Ring Insertion Reactions of Silaaziridines with Aldehydes and Isocyanates

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Silaaziridines **5**, derived from the reactions of silenes with isonitriles, react at room temperature in the dark with aromatic and α,β-unsaturated aldehydes to give 1-sila-2-oxacyclopentan-5-imines **7** and with aromatic isocyanates under photolytic conditions to give substituted 5-methylene-1-sila-2,4-diaza-3-oxocyclopentanes **10**. These new five-membered ring heterocycles have been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and by the crystal structures of three compounds. Mechanisms are proposed to account for the formation of the products.

We have recently reported that silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (**2**) react with isonitriles to yield silaaziridines **5**[1] and not the anticipated silacyclopropanimines **3** (Scheme I). Some evidence was found which suggested that the silacyclopropanimines **3** were unstable intermediates formed in the course of the reaction, and it is significant that a disilacyclopropanimine has been reported as the product obtained from the reaction of a disilene with an isonitrile.[2]

The failure to observe cyclopropanimines **3** as stable products of the reactions suggested that one of the silicon–carbon ring bonds in **3** was easily broken, possibly facilitated by solvent (or some reagent) RS forming a pentacoordinated silicon species which then ring-opened, yielding the charge-delocalized hybrid **4** ↔ **4′**. This species appeared to be a possible intermediate in the conversion of **3** to **5** as shown in Scheme I. It was also shown that aryl isonitriles inserted into the ring Si–N bond of silaaziridines, yielding substituted 1-sila-3-azacyclobutanes **6**.[3] This result suggested that the species **4** ↔ **4′** could also arise from the ring opening of the silaaziridines **5**, followed by insertion of the aryl isonitrile to give **6**. Thus it was of interest to see if the postulated intermediate **4** ↔ **4′** could be trapped from reactions of silaaziridines with other reagents.

When the silaaziridines **5** were treated with aromatic or α,β-unsaturated aldehydes in the dark at room temperature for 1–3 days the heterocycles **7RR′** were formed in good yield (see Scheme II). There was no evidence for the formation of the isomeric heterocycles **8**, although the presence of trace amounts of **8** in the crude reaction mixture cannot be excluded. No reaction occurred in the dark when acetaldehyde or propionaldehyde were used or when ketones such as acetone, methyl vinyl ketone, or benzophenone were employed. However, if the solution containing the silaaziridine and acetaldehyde was photolyzed at ≥360 nm, reaction slowly occurred to give the corresponding insertion compound.

It follows from these observations that the silaaziridines must be able to revert back to their precursor intermediates **4** ↔ **4′** under mild conditions, possibly through a five-coordinated silicon species arising from interaction of the ring silicon atom with the oxygen atom of the carbonyl group. Contributor **4**, formed from reaction of the silaaziridine with an aldehyde, as shown in Scheme II, must then undergo ring closure to the observed adduct **7RR′** as a result of attack by the negatively charged carbon atom of **4** on the positively charged carbon of the aldehyde. The fact that only aryl aldehydes undergo this reaction in the dark suggests that resonance stabilization of the carbocationic center of the intermediate **4** by the aryl group is essential for the reaction to proceed at a reasonable rate. That the reaction with acetaldehyde only occurred when the reaction mixture was photolyzed at wavelengths where the silaaziridine is known to absorb suggests that a different mechanism is probably involved.

When the silaaziridines were treated with aromatic isocyanates (R″ = Ph, *p*-Tol) no reaction occurred in the dark, but when the solution of silaaziridine and isocyanate was photolyzed at ≥360 nm the heterocycles **10RR″** were formed as shown in Scheme III. No reaction was observed when *tert*-butyl isocyanate was employed. The role of the radiation is not presently understood but presumably facilitates opening the silaaziridine ring, thus allowing the formation of the intermediate **9′**, the isocyanate analog of **4′** as shown in Scheme III. Ring closure to **10RR″** then occurs by attack of the charged nitrogen atom in **9′** on the carbonyl carbon atom of the isocyanate moiety. In this case there was no evidence for the formation of **11** in the reactions, which would be derived from the participation of contributor **9** in product formation.

It is of interest that different contributors to **4** ↔ **4′** (or **9** ↔ **9′**) are trapped apparently exclusively by the two different reagents.

Most reactions proceeded in high yield, as indicated by the NMR spectra of the crude reaction mixtures, which showed the absence of more than trace amounts of other products. In a few cases small amounts (<10%) of unidentified reaction products were observed in the crude reaction mixtures.

Most of the compounds which were isolated and purified were air-stable colorless solids, but a few became colored and slowly decomposed over a few weeks. The compounds were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, and the crystal structures of compounds **7aa** (**a** = Ad, **a**

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(1) Brook, A. G.; Kong, Y. K.; Saxena, A. K.; Sawyer, J. F. *Organometallics* 1988, *7*, 2245.

(2) Yokelson, H. B.; Millevolte, A. J.; Haller, K. J.; Wést, R. *J. Chem. Soc. Chem. Commun.* 1987, 1605.

(3) Brook, A. G.; Saxena, A. K.; Sawyer, J. F. *Organometallics* 1989, *8*, 850.

