Reaction of Imines with Silenes. Stable Silazetidines

A. G. Brook,* Wayne J. Chatterton, and Rajkumar Kumarathasan

Lash Miller Chemical Laboratories, University of Toronto, Toronto M5S 1A1, Canada

Received May 7, 1993®

Silenes of the family $(Me_3Si)RSi{=}C(OSiMe_3)R'$, **2**, have been found to undergo both [2+4] and [2+2] cycloadditions with imines $R_2C{=}NR$, **3**, to give cyclic products, silatetrahydroisoquinolines, **4**, or silazetidines, **5**, respectively. If formed, the [2+4] adducts generally rearrange slowly in the dark, or more rapidly when photolyzed, to the [2+2] adducts. When thermally decomposed in solution, the various silazetidines showed different reaction pathways, yielding either the original silene and imine or, in one case, the head-to-tail dimer of a silanimine plus an alkene, nominally derived from the alternative retro [2+2] decomposition.

In continuation of our studies of the reactions of the silicon–carbon double bond in the family of silenes with the general structure $(Me_3Si)RSi{=}C(OSiMe_3)R'$, **2**, we have looked at their reactions with the carbon–nitrogen double bond of some stable imines. Early studies by Sommer[1] with simple silenes $R_2Si{=}CH_2$ (R = Me, Ph), generated thermally at high temperatures, suggested that [2+2] cycloaddition probably occurred, but the anticipated silazetidines were not detected because they apparently underwent retro [2+2] reactions under the high temperatures employed, yielding alkenes and the head-to-tail dimers of the predicted silanimines. More recently, Wiberg reported that the silene $Me_2Si{=}C(SiMe_3)_2$ underwent both [2+2] and [2+4] cycloadditions with the imine $Ph_2C{=}N{-}SiMe_3$ at 0 °C.[2] Both of the products were relatively stable, although at 60 °C the [2+4] adduct was largely converted to the [2+2] adduct, and at 120 °C the products decomposed back to the parent imine and silene, the latter isolated as its head-to-tail 1,3-disilacyclobutane dimer. In 1989 Jones observed that the unstable silene $Me_2Si{=}CHCH_2CMe_3$ underwent both [2+2] and [2+4] cycloadditions with $Ph_2C{=}NMe$ to give thermally stable adducts.[3] Thus the nature and stability of the products of reaction of silenes with imines appears to depend on the structures of the silenes employed, as well as on the imine employed.

In the present study the relatively stable silenes $(Me_3Si)RSi{=}C(OSiMe_3)R'$, **2** (R = Me_3Si, Ph; R' = Ad, *t*-Bu, Mes), derived by photolysis of the parent acylsilanes $(Me_3Si)_2RSiCOR'$, **1**, at wavelengths ≥360 nm, were allowed to react with the imines $R''_2C{=}NR'''$, **3** (R'' = Ph, fluorenyl; R''' = Ph, Me_3Si, Mes) under two different sets of conditions. Cophotolysis of a solution of the acylsilane **1** and the imine in deuteriobenzene gave initial results identical to those from experiments where the silenes **2** were first prepared by photolysis of the acylsilane **1** and then 1 equiv of the imine was added to the silene solution in the dark. Thus the cycloadditions were dark reactions. In most cases the reactions led to relatively unstable [2+4] silatetrahydroisoquinoline adducts **4** (see Scheme I), which usually slowly isomerized spontaneously in the dark, or more rapidly if photolyzed with ≥360-nm radiation, to the related silazetidines, **5**, the expected [2+2] cycloadducts. For example, the silenes **2a** and **2b**, bearing an adamantyl or *tert*-butyl group on carbon, reacted with *N*-phenylimine derived from benzophenone, **3a**, and initially gave the silatetrahydroisoquinolines **4aa** and **4ba**, respectively. (The products of the reaction of silene **2x** with imine **3y** are named as **4xy** or **5xy**, the first letter defining the parent silene and the second letter defining the parent imine.) On standing, or more rapidly, if photolyzed further, these [2+4] adducts isomerized to the silazetidines **5aa** and **5ba**.

Silene **2a** also reacted sluggishly with benzophenone *N*-(trimethylsilyl)imine, **3c**, to yield the tetrahydroisoquinoline **4ac** in low yield.

In contrast, when silenes **2a** or **2b** were allowed to react with the *N*-phenylimine derived from fluorenone, **3b**, while the initially dark red solution suggested formation of the related tetrahydroisoquinolines had occurred, by the time all the parent acylsilane had been consumed the silazetidines **5ab** and **5bb** were the only reaction products observed by NMR spectroscopy. The reactions of silene **2c** having a mesityl group on the carbon with imines **3a** or **3b** gave no evidence for [2+4] cycloaddition, and the silazetidine products **5ca** and **5cb** from [2+2] cycloaddition were apparently formed directly (Scheme II). The latter sterically crowded silazetidine was not very stable and slowly decomposed spontaneously (see below).

There was no evidence for any reaction of either the adamantyl- or mesitylsilenes with the sterically bulky imine **3d** derived from fluorenone and 2,4,6-trimethylaniline, presumably because of steric hindrance. However, if one of the Me_3Si groups on the sp^2-hybridized silicon was replaced by a phenyl group, this less bulky silene **2d** reacted with the imine to give a [2+4] adduct **4dd** (eq 1). Its further photolysis for 72 h effected a 1,3-hydrogen shift, leading to the stable fluorenyl ring system in compound **6**, as shown in eq 1.

