New Azasilatranes: Sterically Induced Transannular Bond Weakening and Cleavage

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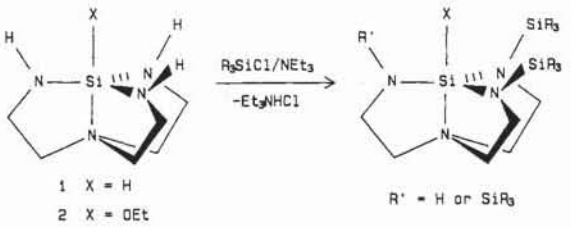
Recently we reported that azasilatranes **1** and **2** retain their structural integrity after undergoing di- or trisubstitution reactions on the equatorial NH functionalities with silyl groups of varying bulk (reaction 1).[1] Here we report that the greatly augmented



(1)

steric encumbrances resulting from the stepwise substitution of

(1) Gudat, D.; Verkade, J. G. *Organometallics*, in press.

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Scheme I

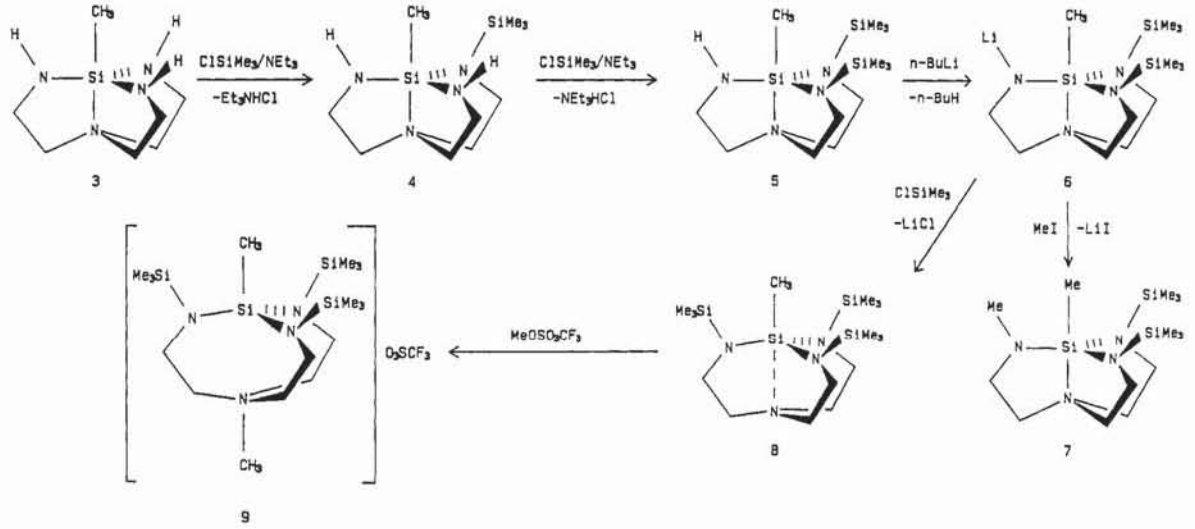

Table I. Selected NMR Data for **3–9**

	R	R′	R″	δ ^{29}Si[a] (ppm) SiCH$_3$	δ ^{29}Si[a] (ppm) Si(CH$_3$)$_3$	$^1J_{Si,C}$ (Hz)	$^2J_{Si,H}$ (Hz)
3[b]	H	H	H	−68.3		66.2	5.87
4	$SiMe_3$	H	H	−56.7	4.00	*c*	5.8
5	$SiMe_3$	$SiMe_3$	H	−36.2[d]	3.20	70.0	6.05
6[e]	$SiMe_3$	$SiMe_3$	Li	−35.9	1.76	67	5.1
7	$SiMe_3$	$SiMe_3$	Me	−25.8	3.15	74.9	6.4
8	$SiMe_3$	$SiMe_3$	$SiMe_3$	−25.7	3.16	72.4	6.50
9[f]	$SiMe_3$	$SiMe_3$	$SiMe_3$	−10.4	6.81	76.8	6.90

