Synthesis of 1,1-Di-*tert*-butylsilirane, the First Silirane with No Substituents on the Ring Carbons

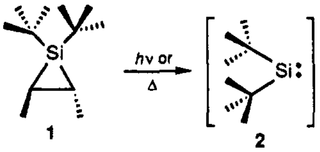
Philip Boudjouk,* Eric Black, and Rajkumar Kumarathasan

Department of Chemistry, North Dakota State University, Fargo, North Dakota 58108

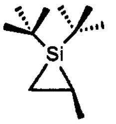
Received April 23, 1991

Summary: 1,1-Di-*tert*-butylsilirane was prepared from thermolysis of 7,7-di-*tert*-butyl-7-silabicyclo[4.1.0]heptane in the presence of ethylene. NMR data as well as thermal and photochemical reactions suggest this silirane is fundamentally different from its more substituted analogues.

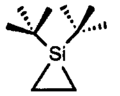
1,1-Di-*tert*-butyl-2,3-dimethylsilirane (1) produces di-*tert*-butylsilylene (2) photochemically and thermally on a preparatively useful scale.[1a] In extending this work, we have prepared two new thermally stable siliranes, 1,1-di-*tert*-butyl-2-methylsilirane (3) and 1,1-di-*tert*-butylsilirane (4), the latter possessing the unique feature of having no substituents on the ring carbons.[1b]



1 2



3



4

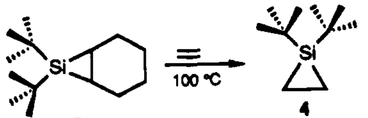
1,1-Di-*tert*-butyl-2-methylsilirane (3)[2] was prepared by condensing propylene (5 mL, 56 mmol) into a 25-mL flask containing a lithium dispersion (1% sodium, 400 mg, 57 mmol) and tetrahydrofuran (12 mL) at −78 °C. Di-*tert*-butyldichlorosilane (4.0 g, 18.6 mmol) was added, and the mixture was stirred for 12 h with gradual warmup to room temperature. After the salts were allowed to settle, the supernatant liquid was removed, concentrated in vacuo, and distilled under vacuum (bp 42 °C, 0.5 Torr), giving 1.8 g of 3 (53%). A similar attempt to prepare 4 by bubbling ethylene through the slurry of lithium, tetrahydrofuran, and di-*tert*-butyldichlorosilane gave no silirane.

Table I. NMR Data for Cyclopropanes

cyclopropane	^{1}H, δ^{a}	^{13}C, δ	^{29}Si, δ^{b}	^{1}J-(^{13}C–^{1}H), Hz
1	0.80	17.4	−43.9	137
3	0.23 (1 H)	4.6 (CH_2)	−49.3	147 (CH_2)
	0.94 (2 H)[c]	6.2 (CH)		137 (CH)
4	0.54	−5.0	−56.8	154
5	1.04	12.4	−54.6	143
cyclopropane[8]	0.22	−2.6		160
ethylene	5.29	122.8		156.2

[a] For the siliranes, only the silacyclopropane ring signals are given. Samples were run in benzene-d_6 on a JEOL GSX400 spectrometer. A 5-mm broad-band probe equipped with a variable-temperature accessory maintained the temperature at 25 °C (with 0.5 °C variance). [b] ^{29}Si NMR spectra were acquired with use of a refocused INEPT pulse sequence,[9] with shifts measured from an external reference of 25% TMS in $CDCl_3$. [c] A ^{13}C{^{1}H} HETCOR experiment shows the methylene protons at 0.23 and 0.94 ppm as complex multiplets. The methine proton overlaps the methylene proton at 0.94 ppm as a complex multiplet.

The preparation of 4[3] involves the use of a novel di-*tert*-butylsilylene generator, 7,7-di-*tert*-butyl-7-silabicyclo[4.1.0]heptane (5),[4] which is prepared by sonication[5] of di-*tert*-butyldichlorosilane (3.0 g, 14.1 mmol) in a slurry of lithium (0.45 g, 64 mmol), tetrahydrofuran (20 mL), and cyclohexene (10 mL, 98.7 mmol). Molecular distillation (65 °C, 2 Torr) yields 1.06 g of 5 (50%). Thermolysis of 5 (50 mg, 0.2 mmol) in benzene (2 mL) saturated with ethylene at 100 °C for 18 h gives 4 in 85% yield.



5 4

Attempts to prepare more highly methylated analogues of 4 from 2-methyl-2-butene and 2,3-dimethyl-2-butene with use of di-*tert*-butyldichlorosilane and lithium or pyrolysis of 5 gave no siliranes. We attribute this to steric inhibition by the *tert*-butyl groups, since it has been shown that dimethylsilylene equilibrates with 2,3-dimethyl-2-butene to give hexamethylsilirane.[6]

Typically, siliranes do not exhibit unusually high ^{13}C chemical shifts relative to those of cyclopropane deriva-

---

(1) (a) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* 1988, *27*, 1355. (b) Some of these results have been reported: Boudjouk, P.; Black, E.; Kumarathasan, R. XXIV Organosilicon Symposium, El Paso, TX, April 1991; Abstract 49.