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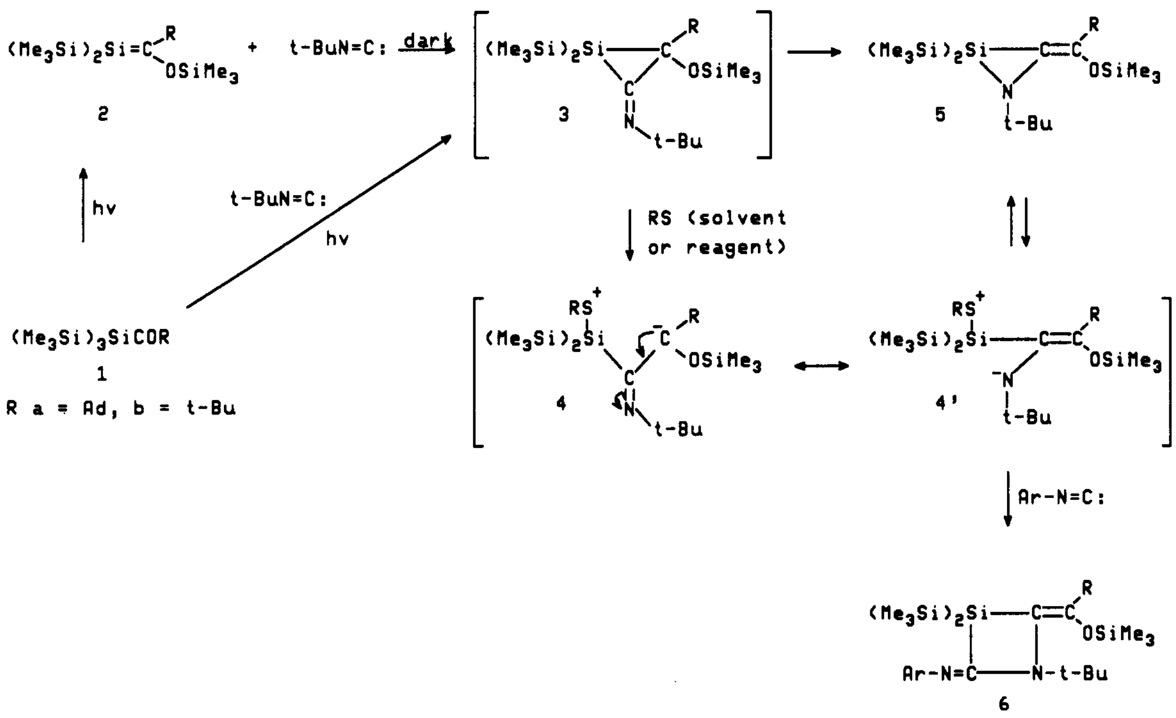
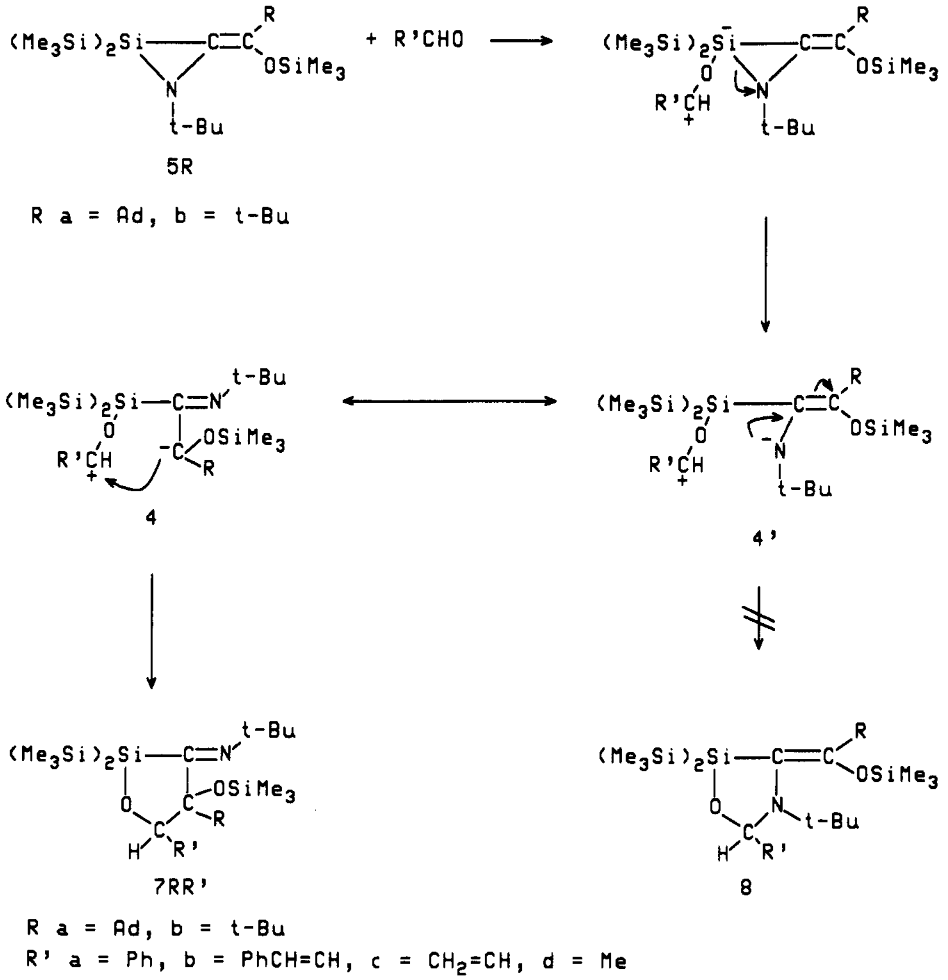
Scheme I



Scheme II



= Ph), **7ab** (**a** = Ad, **b** = PhCH=CH–) and **10ba** (**b** = *t*-Bu, **a** = Ph) were obtained, which established their structures unambiguously. Their ORTEP diagrams are given in Figures 1–3. In the case where the R′ group of R′CHO was CH_2=CH–, the compound **7ac** was a viscous oil which could not be purified by chromatography or distillation; NMR spectroscopy indicated that a compound of similar structure had been formed.

