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Preparation, Stereochemistry, Reactions, and Properties of 3-Silabicyclo[3.2.1]octanes[1]

Sheldon E. Cremer* and Craig Blankenship

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233

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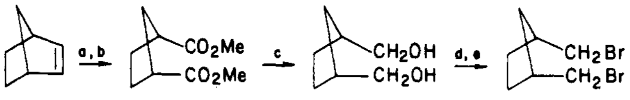
A convenient synthesis of the parent compound 3-silabicyclo[3.2.1]octane (1) and seven derivatives of 3-methyl-3-silabicyclo[3.2.1]octane (7) is described along with 3,3-dichloro-3-silabicyclo[3.2.1]octane (2) and 3-phenyl-3-silabicyclo[3.2.1]octane (5). In most cases the exo and endo isomers were separated by gas chromatography; isomer assignments were based on ^{1}H and ^{13}C NMR spectroscopy and other data. The isomers of 3-chloro-3-methyl-3-silabicyclo[3.2.1]octane (4) equilibrated on distillation. The highly sterespecific lithium aluminum hydride reduction of 3-methoxy-3-methyl-3-silabicyclo[3.2.1]octane (8) was significantly faster for the *endo*-methyl isomer of 8; this enabled the isolation of pure *endo*-methyl 7 as well as the unreacted *exo*-methyl isomer of 8. A number of other highly stereospecific reactions were carried out by using 7 and 8; the stereochemical outcome paralleled that in acyclic organosilicons. Mass spectra were obtained for several of the new compounds; for the isomers of 7, a unique and highly stereodependent fragmentation involving loss of H_2 was observed. Loss of H_2 gave the base peak in the spectrum of the *exo*-methyl isomer of 7, whereas the corresponding peak for the *endo*-methyl isomer was of low intensity.

Introduction

Our investigation of 3-silabicyclo[3.2.1]octanes was initially prompted by the report of Ouellette,[2] who described the stable conformations and steric energies of some of these compounds as well as several other silacyclohexane derivatives by molecular mechanics calculations. This bicyclic system is particularly well-suited for determining the stereochemistry of reactions at silicon since substituents on the heteroatom can have an exo or endo orientation; the energy difference between an exo and endo substituent is much less in the 3-silabicylo[3.2.1]octane system than in the hydrocarbon analogue.[2] An added advantage, common to polycyclic molecules, is the conformational rigidity of the molecular framework. Furthermore, comparison with the recently characterized 2-silabicyclo[2.2.1]heptanes[3] should provide a better understanding of the effect of changing the C–Si–C bond angle on the dynamic stereochemistry of organosilicons during nucleophilic reactions.

For over a decade considerable effort has been made to explore the influence of ring size on the stereochemical outcome of reactions at silicon.[4] In view of the new mechanistic rationales for reactions at silicon proposed by Corriu,[4b,5] stereochemical studies of the title compounds were well-warranted. As noted by other investigators in this field, cyclic organosilicons deserve special attention because, unlike chiral silanes, they do not require aromatic appendages directly bonded to silicon.[5,6] This requirement for chiral silanes precludes simple stereochemical studies in which an aryl group is either an incoming nucleophile or leaving group in a reaction. In light of this background, it is relevant that the only previous stereochemical studies of silacyclohexane derivatives of this nature were conducted by Sakurai and Murakami, who examined the reactions of 4-*tert*-butyl-1-silacyclohexanes.[7]

Scheme I[a]



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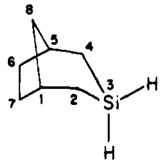
[a] Reagents: (a) $KMnO_4$/isooctane, H_2O; (b) $Me_2C(OMe)_2$, *p*-TsOH/MeOH; (c) LAH/ether; (d) *p*-TsCl/pyridine; (e) LiBr/acetone, Δ.

In previous reports we have described: (a) the molecular structure of the parent compound 3-silabicyclo[3.2.1]octane (1) and its *endo*-3-methyl derivative **7b**, as determined by electron diffraction techniques;[8a] (b) the X-ray crystal structure of *endo*-3-hydroxy-3-methyl-3-silabicyclo[3.2.1]octane (**13b**);[8b] and (c) the fluoride ion catalyzed equilibration of the exo–endo isomers of 3-methyl-3-silabicyclo[3.2.1]octane (7).[8c] This paper gives a complete account of the synthesis, spectral and physical properties, and reaction stereochemistry of 1 and its derivatives. During the course of this investigation, the preparation and detailed ^{1}H NMR analysis of 1 were reported by Anteunis;[9]



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(1) Taken from the Ph.D. Dissertation of Craig Blankenship, "Synthesis, Reactions, and Stereochemical Studies of New Bicyclic Organosilicons: 3-Silabicyclo[3.2.1]octanes and 2-Silabicyclo[2.2.1]heptanes", Marquette University, February, 1982.