[a] In $CDCl_3$ unless stated otherwise. [b] See ref 7. [c] Not determined in this intermediate. [d] −35.6 in benzene. [e] In benzene. [f] In CD_2Cl_2.

the NH functions in **3** with bulky groups (Scheme I) leads to a significant weakening of the Si–N_{ax} bond, facilitating what can be considered to be a retrograde S_N2 reaction. Trimethylsilylation of **3**[2] proceeds stepwise to give **4**[3] and **5**.[3] Deprotonation of **5** gives the isolable intermediate **6**[4] which further silylates to give novel **8** or alkylates to afford unsymmetrical **7**.[5]

Normally silatranes possess robust Si–N_{ax} bonds, displaying upfield ^{29}Si chemical shifts and AA′MM′ ^{1}H NMR spectra for their conformationally mobile CH_2CH_2 protons down to low temperatures.[6] However, increased substitution of the equatorial nitrogens in **3** is accompanied by ^{29}Si deshielding and general increases in $^1J_{SiC}$ and $^2J_{SiH}$ (Table I). Such changes in silatranes have been correlated with weakening of the N_{ax}–Si bond.[7-9] Unlike other symmetrically substituted azasilatranes, the CH_2CH_2 ^{1}H NMR resonances of **8** display an ABMX pattern at −60° with AA′MM′ characteristics becoming fully evident at 100°.

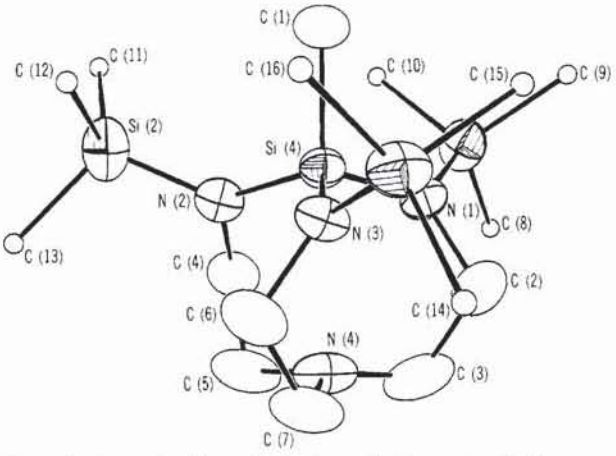

Figure 1. ORTEP drawing and atomic numbering scheme for **8**.

From the structure of **8** (Figure 1) determined by X-ray means,[10] it is evident that the N_{ax}–C_3 geometry is nearly trigonal planar (angle sum = 356.2 (6)°). Although the Si–N_{ax} distance, 2.775 (7) Å, is the longest ever recorded in an azasilatrane,[1] it is 24% shorter than the sum of the relevant van der Waals radii (3.65 Å).[11] This observation along with the slight *upward* protrusion of N_{ax} (by 0.162 (6) Å above the plane of the adjacent carbons) and the larger than tetrahedral NSiN angles (av 112.1 (2)°) suggest the presence of a weak Si–N_{ax} bond. This weak interaction renders N_{ax} sufficiently basic for reaction with $MeOSO_2CF_3$ to give **9**.[12] The further deshielding of the ^{29}Si NMR signal of the bridgehead silicon in **9** with respect to **8** is consistent with the presence of essentially four-coordinate silicon.

(2) Lukevics, E.; Zelchan, G. I.; Solomennikova, I. I.; Liepin'sh, E. E.; Yankovska, I. S.; Mazheika, I. B. *J. Gen. Chem. USSR* **1977**, *47*, 98.

(3) A solution of 10 mmol of **3** in 25 mL of benzene was reacted with a mixture of 30 mmol each of Me_3SiCl and Et_3N for 12 h at room temperature to give **5** which was isolated by filtration of the Et_3NHCl formed followed by fractional distillation of the filtrate. Although monosubstituted **4** was detected spectroscopically, no evidence for trisilylated product was observed (**5**: bp 95–96 °C/0.1 Torr).