Thermal Decomposition of the Silazetidines

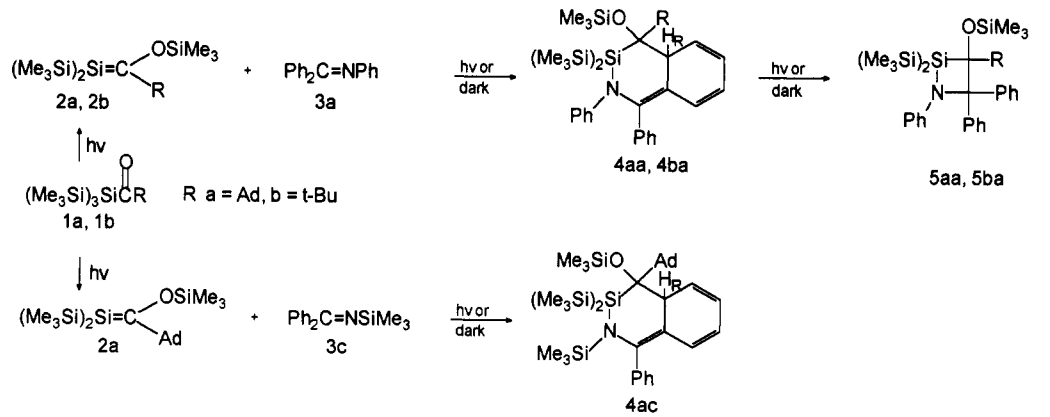
Each of the silazetidines prepared was stable at room temperature in the presence of methanol, unlike the

* Abstract published in *Advance ACS Abstracts*, August 15, 1993.

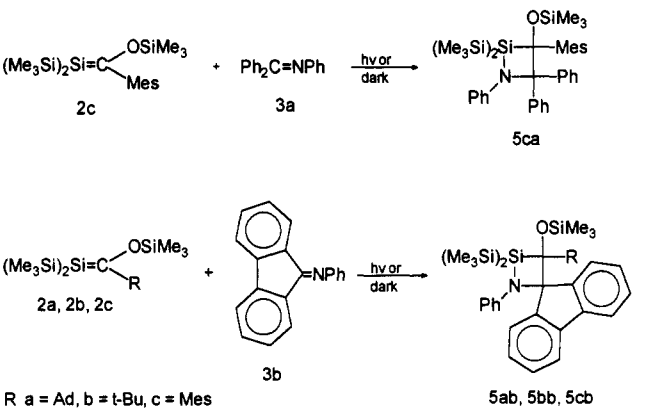
(1) Golino, C. M.; Bush, R. D.; Sommer, L. H. *J. Am. Chem. Soc.* **1974**, *96*, 614.
(2) Wiberg, N.; Preiner, G.; Schieda, O. *Chem. Ber.* **1981**, *114*, 3518.
(3) Jones, P. R.; Uang, S.-N. *Abstracts of the XXIInd Organosilicon Symposium*, Philadelphia, April 7–8, 1989; Abstract F5.
(4) Brook, A. 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.* **1982**, *104*, 5667.
(5) Baines, K. M.; Brook, A. G.; Ford, R. R.; Lickiss, P. D.; Saxena, A. K.; Chatterton, W. J.; Sawyer, J. F.; Behnam, B. A. *Organometallics* **1989**, *8*, 693.
(6) Reddelien, G. *Chem. Ber.* **1910**, *43*, 2476.
(7) Okulo, M.; Hayashi, S.; Matsunaga, M.; Uematsu, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2337.

0276-7333/93/2312-3666$04.00/0

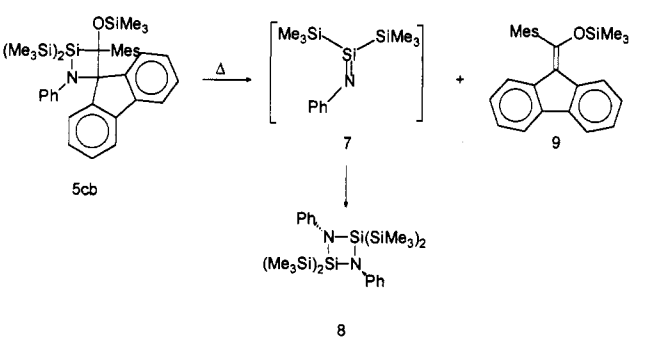
Scheme I



Scheme II



Scheme III



silazetidine reported by Jones.[3] This is probably due to the silazetidines prepared in this study being more sterically hindered than Jones' cycloadducts. The [2+2] cycloadducts were also stable at ambient temperatures in solution, allowing easy analysis by NMR spectroscopy.

When the silazetidines prepared above were heated to 70 °C, two different decomposition pathways were observed, depending on the starting compound.