(2) Ouellette, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 2421.

(3) (a) Cremer, S. E.; Blankenship, C. *J. Org. Chem.* **1982**, *47*, 1626. (b) Hosomi, A.; Mikami, M.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2784. (c) Jones, P. R.; Pierce, R. A.; Cheng, A. H. B. *Organometallics* **1983**, *2*, 12. (d) Jones, P. R.; Lim, T. F. O.; Pierce, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 4970.

(4) For discussions of the effect of angle variation on the stereochemistry of reactions at silicon, see: (a) Roark, D. N.; Sommer, L. H. *J. Am. Chem. Soc.* **1973**, *95*, 969. (b) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231. (c) McKinnie, B. G.; Bhacca, N. S.; Cartledge, F. K.; Fayssoux, J. *J. Org. Chem.* **1976**, *41*, 1534. (d) Cartledge, F. K.; Wolcott, J. M.; Dubac, J.; Mazerolles, P.; Joly, M. *J. Organomet. Chem.* **1978**, *154*, 187. (e) Dubac, J.; Mazerolles, P.; Joly, M.; Cartledge, F. K.; Wolcott, J. M. *J. Organomet. Chem.* **1978**, *154*, 203.

(5) (a) Corriu, R. J. P.; Guerin, C. *Tetrahedron* **1981**, *37*, 2467. (b) Anh, N. T.; Minot, C. *J. Am. Chem. Soc.* **1980**, *102*, 103. (c) Corriu, R. J. P.; Guerin, C. *Adv. Organomet. Chem.*; Stone, F. G. A., West, R., Eds.; Academic: New York, 1982, *20*, 265. (d) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 43.

(6) Sommer, L. H. *Intra-Sci. Chem. Rep.* **1973**, *7*, 1 and references cited.

(7) (a) Sakurai, H.; Murakami, M. *J. Am. Chem. Soc.* **1972**, *94*, 5080. (b) Sakurai, H.; Murakami, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3185.

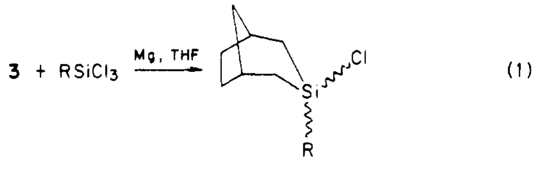
(8) (a) Shen, Q.; Hilderbrandt, R. L.; Blankenship, C.; Cremer, S. E. *J. Organomet. Chem.* **1981**, *214*, 155. (b) Haque, M.; Horne, W.; Cremer, S. E.; Blankenship, C. *J. Chem. Soc., Perkin Trans. 2* **1983**, 395. (c) Cremer, S. E.; Blankenship, C. *Tetrahedron Lett.* **1980**, 3979.

(9) (a) Carleer, R.; Hosten, N.; Anteunis, M. J. O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 709. (b) Carleer, R.; Anteunis, M. J. O. *Org. Magn. Reson.* **1979**, *12*, 673.

the dichlorosilane precursor **2** was the only derivative described.[9a]

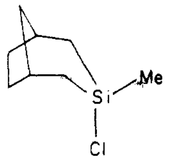
Results and Discussion

Synthesis and Reactions. The precursor to the title compounds, dibromide **3**, was conveniently prepared in quantity by the sequence of reactions shown in Scheme I.[1,10] Dibromide **3** has proven to be a valuable starting material for introducing various heteroatoms into the 3-position of the bicyclic framework.[11] Incorporation of silicon was accomplished by a double-Grignard ring closure reaction[4d,7,9a,12] in which **3** and a polychlorosilane were simultaneously added to a suspension of magnesium powder in tetrahydrofuran (THF) (eq 1). The preparation of dichlorosilane **2** was also carried out by addition of the *preformed* di-Grignard reagent in ether to an ether solution of $SiCl_4$, but no increase in the yield was attained.