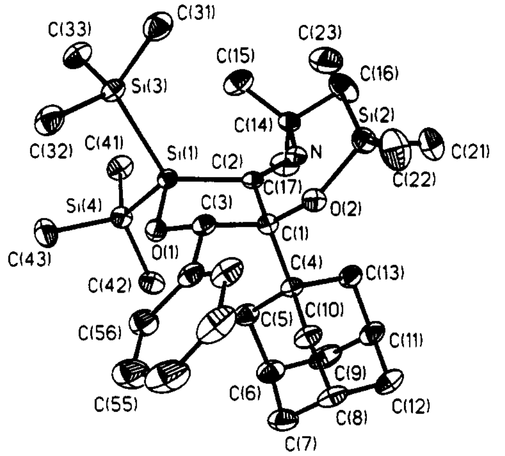


Figure 1. View of the molecule **7aa** showing the atomic labeling scheme. Thermal ellipsoids are at the 25% probability level. For the sake of clarity hydrogen atoms have been omitted.

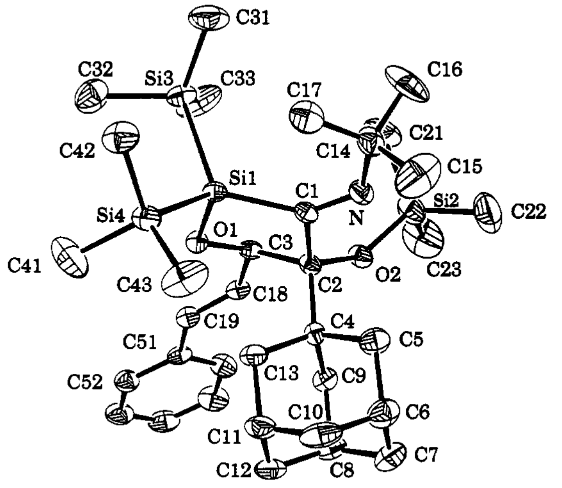
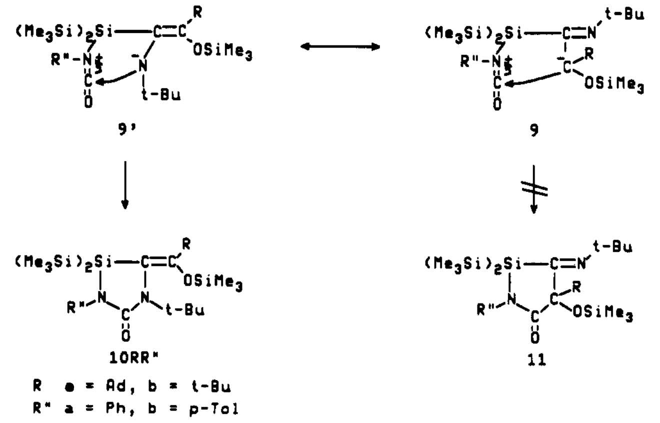


Figure 2. View of the molecule **7ab** showing the atomic labeling scheme. Thermal ellipsoids are at the 25% probability level. For the sake of clarity hydrogen atoms have been omitted.

Scheme III



Discussion of Crystal Structures

The crystal structures of **7aa**, **7ab** and **10ba** were determined to establish unambiguously the structures of these new types of compound. All three compounds contain five-membered rings which adopt envelope conformations. In both **7aa** and **7ab** C(3) is out of the least-squares plane (defined by Si(1), C(1), C(2), and O(1) by -0.644 (4) and -0.609 (6) Å, respectively, and in **10ba** C(2) is 0.440 (5) Å from the plane formed by atoms Si(1), N(1), C(1), and N(2).

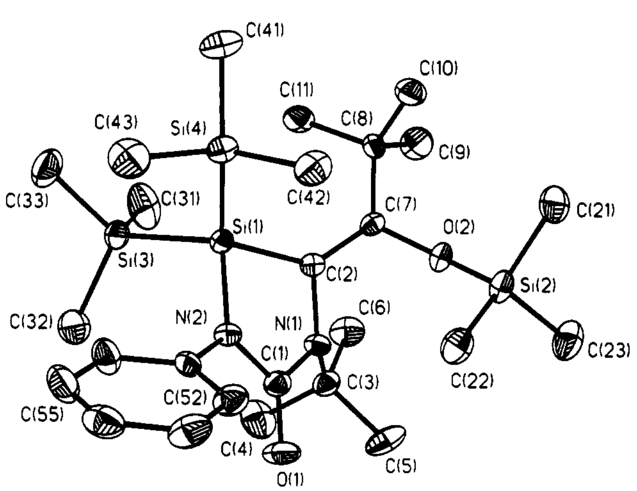


Figure 3. View of the molecule **10ba** showing the atomic labeling scheme. Thermal ellipsoids are at the 25% probability level. For the sake of clarity hydrogen atoms have been omitted.

The Si-Si bond lengths are similar in all the compounds and are in the range 2.3701 (21)-2.388 (3) Å. The Si-C(sp^2) bond lengths of the five-membered rings range from 1.887 (7) to 1.934 (3) Å and these are slightly longer than the Si-C(sp^3) bond lengths of the trimethylsilyl groups, which are in the range 1.829 (8)-1.876 (7) Å. In compound **10ba** the Si(1)-N(2) bond length of 1.797 (5) Å is longer than the average value of 1.748 (22) Å reported for 170 other compounds containing this bond type.[4] The smallest angle in each molecule is the internal ring angle at the silicon atom. These angles are O(1)-Si(1)-C(2) = 91.92 (12)° in **7aa**, O(1)-Si(1)-C(1) = 92.76 (20)° in **7ab**, and N(2)-Si(1)-C(2) = 86.2 (3)° in **10ba**. Some of the external ring angles are larger than expected (on the basis of hybridization principles), namely Si(1)-C(2)-N = 136.63 (25)° in **7aa**, Si(1)-C(1)-N = 138.1 (4)° in **7ab**, and Si(1)-C(2)-C(7) = 131.1 (5)° in **10ba**. These features suggest significant ring strain in each molecule due to large steric interactions between the substituents on the five-membered rings.

