.48 (t, C2, C6), 90.22 (d, CH), 125.31, 125.69, 126.06, 127.43, 128.12, 128.96, 129.10, 129.43, 129.69, 130.72, 133.59, 134.45, 135.08, 136.47, 136.68, 139.44 (Ar). ^{29}Si NMR: δ −5.19 (1-naphthylphenylmethylsilanol).

Addition of Piperidine to Benzoyltrimethylsilane (5g). Following the above procedure, the oil isolated after pumping was found to be essentially pure di(piperidinyl)methylbenzene (**14cm**). ^{1}H NMR (C_6D_6): δ 1.26 (4 H, m, C4), 1.48 (8 H, m, C3, C5) 22.41 (CH_2NCH_2), 3.56 (1 H, s, CH), 7.07−7.33 (5 H, m, Ph). ^{13}C NMR (C_6D_6): δ 25.64 (C4), 26.56 (C3, C5), 50.46 (CH_2NCH_2), 90.15 (CH), 127.42, 128.95, 130.77, 136.52 (Ph).

Attempted Reactions of Diethylamine with Acylsilanes. A solution of benzoyltriphenylsilane and diethylamine in benzene showed no change in the NMR spectra over a period of a week. Similarly, no reaction occurred between *p*-chlorobenzoyltriphenylsilane and diethylamine over a week, although after 2 weeks a minor product (<10%) was detected by NMR.

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Supporting Information Available: ^{1}H, ^{13}C, and ^{29}Si NMR spectra for all new compounds where C,H analyses are not reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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