(2) 3: ^{1}H NMR (399.78 MHz, C_6D_6) δ 0.25 (m, 1 H), 0.95 (m, 2 H), 1.05 (s, 9 H), 1.17 (s, 9 H), 1.53 (d, 6.98 Hz, 3 H); ^{13}C NMR (100.52 MHz, C_6D_6) δ 4.6, 6.2, 17.0, 17.9, 18.7, 29.5, 30.6; ^{29}Si NMR (79.43 MHz, C_6D_6) δ −49.3. The product was further identified by analysis of its methanol addition products, di-*tert*-butylmethoxy-*n*-propylsilane and di-*tert*-butylmethoxyisopropylsilane, prepared as follows: 1,1-di-*tert*-butyl-2-methylsilirane (0.9 g, 4.9 mmol) and methanol (1.26 g, 39.5 mmol) were syringed into a 5-mL sealable tube. The tube was sealed and pyrolyzed for 12 h. GLC showed complete conversion to di-*tert*-butylmethoxy-*n*-propylsilane and di-*tert*-butylmethoxyisopropylsilane in a 55:45 (w/w) ratio (shown also by ^{1}H NMR). The solvent was removed in vacuo, and the products were distilled (bp 36–41 °C/0.2 mmHg) to give 400 mg (38%) of the derivatives. Further separation was done with preparative GC. *n*-Propyl derivative: ^{1}H NMR ($CDCl_3$) δ 0.74 (m, 2 H), 1.01 (s, 18 H), 1.02 (t, 3 H), 1.54 (m, 2 H), 3.59 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 13.2, 17.9, 18.9, 21.2, 28.1, 52.3. Isopropyl derivative: ^{1}H NMR ($CDCl_3$) δ 1.07 (s, 18 H), 1.18 (d, 6 H), 1.34 (m, 1 H), 3.61 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 12.5, 19.0, 22.0, 28.8, 52.1. Anal. Calcd for $C_{12}H_{28}OSi$: C, 66.59; H, 13.04. Found: C, 66.48; H, 13.36.

(3) 4: ^{1}H NMR (C_6D_6) δ 0.54 (s, 4 H), 1.07 (s, 18 H); ^{13}C NMR (C_6D_6) δ −5.0, 17.5, 29.7; ^{29}Si NMR (C_6D_6) δ −56.8. The product was further identified by its methanol addition product, di-*tert*-butylethylmethoxysilane, prepared as follows: Methanol (165 mg, 5 mmol) was added to the tube containing 4. GLC analysis of the solution showed di-*tert*-butylethylmethoxysilane present in 85% yield. Further purification was done with preparative GC: ^{1}H NMR (C_6D_6) δ 0.83 (q, 2 H), 1.23 (s, 18 H), 1.25 (t, 3 H), 3.57 (s, 3 H); ^{13}C NMR (C_6D_6) δ 2.0, 8.0, 20.5, 27.5, 52.3. Anal. Calcd for $C_{11}H_{26}OSi$: C, 65.60; H, 12.51. Found: C, 65.11; H, 12.19.

(4) 5: ^{1}H NMR (C_6D_6) δ 1.01 (s, 9 H), 1.04 (m, 2 H), 1.19 (s, 9 H), 1.6–1.93 (m, 8 H); ^{13}C NMR (C_6D_6) δ 12.41, 18.6, 19.5, 20.7, 23.1, 29.9, 31.5; ^{29}Si NMR (C_6D_6) δ −54.6; UV λ_{max} (hexane) 226 nm ($\epsilon = 3.73 \times 10^2$); HR-MS calcd for $C_{14}H_{28}Si$ *m/e* 224.196, found *m/e* 224.200.

(5) For a review of synthetic applications of ultrasonic waves in heterogeneous systems see: Boudjouk, P. In *Ultrasound: Chemical, Physical and Biological Effects*; Suslick, K. S., Ed.; Verlag Chemie: Deerfield Beach, FL, 1988.

(6) Seyferth, D.; Annarelli, D. C.; Vick, S. C.; Duncan, D. P. *J. Organomet. Chem.* 1980, *201*, 179.