Silazetidine **5cb**, prepared from the mesitylacylsilane and *N*-fluorenylideneaniline **3b**, decomposed slowly at room temperature or rapidly at 70 °C, yielding the dimer 1,1,3,3-tetrakis(trimethylsilyl)-2,4-diphenyl-1,3-disila-2,4-diazacyclobutane, **8**, of the intermediate silanimine monomer **7** (which was not detected) and the siloxyalkene **9**, both in good yields, as shown in Scheme III. This is the same decomposition pathway that Sommer proposed for his postulated intermediate silazetidine.[1] Siloxyalkene **9** had previously been isolated as the result of the thermal decomposition of the siloxetane corresponding to the adduct **5cb** (where O replaced N–Ph).[8]

All of the other silazetidines formed were remarkably stable even at 70 °C. Silazetidine **5aa** was very stable. After 21 days at 70 °C the silazetidine was still present in greater than 30% yield, together with the expected imine **3a** and the adamantylacylsilane **1a** (derived from the precursor adamantylsilene **2a** which is unstable and reverts to its parent acylsilane at elevated temperatures) (see Scheme IV). If the silazetidine was thermolyzed in the presence of methanol for 11 days at 70 °C, the anticipated intermediate silene formed was trapped by methanol as the known adduct **10**, confirming that the silene was an intermediate in the retro [2+2] reaction.

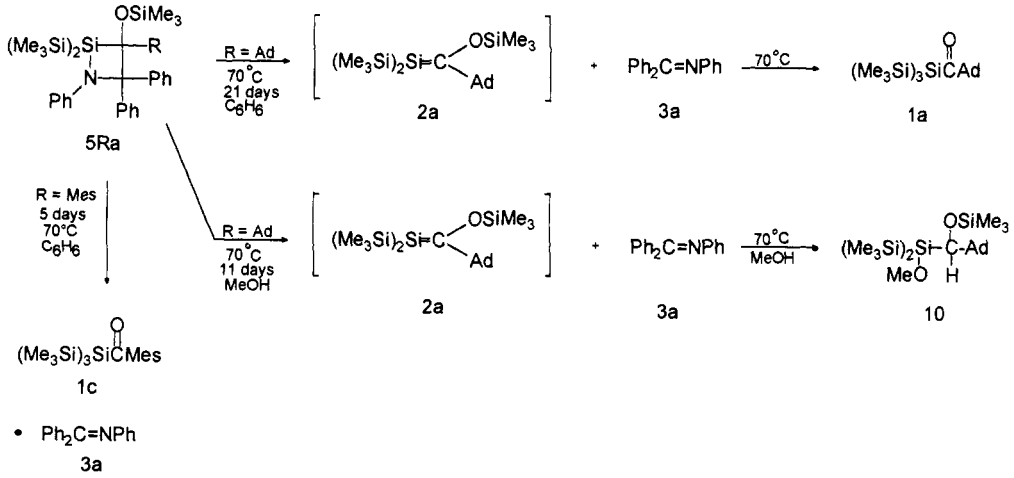
(8) Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246.

Similar behavior was observed for silazetidine **5ca**. At the end of 5 days at 70 °C **5ca** was only 60% decomposed back to the starting imine **3a** and presumably the silene **2c**, which itself is unstable at 70 °C and thus would be completely converted to the parent mesitylacylsilane **1c**, the product actually isolated in about 95% yield. Therefore neither silazetidine **5aa** nor **5ca** are useful thermal sources of a silene; this is in contrast to the behavior of Wiberg's cycloadducts.[2]

Structure Determinations Using NMR Spectroscopy

(i) Silazetidines. All of the silazetidines have very similar NMR spectra, which in turn are very similar to the spectra of analogous siloxetanes described previously.[8] The ^{1}H NMR spectra showed three trimethylsilyl signals in the −0.10 to +1.0 ppm region, adamantyl protons as a broad multiplet between 1.5 and 2.1 ppm or a *tert*-butyl singlet about 1 ppm, and aromatic phenyl and/or fluorenyl protons between 5.95 and 7.83 ppm.

Scheme IV



The ^{13}C NMR spectra of a representative silazetidine, **5ab**, have three trimethylsilyl peaks at 2.03, 3.03, and 5.65 ppm, similar to the range observed in the corresponding siloxetanes.[8] The adamantyl carbon atoms were assigned, using an APT spectrum, to the resonances at 28.86 ppm for the CH carbon atoms, 36.87 and 42.15 ppm for the CH_2 carbon atoms, and 36.96 for the quaternary carbon atom. The quaternary carbon atoms of the four-membered ring were weak resonances at 90.49 and 105.67 ppm (the resonances for the ring carbon atoms in the related siloxetanes occurred in the range 90–107 ppm[8]).

The ^{29}Si NMR spectrum of compound **5ab** had signals at −17.19 and −16.16 ppm (Me_3Si), 5.63 ppm ($OSiMe_3$) (typical positions for these groups), and 23.63 ppm, assigned to the ring silicon atom. This last chemical shift is significantly upfield of the 40–65 ppm range observed for the ring silicon atoms of the corresponding siloxetanes,[8] since nitrogen is less deshielding than oxygen. The above NMR data are in full accord with the assignment of compound **5ab** as a silazetidine, and on the basis of the similarity of the NMR spectra of compounds **5aa**, **5ba**, **5bb**, **5ca**, and **5cb** with compound **5ab**, it is clear that all of these compounds are silazetidines.

(ii) [2+4] Cycloadducts. The compounds described as [2+4] cycloadducts generally could not be completely separated from the starting materials and the silazetidines formed, and hence their NMR spectra were derived from the spectra of mixtures. All of these compounds had very similar NMR spectral data and compound **4aa** will be discussed as a typical example.