(4) Addition of 1.1 equiv of *n*-BuLi as a 0.2 M solution in hexane to 5.0 mmol of **5** in 20 mL of hexane at 50 °C for 20 min gave, after filtration and evaporation, **6** as a colorless, highly moisture-sensitive powder (mp 81–85 °C (dec)).

(5) Solutions of 2.0 mmol of **6** in 20 mL of benzene with excess (10 mmol) of MeI and Me_3SiCl, respectively, were refluxed for 12 h. Cooling the reaction mixture to room temperature, followed by filtration of the lithium salt and fractional distillation of the filtrate afforded **7** and **8** as a colorless liquid and solid, respectively (**7**: bp 94–96 °C/0.1 Torr; **8**: mp 101–103 °C)).

(6) Voronkov, M. G.; Dyakov, V. M.; Kirpichenko, S. V. *J. Organomet. Chem.* **1982**, *233*, 1.

(7) Kupce, E.; Liepin'sh, E. E.; Lapsina, A.; Zelchan, G. I.; Lukevics, E. E. *J. Organomet. Chem.* **1987**, *349*, 23.

(8) Kupce, E.; Liepin'sh, E. E.; Lapsina, A.; Urtane, I.; Zelchan, G. I.; Lukevics, E. *J. Organomet. Chem.* **1985**, *279*, 343.

(9) Sidorkin, F.; Pestunovich, V. A.; Voronkov, M. G. *Magn. Reson. Chem.* **1985**, *23*, 491.

(10) Crystal data: space group $P\bar{1}$ (no. 2) a = 9.382 (4) Å, b = 9.640 (4) Å, c = 14.856 (6) Å, α = 90.13 (3)°, β = 101.72 (2)°, γ = 106.05 (2)°, V = 1261.9 (9) Å^3, Z = 2, d_{calc} = 1.06 g/cm^3, μ(Mo Kα) = 2.36 cm^{-1}; 3287 unique reflections in the $+h,\pm k,\pm l$ hemisphere, 1610 observed ($F_o^2 > 3\sigma(F_o^2)$). The choice of the centric space group was suggested by intensity statistics and was confirmed by successful refinement. The structure was solved by direct methods. The hydrogen atoms were used in idealized positions for structure factor calculations, and the methyl groups were refined rigidly with C–H distances of 1.08 Å. Refinement of 250 parameters converged with agreement factors of $R_1 = \sum|F_o - F_c|/\sum F_o = 0.0466$ and $R_2 = \text{sqrt}[\sum w(F_o - F_c)^2/\sum w(F_o^2)] = 0.0530$. The refinement was carried out with the SHELX-76 package.

(11) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. It should be recognized, however, that at least three lower values down to 2.69 Å have been proposed for this distance (Klaebe, G. *J. Organomet. Chem.* **1985**, *293*, 147.

(12) Addition of 2.5 mmol of MeO_3SCF_3 to 2 mmol of **8** dissolved in 20 mL of benzene at 30 °C produced a colorless precipitate of **9** which was recrystallized from $CHCl_3$ (mp 250–55 °C (dec).

Some silatranes have beneficial biological actions, while others are toxic.[6] The biological properties of the new derivatives reported here are under investigation.

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Registry No. 3 (CC entry), 63344-73-0; **3** (silane entry), 31701-36-7; **4** (CC entry), 122722-12-7; **4** (silane entry), 122699-00-7; **5** (CC entry), 122699-04-1; **5** (silane entry), 122699-01-8; **6** (CC entry), 122699-05-2; **6** (silane entry), 122699-10-9; **7** (CC entry), 122699-06-3; **7** (silane entry), 122699-02-9; **8** (CC entry), 122699-07-4; **8** (silane entry), 122699-03-0; **9**, 122699-09-6.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters, bond lengths, torsion angles, general displacement expressions, and bond angles and a listing of ^1H and ^{13}C NMR data for **4–9**, an elemental analysis for **5**, and high resolution mass spectral data for **5** and **7–9** (9 pages); table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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