In **7aa** and **7ab** the C(sp^3)-O-Si angles of the trimethylsiloxy groups are 143.69 (20)° and 145.3 (3)°, respectively, compared to 130.4 (4)° in **10ba**. The angle widening in the former two compounds can probably be explained in terms of steric interactions of the trimethylsiloxy with the N-*tert*-butyl and adamantyl groups, whereas in **10ba** there is less steric bulk in the vicinity of the trimethysiloxy group.

Summary

It is evident from these results that the ring of silaaziridines is readily opened under mild conditions in the presence of aromatic or α,β-unsaturated aldehydes and aromatic isocyanates, leading after ring closure to new silicon-containing heterocycles. A stepwise process involving charge-delocalized dipolar intermediates ($4 \leftrightarrow 4'$ or $9 \leftrightarrow 9'$) best explains the results. The question of

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[4] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, G. A.; Taylor, R. *J. Chem. Soc. Perkin Trans. 2* 1987, S1-S17.

whether other polar reagents will similarly cause ring opening is being investigated.

Experimental Section

Experiments were performed in oven-dried glassware under argon using standard inert-atmosphere and vacuum line techniques. Solvents were dried before use: diethyl ether and THF were distilled from benzophenone ketyl; hexanes, pentanes, cyclopentane, benzene, and deuteriobenzene were distilled from lithium aluminum hydride. Photolyses employed three 100-W PAR 38 mercury spot lamps which provide radiation of 360 nm and longer wavelengths.

All NMR spectra were obtained on either a Varian XL400 or Gemini 200 spectrometer and were run in C_6D_6. Where necessary, APT[5] and DEPT[6] pulse sequences were used in obtaining ^{13}C NMR spectra and all ^{29}Si NMR spectra were run in the DEPT mode. Mass spectra were obtained on a VG70-2505 mass spectrometer. The data are reported in mass-to-charge units (*m*/*e*) followed by their relative intensities in parentheses. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Acylpolysilanes were prepared according to published procedures.[7,8] Aldehydes were distilled before use.

Reaction of Silaaziridine 5a (R = Ad) with Benzaldehyde. Formation of 7aa. The silaaziridine was prepared by the photolysis at room temperature of a solution of 0.41 g (1.0 mmol) of the adamantylacylsilane **1a** with 0.11 mL (1.1 mmol) of *tert*-butyl isocyanide in 3 mL of C_6D_6 using 3 Par 38 mercury flood lamps ($\lambda \geq 360$ nm). After 2 days of irradiation the reagents had been converted into the silaaziridine **5a**, the light source was removed, and 0.10 mL (1.0 mmol) of freshly distilled benzaldehyde was added. After standing for 3 days in the dark, concentration of the yellow solution under reduced pressure and cooling produced 0.5 g (83% of orange crystals of **7aa**, which after recrystallization from hexane gave colorless crystals with mp 248–250 °C. The ORTEP diagram for **7aa** is shown in Figure 1. Anal. Calcd for $C_{32}H_{57}NO_2Si_4\cdot{}^1/_2C_6H_{14}$: C, 65.42; H, 9.97. Found: C, 65.13; H, 9.67. MS: calcd for MH$^+$ 600.35447, found 600.35463. ^{1}H NMR: δ 0.18, 0.33, 0.47 (each 9H, s, Me$_3$Si), 1.25 (9H, s, *t*-Bu), 1.8–2.1 (15H, m, Ad), 5.02 (1H, s, ring CH), 7.05–8.1 (5H, m, Ph). ^{13}C NMR: δ 0.28, 0.36 (Me$_3$Si), 4.44 (OSiMe$_3$), 29.08 (Ad CH), 30.00 (*Me*$_3$C), 37.16, 37.89 (Ad CH$_2$), 42.89 (Ad quat C), 59.98 (Me$_3$*C*), 84.52 (ring CH), 89.07 (ring quat C), 127.25, 127.52, 127.74 (Ph CH), 142.08 (ipso C), 184.95 (*C*=N). ^{29}Si NMR: δ 4.60 (OSiMe$_3$), −5.05 (ring Si), −13.60, −14.62 (Me$_3$Si). MS (*m*/*e*): 600 (MH$^+$), 584 (6, M$^+$ − Me), 443 (38), 326 (35), 263 (22), 218 (42), 190 (100, (Me$_3$Si)$_2$SiO$^+$), 135 (53, Ad), 93 (19), 73 (90, Me$_3$Si$^+$). IR: none of the **7RR′** compounds showed strong absorptions which could be confidently assigned to the C=N stretching frequency.