The ^1H NMR spectrum of compound **4aa** had signals at 0.24, 0.35, and 0.53 ppm due to the Me_3Si group protons and broad multiplets between 1.5 and 2.3 ppm due to the adamantyl protons, and the vinyl protons were observed as complex multiplets centered at 5.71, 6.20, and 6.48 ppm. The proton on the carbon atom at the ring junction was attributed to the resonance at 4.40 ppm, a chemical shift very similar to the 4.20 ppm observed for the corresponding proton in the analogous [2+4] siloxetane cycloadduct derived from benzophenone and adamantylsilene **2a**.[8]

The ^{13}C NMR spectrum of compound **4aa** exhibited resonances at 3.13, 3.61, and 5.29 ppm due to the Me_3Si groups. The CH carbon atom at the ring juncture was assigned to the resonance at 51.08 ppm (APT), a chemical shift close to the value of 46.21 ppm observed for the corresponding carbon atom in the [2+4] cycloadduct derived from benzophenone and the adamantylsilene.[8] The adjacent sp^3-hybridized carbon atom bearing the adamantyl and trimethylsiloxy groups was assigned to the weak resonance at 116.23 ppm.

The ^{29}Si NMR spectrum of compound **4aa** had resonances attributable to the Me_3Si silicon atoms at −17.35 and −15.20 ppm, a typical range for this type of silicon atom.[8] The trimethylsiloxy silicon atom adsorbed at 6.23 ppm, and the central silicon atom was assigned the resonance at −3.17 ppm, in the range −7 to +3 ppm observed for the corresponding ring silicon atoms in the oxygen analogs of these compounds.[8]

Taking the above NMR data into account, it is evident that compound **4aa** is a [2+4] cycloadduct and, on the basis of the similarity of the NMR data of compounds **4ba** and **4dd** with compound **4aa**, each of these compounds must be [2+4] cycloadducts.

Compound **6**, derived from **4dd** by a 1,3-H migration, is also a [2+4]-"like" cycloadduct. Its ^1H NMR spectrum was quite similar to that of the [2+4] adduct compound **4dd** except that the proton on carbon at the ring junction resonated at 5.48 ppm, reflecting its position adjacent to a more electronegative nitrogen atom. In the ^{13}C NMR spectrum this CH carbon (APT) resonated at 46.92 ppm. The other sp^3-hybridized ring quaternary carbon atom resonated at 78.05 ppm. The ^{29}Si NMR spectrum was quite similar to that of compound **4dd**, as expected, since changes in the molecule are remote from the silicon atoms and thus the positions of the peaks are only affected minimally.

(iii) 1,3-Disila-2,4-diazacyclobutane. The silanimine dimer **8** (R = Me_3Si), formed on thermolysis of silazetidine **5cb**, exhibited only one Me_3Si signal in the ^1H NMR and ^{13}C NMR spectra and only one set of signals for the two phenyl groups in both the proton and carbon NMR spectra. There was also only one peak for the Me_3Si groups attached to silicon at −18.77 ppm in the ^{29}Si NMR spectrum, along with a peak for the central silicon atom at −21.20 ppm. The simplicity of the spectra indicated that the structure must be that of the all "trans" dimer, as shown in Scheme III, or that the nitrogen atoms in the ring were rapidly inverting.

Summary and Conclusions

It has been shown above that the addition of an imine to a silene is analogous to the addition of a carbonyl compound to a silene;[8] in each case it is often possible to

observe both [2+2] and [2+4] cycloadducts being formed. The [2+4] adducts are not the end products, since they rearrange spontaneously to the more stable silazetidines.

The generation of a silene from a silazetidine "store", as employed by Wiberg[2] with his compounds, is not very useful with the present group of silazetidines because the [2+2] cycloadduct must be heated for extended periods to liberate the silene from the silazetidine, during which time the silene rapidly reverts back to its acylsilane precursor.

The generation of a stable silanimine from a silazetidine is, however, a more interesting problem, unfortunately not achieved in this study because an appropriately bulky silazetidine precursor was not prepared.

Experimental Section

All NMR spectra were run either on a Varian XL400 spectrometer or a Varian XL200 NMR spectrometer in C_6D_6 unless otherwise noted using TMS as reference. Where appropriate, APT[9] or DEPT[10] NMR pulse sequences were employed for ^{13}C NMR spectra. ^{29}Si NMR spectra were run in the DEPT mode or were run 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.

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 ≥360 nm.

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

General Procedure for Imine Formation. To 2 mol equiv of the primary amine and 1 mol equiv of the ketone was added about 150 mg of zinc bromide as a Lewis acid catalyst. The system was heated to 170 °C for 1 h, after which time the reaction mixture was allowed to cool. About 150 mL of dry benzene was added to the reaction mixture, and the benzene solution was dried over magnesium sulfate and filtered. Removal of the solvent and recrystallization from ethanol gave the pure imines.

Preparation of *N*-(Diphenylmethylidene)aniline (3a). Following the general procedure above using 10 g (0.11 mol) of aniline and 9.8 g (0.05 mol) of benzophenone gave a 72% yield of imine **3a**: mp 114 °C (lit.[6] mp 117 °C); ^1H NMR δ 7.0–8.3 ppm (15H, m, Ph); ^{13}C NMR δ 123.30, 128.43, 130.78 (each *p*-CH sp^2), 121.21, 128.09, 128.33, 128.74, 129.59, 129.73 (each *o*- or *m*-CH sp^2), 136.73, 140.09, 152.05 (each ipso-C sp^2), 167.74 (C=N); UV_{max} = 344 nm, ε = 2300.