0276-7333/91/2310-2095$02.50/0

Table II. Thermolysis and Photolysis of Siliranes in the Presence of Et$_3$SiH

$$1, 3, 4, \text{ or } 5 + \mathrm{Et_3SiH} \xrightarrow[\Delta]{h\nu} \mathrm{Et_3Si{-}Si}(t\text{-}\mathrm{Bu})_2\mathrm{{-}H}$$

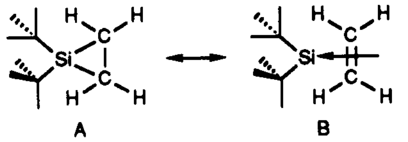
compd	conditions	products; yield, %
1	$h\nu$, 3 h[a]	1,1,1-triethyl-2,2-di-*tert*-butyldisilane;[c] 69%
	180 °C, 18 h[b]	1,1,1-triethyl-2,2-di-*tert*-butyldisilane; 71%
3	$h\nu$, 3 h	1,1,1-triethyl-2,2-di-*tert*-butyldisilane; 89%
	180 °C, 18 h	viscous liquid[d]
4	$h\nu$, 3 h, THF	white solid[e]
	100 °C, 18 h, benzene	white solid[e]
5	$h\nu$, 3 h	1,1,1-triethyl-2,2-di-*tert*-butyldisilane; 50%
	100 °C, 18 h[13]	1,1,1-triethyl-2,2-di-*tert*-butyldisilane; 80%

[a] In a typical experiment, the silirane is transferred to a quartz test tube under N$_2$ and photolyzed in the presence of excess triethylsilane at 254 nm with use of a Rayonet Model RPR 1000 reactor. Cyclohexane is the solvent unless otherwise noted. [b] In a typical experiment the silirane is thermalized in a sealable tube with excess triethylsilane. Cyclohexane is the solvent unless otherwise noted. [c] See ref 1a. [d] A high-boiling liquid exhibiting several *tert*-butyl signals in the ^{1}H NMR spectrum. No Si–O or Si–H bands are noted in the IR spectrum. [e] The solid is insoluble in benzene, THF, hexane, and H$_2$O. It does not melt below 230 °C, and its IR spectrum (Nujol) shows no Si–O or Si–H bands.

tives.[7] Removal of substituents on carbon result in a significant upfield shift for the ^{13}C NMR signal for the ring carbons of 4, which is at −5 ppm relative to tetramethylsilane, compared to 4.6 and 6.2 ppm for the methylene and methine carbons, respectively, of 3 (Table I). This is the largest upfield shift reported for a ring carbon in silacyclopropanes.

Also noteworthy is that, with only hydrogens on the ring carbons, the $^1J(^{13}\mathrm{C}{-}^1\mathrm{H})$ coupling constant is 154 Hz compared to 137 and 147 Hz for the methylene and methine groups of 3. This implies a 117° H–C–H$_{\mathrm{ring}}$ bond angle in 4, which differs from the value 112.4° predicted for silirane[10] and the values 109.54 and 113.63° found experimentally by Ando et al.[11] for a silirane with bulky substituents. The different $^1J(^{13}\mathrm{C}{-}^1\mathrm{H})$ coupling constants observed in 3 may reflect some steric interaction of the methyl group on the ring carbon with the *tert*-butyl groups on silicon as well as the electronic effect of the carbon substituent. Since coupling constants reflect percent s character, and 160 Hz is the value for a typical sp^2 or cyclopropane system, our data suggest that 4 is the silirane closest in structure to cyclopropane.

^{13}C shifts for ethylenic carbons in typical metal ethylene π-complexes are δ 35–70 and proton chemical shifts δ 2–4,[12] both quite far from those listed in Table I. Additionally, ab initio calculations on siliranes indicate that electron density is concentrated on the perimeter of the ring and not in its center.[10] These data provide strong support for structure A as the primary contributor to the ground-state picture of siliranes.



We compared the photochemical and thermal reactions of 3 and 4 to those of other siliranes and found significant differences. Decreasing substitution on the carbon atoms reduces the tendency of the siliranes to undergo the extrusion reaction to give silylenes. For example 3, will generate di-*tert*-butylsilylene (2) in high yield under photolysis, as evidenced by the isolation of 1,1,1-triethyl-2,2-di-*tert*-butyldisilane in 89% yield (Table II), but it produces only a nondistillable viscous liquid when pyrolyzed in the presence of triethylsilane. Silirane 4, on the other hand, does not produce 2 photochemically or thermally.

These results imply fundamental relationships influencing the properties of siliranes via the ring carbon substituents not previously observed and are worthy of further study.

Acknowledgment. We wish to thank Steve Castellino for his assistance in obtaining NMR results. This work was supported by the Air Force Office of Scientific Research through Grant No. 88-0060.

---

(7) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 1, Chapter 8.

(8) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; Chapter 10.

(9) Blinka, T. A.; Helmer, B. J.; West, R. *Adv. Organomet. Chem.* **1984**, *23*, 193.

(10) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 3025.

(11) Ando, W.; Fujita, M.; Yoshida, H.; Sekiguchi, A. *J. Am. Chem. Soc.* **1988**, *110*, 3310 (the angles given are CH$_3$–C–H angles in this case).

(12) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135. Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1975**, 449; *J. Chem. Soc., Dalton Trans.* **1977**, 271.

(13) 5 (50 mg, 0.2 mmol) and triethylsilane (0.2 mL, 1.45 mmol) in 1 mL of hexane were heated in a sealed tube at 100 °C for 18 h. 1,1,1-Triethyl-2,2-di-*tert*-butyldisilane was produced in 80% yield (GC) and was identified by comparison with an authentic sample.[1a]