Reaction of Silaaziridine 5b with Benzaldehyde. Formation of 7ba. The silaaziridine **5b** (R = *t*-Bu) was prepared as above by irradiation over 2 days of 0.5 g (1.5 mmol) of acylsilane **1b** and 0.13 g (1.57 mmol) of *tert*-butyl isocyanide in 4 mL C_6D_6. The resulting yellow solution was concentrated under vacuum to remove excess isocyanide and then was redissolved in 4 mL C_6D_6 to which 0.16 g (1.5 mmol) of benzaldehyde was added. After standing for 2 days in the dark at room temperature, NMR spectra revealed that the adduct **7ba** had formed quantitatively. Removal of the solvent and recrystallization of the oily residue from heptane at −20 °C gave colorless crystals of **7ba**; mp 122–125 °C. Anal. Calcd for $C_{26}H_{51}O_2NSi_4$: C, 59.88; H, 9.79; N, 2.69. Found: C, 58.61; H, 9.99; N, 2.57. MS: calcd for M$^+$ − Me 506.2762, found 506.2775. ^{1}H NMR: δ 0.18, 0.30, 0.47 (each 9H, s, Me$_3$Si), 0.93 (9H, s, *Me*$_3$C-C), 1.22 (9H, s, *Me*$_3$C-N), 5.05 (1H, s, ring CH), 7.15–8.02 (5H, s, Ph). ^{13}C NMR: δ 0.64, 0.66 (Me$_3$Si), 4.68 (OSiMe$_3$), 28.34 (*Me*$_3$C-C), 30.13 (*Me*$_3$C-N), 40.43 (Me$_3$*C*-C), 60.05 (Me$_3$*C*-N), 84.66 (ring CH), 89.46 (quat ring C), 127.26, 127.60, 127.80 (CH Ph), 141.90 (ipso C Ph), 184.70 (C=N). ^{29}Si NMR: δ 4.65 (0SiMe$_3$), −4.98 (ring Si), −13.97, −14.64 (Me$_3$Si). MS (*m*/*e* (%)): 506 (3, M$^+$ − Me), 450 (8), 365 (35), 190 (100, (Me$_3$Si)$_2$SiO$^+$), 73 (97, Me$_3$Si$^+$).

Reaction of Silaaziridine 5a with Cinnamaldehyde. Formation of 7ab. A solution of 0.5 g (1.22 mmol) of the acylsilane **1a** (R = Ad) and 0.14 mL (1.24 mmol) of *tert*-butyl isocyanide in 4 mL of C_6D_6 was sealed under argon and photolyzed at 10 °C. After 2 days the acylsilane had been fully converted into silaaziridine **5a**, as shown by the NMR spectrum of the yellow solution. To the solution was added 0.15 mL (1.22 mmol) of cinnamaldehyde in the dark. After standing for 3 days in the dark, the ^{1}H NMR spectrum indicated that the silaaziridine had been completely converted to the adduct **7ab**. After removal of the solvents under reduced pressure recrystallization of the residue from hexanes at −20 °C gave colorless crystals; mp 136–138 °C. The ORTEP diagram for the compound is shown in Figure 2. Anal. Calcd for $C_{34}H_{59}O_2NSi_4$: C, 65.28; H, 9.44; N, 2.24. Found: 64.98; H, 9.70; N, 1.94. MS: calcd for M$^+$ − H 624.3545, found 624.3576. ^{1}H NMR: δ 0.25, 0.34, 0.41 (each 9H, s, Me$_3$Si), 1.24 (9H, s, *t*-Bu), 1.6–2.2 (15H, m, Ad), 4.54 (1H, d × d, H$_A$ of AXY system ring-CH$_A$-CH$_B$=CH$_C$-Ph, J_{AB} = 3.4, J_{AC} = 2.2 Hz), 6.93 (1H, d × d, H$_B$, J_{BC} = 16.0 Hz), 7.0–7.5 (6H, m, Ph + H$_C$ overlapped). ^{13}C NMR: δ 0.71, 0.76 (Me$_3$Si), 4.32 (OSiMe$_3$), 29.48 (Ad CH), 30.23 (*Me*$_3$C), 37.58, 38.67 (Ad CH$_2$), 42.85 (Ad quat C), 59.97 (Me$_3$*C*), 84.59 (ring CH), 88.52 (ring quat C), 127.20, 127.27 (*C*H=*C*HPh), 126.61, 128.91, 130.21 (Ph CH), 138.12 (ipso C Ph), 183.81 (*C*=N). ^{29}Si NMR: δ 4.94 (OSiMe$_3$), −4.15 (ring Si), −13.92, −14.55 (Me$_3$Si). MS (*m*/*e* (%)): 625 (0.5, M$^+$), 610 (7, M$^+$ − Me), 568 (2.5, M$^+$ − CMe$_3$), 542 (14, M$^+$ − Me$_3$C—N=C), 469 (82), 352 (100), 190, (44, (Me$_3$Si)$_2$SiO)$^+$), 135 (48, Ad$^+$), 73 (92 (Me$_3$Si)$^+$).

Reaction of Silaaziridine 5b (R = *t*-Bu) with Cinnamaldehyde. Formation of 7bb. A yellow solution of the silaaziridine **5b** was prepared as above from 1.5 mmol of reagents, and the solution was then concentrated under reduced pressure to remove excess isocyanide. After it was redissolved in 4 mL of C_6D_6, 0.2 g (1.5 mmol) of cinnamaldehyde was added in the dark at room temperature. After 2 days the NMR spectrum of the solution indicated that all the silaaziridine had been converted into the adduct **7bb**. Concentration followed by recrystallization from hexanes at −20 °C gave pale yellow crystals; mp 127–128 °C. Anal. Calcd for $C_{28}H_{53}O_2NSi_4$: C, 61.43; H, 9.69; N, 2.56. Found: C, 60.19; H, 9.82; N, 2.50. MS: calcd for MH$^+$ 548.3232, found 548.3231. ^{1}H NMR: δ 0.24, 0.30, 0.38 (each 9H, s, Me$_3$Si), 1.19 (9H, s, *Me*$_3$C-C), 1.21 (9H, s, *Me*$_3$C-N), 4.54 (1H, d × d, H$_A$ of AXY system CH$_A$—CH$_B$=CH$_C$Ph), J_{AB} = 3.7, J_{AC} = 2.1 Hz), 6.86 (1H, d × d, H$_B$, J_{BC} = 16.0 Hz), 7.01–7.43 (6H, m, Ph + H$_C$ overlapped). ^{13}C NMR: δ 0.66, 0.72 (Me$_3$Si), 4.24 (OSiMe$_3$), 28.55 (*Me*$_3$C-C), 30.10 (*Me*$_3$C-N), 40.31 (Me$_3$*C*-C), 59.87 (Me$_3$*C*-N), 84.59 (ring CH), 88.71 (quat ring C), 126.66, 128.88, 130.03 (CH Ph), 127.24, 127.64 (*C*H=*C*HPh), 138.01 (ipso C Ph), 183.75 C=N). ^{29}Si NMR: δ 4.97 (OSiMe$_3$), −4.11 (ring Si), −14.27, −14.57 (Me$_3$Si). MS (*m*/*e* (%)): 532 (5, M$^+$ − Me), 464 (10, M$^+$ − Me$_3$Si), 391 (42), 275 (75), 263 (65), 190 (60, (Me$_3$Si)$_2$SiO$^+$), 73 (100, Me$_3$Si$^+$).