Preparation of *N*-Fluorenylideneaniline (3b). Utilizing the general procedure above with 10 g (0.11 mol) of aniline and 10 g (0.055 mol) of fluorenone yielded 9.97 g (71%) of the desired imine: mp 89 °C (lit.[6] 89 °C); ^1H NMR δ 6.5–8.2 ppm (m, Ar); ^{13}C NMR δ 118.50 (2C), 119.78, 120.42, 123.82, 123.98, 127.35, 127.79, 128.66, 129.53 (2C), 131.76, 131.88 (CH sp^2), 134.29, 138.27, 142.20, 144.26, 152.69 (q-C sp^2), 162.79 (C=N); UV_{max} = 387 nm, ε = 1500.

Preparation of *N*-Fluorenylidene-2,4,6-trimethylaniline (3d). Following the general procedure above with 10 g (0.077 mol) of 2,4,6-trimethylaniline and 6.5 g (0.036 mol) of fluorenone led to the desired imine, **3d**, in 64% yield: mp 194–195 °C (lit.[7] mp 159–162 °C); ^1H NMR δ 2.35 (6H, s, *o*-Me Mes), 2.51 (3H, s, *p*-Me Mes), 6.8–8.5 (10H, b, Ar); ^{13}C NMR δ 18.37 (*o*-Me Mes), 21.20 (*p*-Me Mes), 129.37 (CH sp^2 Mes), 119.88, 120.33, 123.66, 125.85, 128.54, 128.74, 131.79, 131.92 (CH sp^2 Fl), 124.97, 132.61, 132.64, 138.04, 142.22, 143.45, 147.47 (q-C sp^2), 163.25 (C=N); UV_{max} = 415 nm, ε = 870; high resolution mass spectrum calcd for $C_{22}H_{19}N$ M^+, *m/e* 297.1517, found *m/e* 297.1519.

(9) Patt, S. L.; Shoolery, T. N. *J. Magn. Reson.* **1982**, *46*, 535.
(10) Pegg, D. T.; Doddrell, D. M.; Bendall, M. R. *J. Chem. Phys.* **1982**, *77*, 2745.

Preparation of Silatetrahydroisoquinoline 4aa. Equimolar amounts of the adamantylacylsilane **1a** (0.11 g, 0.27 mmol) and *N*-(diphenylmethylidene)aniline, **3a** (0.071 g, 0.27 mmol), were cophotolyzed in C_6D_6 at room temperature for 48 h, and the [2+4] cycloadduct **4aa** was produced in near quantitative yield along with a small amount of the silazetidine **5aa**. **4aa**: ^1H NMR δ 0.24, 0.35, 0.53 (each 9H, s, Me_3Si), 1.5–2.3 (15H, Ad), 4.40 (1H, ring CH_R), 5.71, 6.20, 6.48 (each 1H, br m, vinyl CH), 7.0–8.1 (br m, vinyl CH + Ph); ^{13}C NMR δ 3.13, 3.61, 5.29 (Me_3Si), 29.41 (CH Ad), 37.33, 40.29 (CH_2 Ad), 42.74 (q-C Ad), 51.08 (ring CHR), 116.23 (ring C–$OSiMe_3$), 118.55, 123.53, 123.77, 126.98 (2C), 127.70 (2C), 128.53 (2C), 129.94, 131.39, 131.77 (2C) (CH sp^2), 124.15, 137.14, 148.05, 149.25 (q-C sp^2); ^{29}Si NMR δ −17.35, −15.20 (each Me_3Si), −3.17 (ring Si), 6.18 ($OSiMe_3$).

Preparation of the Silazetidine 5aa. Following the above procedure but irradiating for 72 h instead indicated, on the basis of NMR evidence, that both the [2+4] cycloadduct **4aa** and the silazetidine **5aa** were present in the solution. If the sample was photolyzed for an additional 48 h, the [2+4] adduct was completely converted to the stable silazetidine in an overall yield of 94%. **5aa**: mp 176–178 °C; ^1H NMR δ 0.06, 0.45, 0.60 (each 9H, s, Me_3Si), 1.4–2.1 (15H, b, Ad), 6.2–8.1 (15H, b, Ar); ^{13}C NMR δ 2.99, 3.74, 5.32 (Me_3Si), 29.30 (CH Ad), 36.71, 42.59 (CH_2 Ad), 41.57 (q-C Ad), 88.70 (ring CPh_2), 107.55 (ring C–$OSiMe_3$), 117.29, 118.71, 125.97, 126.84, 127.48, 128.03, 128.40, 131.77, 132.77 (CH sp^2), 138.96, 140.94, 146.39 (q-C sp^2); ^{29}Si NMR δ −16.91, −16.06 (Me_3Si), 6.23 ($OSiMe_3$), 21.21 (ring Si). Anal. Calcd for $C_{39}H_{57}NOSi_4$: C, 70.10; H, 8.60. Found: C, 70.12; H, 8.80. HR-MS: calcd for M^+, *m/e* 667.3517; found, *m/e* 667.3536.