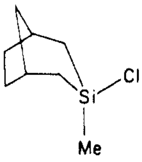


2, R = Cl, 20% yield
4, R = Me, 50-60% yield
5, R = Ph, 50% yield

The preparation of methylchlorosilane **4** was performed several times, and the two isomers, **4a** (*exo*-Me) and **4b** (*endo*-Me),[13] were obtained reproducibly in a 60:40 ratio, respectively. One preparation of **4** was run in ether, but the yield was only half that obtained in THF. In two preparations of **4**, the higher boiling 3-bromo-3-methyl-3-silabicyclo[3.2.1]octane (**6**) was also collected. Halosilanes are known to undergo halide exchange with magnesium salts,[14] and isolation of **6** occurred when the magnesium salts had not been as effectively removed before final distillation. Bromosilane **6** was characterized by ^1H and ^{13}C NMR spectroscopy and was identical with a sample made from the reaction of bromine with methylsilane **7**.[15]

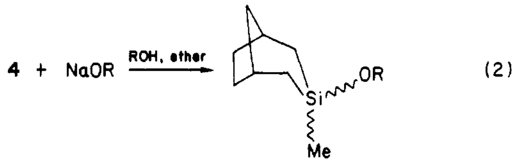


4a



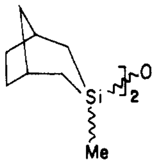
4b

Methylchlorosilane **4** was converted into alkoxysilanes **8**, **9**, and **10** in 80–95% yields by reaction with the appropriate sodium alkoxide (eq 2).[16] Similarly, phenylchlorosilane **5** was transformed into 3-methoxy-3-phenyl-3-silabicyclo[3.2.1]octane (**11**) in 75% yield.



8, R = Me
9, R = Et
10, R = *i*-Pr

The yield of methoxysilane **8** was dependent upon the work-up conditions. A mixture of isomers was obtained quantitatively prior to distillation. Upon distillation, 75–95% of **8** was collected, but a residue was obtained which sometimes contained a small amount of siloxane **12**, together with the major product, silanol **13**. The extent of this apparent "hydrolysis" of **8** increased at higher distillation temperatures. Subsequently, it was found that treatment of **8** with silica gel in refluxing ethyl acetate gave **13** in good yield.[8b] Reversible chemical reactions can occur between an alkoxysilane and a silica gel surface;[17] a similar reaction of **8** with the glass surface during distillation to give **13** is likely. In an attempt to generalize upon this type of reaction, racemic α-naphthylphenylmethylmethoxysilane[18] was treated with silica gel in relfuxing ethyl acetate for several days, but no reaction was observed, and the starting material was recovered intact.



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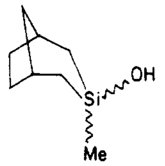

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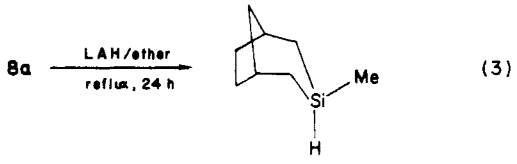
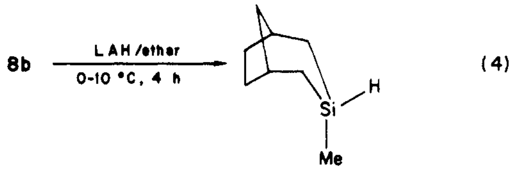
Methoxysilanes **8** and **11** were reduced with lithium aluminum hydride (LAH) in ether to give silanes **7** and 3-phenyl-3-silabicyclo[3.2.1]octane (**14**), respectively. A significant difference in reactivity of **8a** and **8b** (eq 3 and 4) led to the selective reduction of **8b** in the presence of the former isomer. When a 50:50 mixture of **8a** and **8b** was treated with LAH/ether at 0–10 °C for 4 h nearly complete reduction of **8b** occurred with negligible reduction of **8a**. Methylsilane **7a** was obtained from **8a** under the conditions shown (eq 3). Reduction of either isomer



7a



7b

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[10] (a) The synthesis is based on that used to prepare the ditosylate, see: Birch, S. F.; Dean, R. A. *J. Chem. Soc.* **1953**, 2477. (b) Conversion of the ditosylate to *3* has been reported: Haque, M.; Horne, W.; Cremer, S. E.; Kremer, P. W.; Most, J. T. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1467.

[11] For incorporation of phosphorus, see ref 10b; for incorporation of tin see: Borsub, L. Ph.D. Dissertation, Marquette University, Dec 1984.

[12] (a) West, R. *J. Am. Chem. Soc.* **1954**, *76*, 6012. (b) Franke, F.; Wells, P. R. *J. Og. Chem.* **1979**, *44*, 244. (c) Eaborn, C.; Bott, R. W. In "Organometallic Compounds of the Group IV Elements; The Bond to Carbon"; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, 1968; Vol. 1, Part I, p 119 and references cited.

[13] For these and the other methylsilane derivatives in this paper, the "a" designation, as in **4a**, refers to the isomer with an *exo*-methyl group; the "b" designation corresponds to the *endo*-methyl isomer. Isomer ratios and identification were determined by NMR and GC techniques.