Reaction of Silaaziridine 5a with Propenal. Formation of 7ac. Using the general conditions described above, an excess of propenal (distilled from a 33% aqueous solution and dried over MgSO$_4$) was added to silaaziridine **5a**. After 48 h the reaction was complete and the excess propenal was pumped off to leave **7ac** as a viscous oil which failed to crystallize. ^{1}H NMR: δ 0.20, 0.28, 0.36 (each 9H, s Me$_3$Si), 1.22 (9H, s, *t*-Bu), 1.6–2.1 (15H, m, Ad), 4.26 (1H, d × d × d (appeared as d × d until high resolution or spin decoupling experiments were done, H$_A$ of O—C$_{ring}$H$_A$—CH$_D$=CH$_B$H$_C$, J_{AB} = 2.6, J_{AC} = 2.5. J_{AD} = 3.4 Hz), 5.18 (1H, H$_B$, d × d × d (appeared as d × t), J_{BC} = 2.6, J_{BD} = 10.6 Hz (cis)), 5.71 (1H, H$_C$, d × d × d (appeared as d × t, J_{CD}

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(5) Patt, S. I.; Shoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 535.

(6) Pegg, D. T.; Doddrell, D. M.; Bendell, M. R. *J. Phys. Chem.* **1982**, *77*, 2745.

(7) Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83.

(8) 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.

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

compd	**7aa**	**7ab**	**10ba**
empirical formula	$C_{32}H_{57}NO_2Si_4$	$C_{34}H_{59}NO_2Si_4$	$C_{26}H_{50}N_2O_2Si_2$
M_r	600.1	626.2	535.0
cryst size, mm	0.30 × 0.25 × 0.35	0.30 × 0.15 × 0.20	0.20 × 0.15 × 0.20
cryst class	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/c$	$P2_1/n$
a, Å	11.797 (2)	17.240 (2)	9.209 (2)
b, Å	17.705 (2)	11.888 (2)	18.554 (3)
c, Å	17.604 (3)	19.223 (4)	19.140 (4)
β, deg	101.45 (1)	98.99 (1)	90.62 (2)
V, Å^3	3603.7 (1)	3891.3 (11)	3270.1 (16)
Z	4	4	4
D_{calc}, g cm^{-3}	1.11	1.07	1.09
μ(Mo Kα), cm^{-1}	1.8	1.7	2.1
F(000)	1312	1368	1168
ω scan width, deg	$0.6 + 0.35 \tan \theta$	$0.6 + 0.35 \tan \theta$	$0.7 + 0.35 \tan \theta$
range θ collected, deg	1–25 ($\pm h,k,l$)	1–22.5 ($\pm h,k,l$)	1–22.5 ($\pm h,k,l$)
total no. rflns	6516	5260	4397
no. of unique rflns	6308	5090	4257
R_{int}	0.025	0.037	0.021
no. of obsd data [$I > 3\sigma(I)$]	3655	2637	1746
weighting g	0.0004	0.0004	0.0006
R	0.040	0.050	0.046
R_w	0.047	0.053	0.049
goodness of fit	1.39	1.41	1.18
largest Δ/σ	0.001	0.002	0.015
no. of params refined	352	371	308
max density in ΔF map, e/Å^3	0.28	0.25	0.24

= 17.2 Hz (trans)), 6.51 (1H, H_D, d × d × d). ^{13}C NMR: δ 0.70, 0.76 (Me_3Si), 4.27 ($OSiMe_3$), 29.53 (Ad CH), 30.27 (*Me*C-N), 37.64, 38.42 (Ad CH_2), 42.85 (Ad quat C), 59.94 (Me_3*C*-N), 84.47 (ring CH), 87.74 (ring *C*-$OSiMe_3$), 112.31 (CH_2=), 138.11 (=CH-), 184.95 (C=N). ^{29}Si NMR: δ 4.64 ($OSiMe_3$), −4.54 (ring Si), −13.99, −14.64 (Me_3Si).

Reaction of Silaaziridine 5a with Acetaldehyde. Formation of 10ad. A solution of 0.025 mmol of silaaziridine **5a** was prepared as above, and then 0.028 mmol of acetaldehyde was added by microsyringe in the dark. The reaction was monitored by ^{1}H NMR spectroscopy, and no reaction occurred over 2 days. The reaction mixture was then photolyzed over 4 days at room temperature by which time most of the reagents had been converted to **10ad**. Removal of the solvents gave a viscous oil which failed to crystallize. ^{1}H NMR: δ 0.30, 0.31, 0.33 (each 9H, s, Me_3Si), 1.19 (>9H, s, *t*-Bu), 1.20 (d partly overlapped with *t*-Bu, Me), 1.6–2.0 (15H, m, Ad), 5.22 (1H, q, ring CH, J = 5.8 Hz). ^{13}C NMR: δ 0.31, 1.13 (Me_3Si), 2.02 ($OSiMe_3$), 26.23 (*Me*-CH), 28.60, 28.92 (Ad CH and *Me*$_3$C), 36.85, 40.44 (Ad CH_2), 39.96 (Ad quat C), 59.50 (Me_3C), 86.89 (ring CH), 119.89 (ring quat CO), 188.22 (C=N). ^{29}Si NMR: δ 12.54 ($OSiMe_3$), −5.68 (ring Si), −16.14, −16.78 (Me_3Si).