Preparation of Silatetrahydroisoquinoline 4ba and Silazetidine 5ba. The *tert*-butylacylsilane **1b** (0.1 g, 0.3 mmol) was photolyzed in 0.5 mL of C_6D_6 for 15 h at ambient temperature, yielding a mixture of the silene **2b** and its head-to-head dimer. The mixture was added to 0.08 g (0.3 mmol) of *N*-(diphenylmethylidene)aniline, **3a**, in the dark under argon. The ^1H NMR spectrum showed the presence of the [2+4] cycloadduct **4ba** and unreacted reagents, but there was no evidence for the [2+2] adduct. When the mixture was kept in the refrigerator for 2 weeks, the silene and its dimer were completely converted to the [2+4] adduct with a trace of [2+2] adduct. The product **4ba** was isolated in 73% yield and about 90% purity by passing the crude mixture through a Me_3SiCl-treated silica gel column. **4ba**: ^1H NMR δ 0.21, 0.32, 0.47 (each 9H, s, Me_3Si), 1.31 (9H, s, *t*-Bu), 4.38 (1H, br m, ring sp^3 CH_R), 5.67 (1H, d x d x t?, J = 1.2, 5.6, 9.5 Hz, H_A), 6.14 (1H, d x d x m, J = 2.3, 5.5, 9.8 Hz, H_B), 6.49 (1H, d x d, J = 1.1, 9.5 Hz, H_C), 6.6–7.0, 7.4–7.5, 7.8–8.0 (11H, m, Ph + one CH sp^2); ^{13}C NMR δ 3.31, 3.58 (Me_3Si), 5.07 ($OSiMe_3$), 30.73 (Me_3C), 40.46 (Me_3C), 51.32 (ring CH_R), 115.41 (ring C–$OSiMe_3$), 118.48, 123.90, 124.02, 127.46, 127.65, 128.55, 131.17, 131.99 (sp^2 CH), 123.81, 136.96, 148.04, 149.85 (C quat); ^{29}Si NMR δ −17.03, −15.58 (Me_3Si), −3.54 (ring Si), 5.94 ($OSiMe_3$); HR-MS calcd for M^+ − Me, *m/e* 574.2813, found, *m/e* 574.2827.

Preparation of Silazetidine 5ba. Equimolar quantities of the *tert*-butylacylsilane **1b** (0.1 g, 0.3 mmol) and *N*-(diphenylmethylidine)aniline, **3a** (0.08 g, 0.3 mmol), were cophotolyzed in 0.4 mL of C_6D_6 at room temperature for 46 h. The NMR spectra showed the presence of both the [2+4] and the [2+2] cycloadducts at this stage of photolysis. Further photolysis of the sample for an additional 24 h completely converted the [2+4] adduct to the stable silazetidine **5ba**, which was isolated in 50% yield. **5ba**: ^1H NMR δ 0.04, 0.41, 0.57 (each 9H, s, Me_3Si), 0.93 (9H, s, CMe_3), 6.2–8.1 (15 H, m, Ph); ^{13}C NMR δ 3.05, 3.35, 4.79 (Me_3Si), 30.75 (Me_3C), 39.95 (Me_3C), 88.34 (ring CPh_2), 105.45 (ring C–$OSiMe_3$), 117.32, 118.31, 126.02, 126.90, 127.38, 128.16, 128.29, 131.64, 132.38 (CH, sp^2), 139.03, 141.15, 146.45 (quat C, sp^2); ^{29}Si NMR δ −16.93, −15.88 (Me_3Si), 6.30 ($OSiMe_3$), 21.52 (ring Si); HR-MS calcd for M^+ *m/e* 589.3047, found *m/e* 589.3021.

Preparation of Silazetidine 5ab. Equimolar amounts of the adamantylacylsilane **1a** (0.115 g, 0.27 mmol) and *N*-fluorenylideneaniline, **3b** (0.070 g, 0.27 mmol), together with 0.3 mL of C_6D_6 were photolyzed for 72 h in a 5-mm NMR tube sealed under argon. The solution initially became deep red in color

before becoming colorless during photolysis. NMR spectroscopy of the colorless solution indicated that the [2+2] cycloadduct **5ab** was present in solution. **5ab**: mp 188–189 °C; ^{1}H NMR δ 0.10, 0.51, 0.58 (each 9H, s, Me_3Si), 1.5–2.0 (15H, b, Ad), 5.95–7.83 (13H, b, Ar); ^{13}C NMR δ 2.03, 3.03, 5.65 (Me_3Si), 28.86 (CH Ad), 36.87, 42.15 (CH_2 Ad), 36.96 (q-C Ad), 90.49, 105.67 (ring C's), 116.54 (2C), 117.26, 120.58, 121.14, 124.48, 126.62, 128.71 (2C), 128.74, 128.90, 128.93, 129.99 (CH sp^2), 141.36, 141.57, 145.69, 147.99, 149.64 (q-C sp^2); ^{29}Si NMR δ −17.19, −16.16 (Me_3Si), 5.63 ($OSiMe_3$), 23.63 (ring Si). Anal. Calcd for $C_{39}H_{55}NOSi_4$: C, 70.31; H, 8.32; N, 2.10. Found: C, 70.24; H, 8.44; N, 2.01.