[14] Van Dyke, C. H. In "*Organometallic Compounds of the Group IV Elements*; *The Bond to Halogens and Halogenoids*"; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, 1972; Vol. 2, Part I, p 110.

[15] (a) Reference 14, pp 47–51. (b) Fleming, I. In *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon: Oxford, 1979; Vol. 3, p 566. (c) El-Durini, N. M. K.; Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1275.

[16] Reference 12c, p 184.

[17] Waddell, T. G.; Leyden, D. E.; DeBelle, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 5303.

[18] Sommer, L. H.; Frye, C. L.; Parker, G. A.; Michael, K. W. *J. Am. Chem. Soc.* **1964**, *86*, 3271.

was highly stereospecific; retention of configuration at silicon was observed, which is the expected result in ether solvent.[5,6,19] Another method for the selective reduction of **8b** in an isomeric mixture involved modification of the reducing agent. Thus, $LiAlH(OMe)_3$[20] in refluxing ether stereospecifically converted **8b** to **7b**; no reduction of **8a** took place.

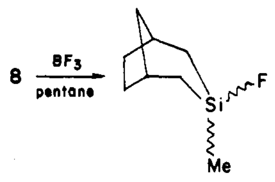
The isomeric 4-*tert*-butyl-1-isopropoxy-1-methyl-1-silacyclohexanes investigated by Sakurai and Murakami[7] also showed significant differences in reactivity toward LAH reduction. The equatorial isopropoxy group was substituted by hydride much more readily than the axial one. These reductions are commonly postulated to proceed through a four-centered transition state or intermediate.[6,19,21] Unfavorable 1,3-diaxial steric interactions were invoked to rationalize the slower reduction of the axial leaving group. A similar steric effect between the *endo*-methoxy group and bimethylene bridge in **8a** would inhibit the substitution reaction relative to **8b**.

Qualitatively, there was a significant solvent effect on the rate of LAH reduction of **8**. Two parallel reactions were run on a 50:50 ratio of **8a**:**8b**; one was carried out in ether and the other in diglyme. While the former reaction required 2 days at reflux temperatures for completion, the latter was finished after 12 h at ambient temperature. A similar rate enhancement in diglyme has been observed for LAH reductions of alkyl halides.[22] The proposed explanation for the rate increase was based on the more effective complexation of Li^+ by diglyme to give a higher proportion of "free" AlH_4^-, which is a better nucleophile than ion paired or aggregated LAH. For LAH reduction of methoxysilanes there is a marked rate increase when Li^+ is more effectively complexed.[5a] In addition, Corriu and Guerin have shown that the "freeness" of AlH_4^- can alter the stereochemical outcome of certain reductions of organosilanes.[5a]

The selective reductions of the isomers of **8** allowed the isolation of **7a**, **7b**, and **8a** in high isomeric purity. Furthermore, the pure isomers **8a** and **8b** were easily separated from a mixture by preparative GC. Thus, it is possible to selectively prepare individual isomers of the 3-methyl-3-silabicyclo[3.2.1]octane family from these key substrates.

The reaction of **8a** with phenyllithium gave *exo*-3-methyl-*endo*-3-phenyl-3-silabicyclo[3.2.1]octane (**15a**) in high yield with 100% retention of configuration. Moreover, isomer **15b** was prepared in high yield by the reaction of phenyllithium with methylsilane **7b**; predominant retention of configuration was again observed. Reactions of both alkoxy- and hydrosilanes with simple alkyl- and aryllithiums are known to proceed with a high degree of retention of configuration at silicon;[4b,5a,6] also, displacement of hydride by phenyllithium was reported to take place with 100% retention of configuration in a silacyclopentane.[4d]

Fluorosilanes **16** were quantitatively prepared by treatment of a pentane solution of methoxysilane **8a** and **8b** with gaseous BF_3 (eq 5). The substitution proceeded with predominant (80%) inversion of configuration at silicon, but the stereospecificity was not as high as in acyclic methoxysilanes[5a,6,23] or silacyclopentanes.[24]



16

(5)

Starting with **8a** (4% **8b** present) a 25:75 ratio of **16a**:**16b** was found; **8b** (8% **8a** present) gave a 75:25 ratio of **16a**:**16b**. The isomer ratios did not measurably change on prolonged contact with BF_3.