Reaction of Silaaziridine 5a with Phenyl Isocyanate. Formation of 10aa. A solution of 0.25 mmol of acylsilane **1a** and 0.25 mmol *t*-BuN=C: in 0.6 mL of C_6D_6 was photolyzed for 2 days. NMR spectroscopy indicated that all the acylsilane had been converted to silaaziridine **5a**. To this solution was added 0.25 mmol of phenyl isocyanate by microsyringe, and the solution was photolyzed for about 24 h, at which time all reagents had been converted into product **10aa**. The reaction mixture was concentrated under reduced pressure, and the residue was chromatographed on silica gel using hexanes/ether (70:30) followed by recrystallization from hexanes to yield colorless adduct; mp 170–173 °C. Anal. Calcd for $C_{32}H_{56}N_2O_2Si_4$: C, 62.74; H, 9.19; N, 4.57. Found: C, 62.59; H, 9.40; N, 4.56. MS: calcd 612.34189, found 612.33830. ^{1}H NMR: δ −0.04, 0.32, 0.39 (each 9H, s Me_3Si), 1.68 (9H, s, *t*-Bu), 1.6–1.95 (15H, m, Ad), 6.5–7.4 (5H, m, Ph). ^{13}C NMR: δ 0.44, 1.29 (Me_3Si), 2.34 ($OSiMe_3$), 28.41, 29.76 (Ad CH and *Me*$_3$C), 36.56, 40.66 (Ad CH_2), 40.04 (Ad quat C), 61.03 (Me_3*C*-N), 115.58 (ring C=), 125.28, 128.44, 128.82 (Ph CH), 142.77 (Ph ipso C), 160.43, 163.63 (*C*=C, *C*=O). ^{29}Si NMR: δ 16.30 ($OSiMe_3$), −8.65 (ring Si), −14.12, −18.20 (Me_3Si). IR (KBr): 1679 cm^{-1} (C=O). MS (*m/e* (%)): 612 (18, M$^+$), 556 (24, M$^+$ − C_4H_8), 540 (59, M$^+$ + H − Me_3Si), 483 (41, 556 − Me_3Si), 468 (45), 467 (70), 73 (100, Me_3Si^+).

Reaction of Silaaziridine 5b with Phenyl Isocyanate. Formation of 10ba. A solution of 0.4 g (1.20 mmol) of acylsilane **1b** and 0.105 g of *tert*-butyl isocyanide in 4 mL of C_6D_6 was photolyzed for 2 days, during which time the acylsilane was converted to silaaziridine **5b** as shown by NMR spectroscopy. The resulting yellow solution was then concentrated under reduced pressure to remove the residual isonitrile. The residue was redissolved in 4 mL of C_6D_6, 0.15 g (2.42 mmol) of phenyl isocyanate was added, and the reaction was left for 24 h, by which time no reaction had occurred. The solution was then photolyzed for 3 days, by which time the silaaziridine had been converted to adduct **10ba** essentially quantitatively. The yellow oily residue remaining after removal of the solvent under reduced pressure was recrystallized from hexane at about −20 °C to produce colorless crystals: mp 126–128 °C. Anal. Calcd for $C_{26}H_{50}O_2N_2Si_4$: C, 58.43; H, 9.36; N, 5.24. Found: C, 58.07; H, 9.20, N, 5.29. MS: calcd for M$^+$ 534.2949, found 534.2956. ^{1}H NMR: δ −0.02, 0.28, 0.35 (each 9H, s, Me_3Si), 1.14, (9H, s, *Me*$_3$C-C), 1.64 (9H, s, *Me*$_3$C-N), 6.93–7.26 (5H, m, Ph). ^{13}C NMR: δ 0.67, 1.39 (Me_3Si), 2.14 ($OSiMe_3$), 29.44 (*Me*C-C), 29.95 (*Me*$_3$C-N), 37.05 (Me_3*C*-C), 60.67 (Me_3*C*-N), 115.80 (ring C=), 125.31, 128.50, 128.73 (Ph CH), 142.46 (Ph ipso C), 160.01, 163.68 (*C*=C, *C*=O). ^{29}Si NMR: δ 16.06 ($OSiMe_3$), −8.86 (ring Si), −14.47, −18.41 (Me_3Si). MS (*m/e* (%)): 534 (21, M$^+$), 519 (1, M$^+$ − Me), 478 (26, M$^+$ − C_4H_8), 463 (M$^+$ − $NCMe_3$), 405 (60), 389 (93), 73 (100, Me_3Si^+). IR: (KBr) 1673 cm^{-1} (C=O).