Preparation of the Silatetrahydroisoquinoline 4ad. Equimolar amounts of the adamantylacylsilane **1a** (0.1 g, 0.24 mmol) and benzophenone *N*-(trimethylsilyl)imine, **3c** (0.06 g, 0.24 mmol), in 0.5 mL of C_6D_6 were photolyzed at room temperature for 17 h. The proton NMR spectrum showed the presence of the [2+4] cycloadduct (about 36%) and starting materials. The success of this experiment depended on the purity of the parent acylsilane. Neither extended photolysis (72 h) nor thermolysis at 70 °C showed evidence for the conversion of the [2+4] adduct **4ad** to its [2+2] isomer. **4ad**: ^{1}H NMR δ 0.18 (9H, s Me_3Si), 0.27 (18H, s, Me_3Si, accidental overlap), 0.41 (9H, s, Me_3Si), 1.5–2.2 (15H, br m, Ad), 4.50 (1H, br m, ring CH_R), 5.36–7.56 (9H, br m, CH sp^2); ^{13}C NMR δ 0.27, 0.88, 2.12, 4.74 (Me_3Si), 29.52 (CH Ad), 37.42, 41.02 (CH_2 Ad), 41.60 (quat C, Ad), 47.66 (ring CH), 90.16 (ring C–$OSiMe_3$), 113.80, 125.65, 126.57, 128.60, 129.98, 130.7 (CH sp^2), 108.18, 127.59, 145.40 (quat C sp^2); ^{29}Si NMR δ −18.94, −17.21 (Me_3Si), 6.03, 7.45 ($OSiMe_3$ and N–$SiMe_3$), −16.35 (ring Si).

Preparation of Silazetidine 5bb. A sample (0.1 g, 0.3 mmol) of the *tert*-butylacylsilane **1b** in 0.5 mL of C_6D_6 was photolyzed for 15 h, yielding the silene **2b** and its dimer. To this was added 0.077 g (0.3 mmol) of *N*-fluorenylidineaniline, **3b**, in the dark at room temperature. The solution turned red, but the ^{1}H NMR spectrum indicated the presence of only the [2+2] adduct **5bb** and the silene dimer. After 3 days in the refrigerator the silene dimer had been completely converted to **5bb**. Removal of the benzene and washing with hexane led to the isolation of pure **5bb** in about 40% yield. Mp: 195–197 °C. ^{1}H NMR: δ 0.01, 0.45, 0.55 (each 9H, s, Me_3Si), 0.98 (9H, s, Me_3C), 5.97–7.80 (13H, br m, Ar). ^{13}C NMR: δ 2.01, 2.92, 5.03 (Me_3Si), 31.91 (Me_3C), 39.42 (Me_3C), 90.38, 103.61 (ring C's), 116.39 (2C), 117.27, 120.36, 120.96, 124.73, 126.56, 128.52, 128.75 (2C), 128.80, 129.09, 129.66 (CH, sp^2), 141.25, 141.60, 145.73, 147.53, 149.42 (quat C, sp^2). ^{29}Si NMR: δ −17.40, −16.10 (Me_3Si), 5.90 ($OSiMe_3$), 24.29 (ring Si). Anal. Calcd for $C_{33}H_{49}NOSi_4$: C, 67.46; H, 8.34. Found: C, 67.31; H, 8.33.

Preparation of Silazetidine 5ca. Equimolar amounts of the mesitylacylsilane **1c** (0.13 g, 0.33 mmol), *N*-(diphenylmethylidene)aniline, **3a** (0.086 g, 0.33 mmol), and 0.3 mL of C_6D_6 were added under an argon atmosphere to an NMR tube which was sealed. The sample was photolyzed for 24 h at 10 °C, after which time the only observable product by NMR spectroscopy was silazetidine **5ca** in greater than 94% yield. **5ca**: ^{1}H NMR δ −0.17, 0.40, 0.81 (each 9H, s, Me_3Si), 2.17, 2.59, 2.86 (each 3H, s, Me Mes), 6.6–8.4 (17H, b, Ar); ^{13}C NMR δ 1.96, 2.54, 3.43 (Me_3Si), 20.21, 23.46, 25.75 (Me Mes), 88.48 (ring CPh_2), 93.88 (ring C-$OSiMe_3$), 117.31, 118.07, 126.76, 126.83, 126.97, 127.25, 127.84, 129.24, 130.46, 131.57, 134.09 (CH sp^2), 137.26, 137.70, 138.11, 138.67, 139.26, 141.90, 145.05 (q-C sp^2); ^{29}Si NMR δ −14.22, −12.36 (Me_3Si), 10.85 ($OSiMe_3$), 18.01 (central Si).