Reaction of Silaaziridine 5a with *p*-Tolyl Isocyanate. Formation of 10ab. The same methodology was employed as described above for **10ba** (including the photolysis) except that *p*-tolyl isocyanate was employed. Workup gave a solid material, which was chromatographed on silica gel using hexane/ether (70:30) and then recrystallized from hexanes to give colorless crystals: mp 158–159 °C. Anal. Calcd for $C_{33}H_{58}N_2O_2Si_4$: C, 63.26; H, 9.26; N, 4.47. Found: C, 63.25; H, 9.44; N, 4.43. MS: calcd for M$^+$ 626.35754, found 626.35522. ^{1}H NMR: δ 0.03, 0.36, 0.42 (each 9H, s Me_3Si), 1.72 (9H, s, Me_3C), 1.6–2.1 (Ad), 2.06 (3H, s, Me of *p*-tol), 6.93 (2H, d, A part of aryl A_2B_2 system, J = 8.1 Hz), 7.17 (2H, d, B part). ^{13}C NMR: δ 0.51, 1.33 (Me_3Si), 2.35 ($OSiMe_3$), 20.61 (Me), 29.77 (*Me*$_3$C-N), 28.41 (Ad CH), 36.57, 40.67 (Ad CH_2), 40.02 (Ad quat), 60.96 (Me_3*C*-N), 115.68 (ring C=), 128.32, 129.47 (each 2C of *p*-tol), 134.68, 139.99 (quat C *p*-tol), 160.34, 163.78 (C=C and C=O). ^{29}Si NMR: δ 16.16 ($OSiMe_3$), −9.16 (ring C), −14.22, −18.33 (Me_3Si). IR (Nujol): 1681 cm^{-1} (C=O). MS (*m/e* (%)): 626 (11, M$^+$), 570 (22, M$^+$ −

C_4H_8), 555 (47), 554 (49, $M^+ + H - Me_3Si$), 497 (44), 481 (70), 135 (49, Ad), 73 (100, Me_3Si^+).

Reaction of Silaaziridine 5b with *p*-Tolyl Isocyanate. Formation of 10bb. Following the preceding methodology but using *p*-tolyl isocyanate, reaction led to the formation of **10bb** in near-quantitative yield. After concentration, chromatography on silica gel using hexanes/ether (80:20) followed by recrystallization from hexanes gave colorless crystals: mp 137–139 °C. Anal. Calcd for $C_{27}H_{52}N_2O_2Si_4$: C, 59.12; H, 9.49; N, 5.11. Found: C, 58.96, H, 9.71; N, 5.09. MS: calcd for M^+ 548.31059, found 548.30943. ^1H NMR: δ 0.04, 0.32, 0.38 (each 9H, s, Me_3Si), 1.17 (9H, s, *Me*C-C), 1.68 (9H, s, *Me*$_3$C-N), 2.07 (Me of *p*-tol), 6.95 (2H, d, H_A of A_2B_2 system, J = 8.1 Hz), 7.17 (2H, d, H_B of A_2B_2. ^{13}C NMR: δ 0.68, 1.40 (Me_3Si), 2.11 ($OSiMe_3$), 20.61 (Me), 29.45, 29.94 (*Me*$_3$C-C and *Me*$_3$C-N), 37.02 (Me_3C-C), 60.64 (Me_3*C*-N), 115.88 (ring C=), 128.44, 129.42 (CH of *p*-tol), 135.79, 139.68 (quat C of *p*-tol), 159.90, 163.92 (C=O and C=C). ^{29}Si NMR: δ 16.01 ($OSiMe_3$), −9.33 (ring Si), −14.53, −18.48 (Me_3Si). IR (Nujol): 1672 cm^{-1} (C=O). MS (*m/e* (%)): 548 (27, M^+), 492 (29, $M^+ - C_4H_8$), 477 (70), 476 (69), 419 (61), 403 (100, $M^+ + H - 2Me_3Si$?), 73 (92, Me_3Si^+).

Attempted Reaction of Silaaziridine 5a with *tert*-Butyl Isocyanate or Phenyl Isothiocyanate. When silaaziridine **10aa** prepared as described above was treated with excess *tert*-butyl isocyanate, or phenyl isothiocyanate, no reaction occurred over 48 h in the dark, as shown by the ^1H NMR spectrum. Extending the time, or photolyzing the solution for 24 h, failed to effect any reaction.

X-ray Structural Determinations. Compounds **7aa**, **7ad**, and **10ba** were stable to air exposure during the course of the structure determination. Intensity data for the compounds were collected on a Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The ω–2θ scan technique was applied with variable scan speeds. The intensities of three standard reflections measured every 2 h showed no decay.

The structures were solved by direct methods. C, O, and Si atoms were refined anisotropically by full-matrix least-squares to minimize $\sum w(F_o - F_c)^2$, where $w^{-1} = \sigma^2(F) + gF^2$. Hydrogen atoms were positioned on geometric grounds (C–H = 0.95 Å, U(H) = U(C) + 0.01 Å^2) for **7aa** and **7ab**, and for **10ba** an overall hydrogen atom thermal parameter was refined to 0.105 (4) Å^2. Crystal data, data collection, and least-squares parameters are listed in Table I. All calculations were performed using SHELX76[9] and SHELXS86,[10] SHELXTLPC,[11] and NRCVAX[12] on a 486-33 personal computer and an Apollo computer. Ortep[13] diagrams of the structures are given in Figures 1–3.

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Supplementary Material Available: Tables of atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, and least-squares planes for **7aa**, **7ab**, and **10ba** (23 pages). Ordering information is given on any current masthead page.

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(9) Sheldrick, G. M. SHELX76, Program for Crystal Structure Determination; Cambridge University: Cambridge, England, 1976.

(10) Sheldrick, G. M. SHELXS86, Program for Crystal Structure Determination; University of Göttingen: Federal Republic of Germany, 1986.

(11) Sheldrick, G. M. SHELXTL PC Rel. 4.2., Siemens Analytical X-Ray Instruments, Inc., Karlsruhe, Germany.

(12) Larson, A. C.; Lee, F. L.; Le Page, Y.; Webster, M.; Charland, J. P.; Gabe, E. J. The NRCVAX Crystal Structure System; Chemistry Division, NRC, Ottawa, Canada K1A 0R6, 1990.

(13) Johnson, C. K. ORTEPII; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.