Preparation of Silazetidine 5cb. Equimolar amounts of the mesitylacylsilane **1c** (0.11 g, 0.27 mmol) and *N*-fluorenylideneaniline, **3b** (0.07 g, 0.27 mmol), were cophotolyzed in 0.3 mL of C_6D_6 for 24 h at ambient temperatures. The progress of the reaction was followed by NMR spectroscopy ever 6 h, as the silazetidine **5cb** initially formed started to decompose even at ambient temperatures to the dimer **8** of the silanimine and the siloxyalkene **9**. After 24 h in the dark at room temperature the silazetidine **5cb** could not be detected in the NMR spectrum and only the dimer and siloxyalkene were observed (see below). **5cb**: ^{1}H NMR δ −0.25, 0.22, 0.64 (each 9H, s, Me_3Si), 1.25, 2.02, 2.49 (each 3H, s, Me Mes), 6.4–8.4 (sp^2 CH); ^{13}C NMR δ 2.54, 2.67, 2.72 (Me_3Si), 20.47, 22.86, 23.76 (Me Mes), 87.75, 91.61 (ring C–$OSiMe_3$), 116.45 (2C), 117.31, 119.13, 120.03, 126.22, 127.13, 127.52, 128.96 (2C), 129.50 (2C), 130.62, 130.84 (CH sp^2), 131.06, 136.09, 137.00, 137.57, 138.22, 138.39, 139.49, 143.28, 145.49 (q-C sp^2); ^{29}Si NMR δ −14.53, −13.91 (Me_3Si), 11.28 ($OSiMe_3$), 23.12 (central Si).

Preparation of [2+4] Cycloadducts 4dd and 6. Equimolar amounts of (1-adamantylcarbonyl)phenylbis(trimethylsilyl)-silane, **1d**[5] (0.125 g, 0.30 mmol), and *N*-fluorenylidene-2,4,6-trimethylaniline, **3d** (0.090 g, 0.30 mmol), together with 0.25 mL of C_6D_6 were added to a 5-mm NMR tube under an argon atmosphere. The tube was photolyzed for 24 h at room temperature, after which time the major product present was the [2+4] cycloadduct **4dd**. If the tube was photolyzed for an additional 3 days almost all of **4dd** was converted to compound **6**. **4dd**: ^{1}H NMR δ 0.47, 0.61 (each 9H, s, Me_3Si), 1.7–2.5 (24H, b, Me Mes & Ad), 4.83 (1H, ring CH_R), 6.4–8.5 (15H, b, Ar); ^{13}C NMR δ 3.62, 4.06 (Me_3Si), 20.01, 20.18, 21.03 (Me Mes), 29.32 (CH Ad), 42.53, 42.91 (CH_2 Ad), 40.92 (q-C Ad), 45.77 (ring CH), 93.68 (ring C–$OSiMe_3$), 111.30, 119.22, 119.74, 124.16, 126.76, 127.61, 127.65, 129.62, 129.83, 130.42, 130.70, 137.12 (CH sp^2), 113.38, 136.11, 136.23, 138.70, 138.87, 139.29, 139.57, 139.62, 143.61, 147.61 (q-C sp^2); ^{29}Si NMR δ −16.63 (Me_3Si), 7.00 ($OSiMe_3$), −15.94 (central Si). **6**: ^{1}H NMR δ 0.19, 0.49 (each 9H, s, Me_3Si), 1.7–2.5 (24H, Me Mes & Ad), 5.48 (1H, m, ring CH_R), 6.4–8.4 (15H, b, Ar); ^{13}C NMR δ 1.77, 3.23 (Me_3Si), 20.84, 23.32, 23.69 (Me Mes), 29.72 (CH Ad), 37.31, 39.98 (CH_2 Ad), 40.99 (q-C Ad), 46.92 (ring CH), 78.05 (ring C–$OSiMe_3$), 113.18, 118.88, 119.83, 122.78, 124.22, 127.29, 127.52, 129.73 (2C), 130.01, 131.64, 137.04 (CH sp^2), 111.96, 135.90, 136.82, 137.83, 138.26, 138.70, 139.02, 139.16, 140.49, 143.98 (q-C sp^2); ^{29}Si NMR δ −12.34 (Me_3Si), 7.42 ($OSiMe_3$), −21.58 (central Si).

General Procedure for Silazetidine Thermolysis in Solution. The silazetidines were thermolyzed in a temperature-controlled oven at 70 °C in C_6D_6 in an NMR tube under an argon atmosphere. The progress of the decomposition was monitored by NMR spectroscopy.

Thermolysis of Silazetidine 5aa. Heating silazetidine **5aa** for 21 days under the general procedure described above gave a solution containing 30% of recovered silazetidine together with the starting imine **3a** and the starting acylsilane **1a**, as determined by NMR spectroscopy. No other products were observed. The thermolysis was also carried out in the presence of excess methanol under the same conditions. After 11 days the silazetidine was present in 36% of the original concentration along with the imine **3a** and the methanol adduct **10** of the adamantylsilene **2a**, identified by NMR spectroscopy.[4]

Thermolysis of Silazetidine 5ca. Following the general procedure described above, silazetidine **5ca** was thermolyzed for 5 days, after which time the only observable products using NMR spectroscopy were imine **3a** and the starting mesitylacylsilane **1b**, both present in essentially quantitative yields.

Thermolysis of Silazetidine 5bb. This unstable silazetidine spontaneously decomposed at room temperature to the dimer **8** of the silanimine and to the siloxyalkene **9**, a previously known compound, as shown by the identity of its NMR spectra with published data.[8] However, the decomposition was accelerated by heating at 70 °C, as described above. Dimer **8**: ^{1}H NMR δ 0.40 (36H, s, Me_3Si), 6.8–8.2 (10H, b, Ph); ^{13}C NMR δ −0.54 (Me_3Si), 117.73 (2C), 119.36 (*p*-CH), 129.41 (2C) (CH sp^2), 148.21 (ipso-C sp^2); ^{29}Si NMR δ −18.77 (Me_3Si), −21.20 (central Si).

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

OM9303055