Three different methods for converting the isomers of 3-methyl-3-silabicyclo[3.2.1]octane (**7**) into chlorosilanes **4** were examined to determine which was the most stereospecific. The best method was benzoyl peroxide initiated free radical chlorination in CCl_4,[25] a reaction known to proceed with a high degree of retention of configuration in acyclic[26] and cyclic organosilicons.[4c,d,7b,27] Under these conditions each isomer of **7** was converted to the corresponding isomer of **4** with greater than 95% stereospecificity (^1H NMR monitor). Both isomers of **4** were stable to the reaction conditions, and prolonged heating of the reaction mixture only slowly altered the isomer ratio. However, when **4b** was distilled from the original reaction, a mixture of **4a**:**4b** (60:40) was isolated.

The ease of product isomerization was evident in the other chlorination methods. When either **7a** or **7b** was treated with Pd/C in CCl_4 at room temperature, a predominance of **4a** or **4b**, respectively, was initially formed; however, isomerization readily occurred to give a mixture. No other silicon-containing products were detected by ^1H or ^{13}C NMR spectroscopy. This conversion was previously reported to proceed with predominant retention of configuration at acyclic silicon.[28] It was apparent that $CHCl_3$ was generated in the conversion of **7** to **4** by the growth of a peak at 7.2 ppm (singlet) in the NMR spectrum. In earlier studies of this type of reaction, $CHCl_3$ was *not* detected, which complicated its mechanistic understanding.[28]

A slow reaction of **7b** and Ph_3CCl occurred at room temperature which produced **4a** and **4b** (60:40 ratio) and Ph_3CH. No side products were evident in the NMR spectrum of the product. Both isomers of **4** appeared to form simultaneously; it was not clear whether the reaction was nonstereospecific or if a stereospecific conversion took place followed by rapid isomerization. This type of reaction was reported to proceed with a high degree of retention of configuration in an acyclic silane,[29] but a later study showed that the outcome was very sensitive to reaction conditions.[30] The chlorination was judged to be nonstereospecific for a silacyclopentane.[27b]

Since it was possible to prepare the chlorosilanes **4** in high isomeric purity, an overall inversion sequence for conversion of **7a** to **7b** was achieved (eq 6). Isomerically

$$\mathbf{7a}\ \text{(pure)} \xrightarrow[\text{CCl}_4]{\text{benzoyl peroxide}} \mathbf{4a}:\mathbf{4b}\ (19{:}5) \xrightarrow{\text{LAH, ether}} \mathbf{7a}:\mathbf{7b}\ (15{:}85) \quad (6)$$

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[19] (a) Sommer, L. H. *Stereochemistry, Mechanism, and Silicon*; McGraw-Hill: New York, 1965; pp 51–53. (b) Sommer, L. H.; Frye, C. L.; Parker, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 3276.

[20] Haubenstock, H.; Mester, T., Jr. *J. Org. Chem.* **1983**, *48*, 945.

[21] For an alternative mechanistic proposal, see ref 5a.

[22] Krishnamurthy, S. *J. Org. Chem.* **1980**, *45*, 2550.

[23] Sommer, L. H.; Citron, J. D.; Parker, G. A. *J. Am. Chem. Soc.* **1969**, *91*, 4729.

[24] Dubac, J.; Mazerolles, P.; Cavezzan, J.; Quintard, J.; Pereyre, M. *J. Organomet. Chem.* **1980**, *197*, 261.

[25] Nagai, Y.; Yamazaki, K.; Shiojima, I.; Kobori, N.; Hayashi, M. *J. Organomet. Chem.* **1967**, *9*, P21.

[26] (a) Sakurai, H.; Murakami, M.; Kumada, M. *J. Am. Chem. Soc.* **1969**, *91*, 519. (b) Sommer, L. H.; Ulland, L. A. *J. Org. Chem.* **1972**, *37*, 3878.

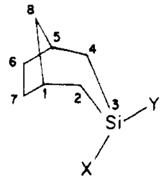
[27] (a) Roark, D. N.; Sommer, L. H. *J. Am. Chem. Soc.* **1973**, *95*, 969. (b) Franke, F.; Wells, P. R. *J. Org. Chem.* **1979**, *44*, 4055.

[28] Citron, J. D.; Lyons, J. E.; Sommer, L. H. *J. Org. Chem.* **1969**, *34*, 638.

[29] Austin, J. D.; Eaborn, C. *J. Chem. Soc.* **1964**, 2279.

[30] Sommer, L. H.; Bauman, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 7076.

Table I. ^{13}C NMR Data for 3-Silabicyclo[3.2.1]octanes and Relevant Carbon Analogues



compd	C-1,5	C-2,4	C-6,7	C-8	X	Y
1, X = Y = H	34.3	15.7	31.3	41.7		
2, X = Y = Cl	34.5	30.2[a]	30.6	40.4		
4a, X = Cl, Y = Me	34.1	26.4	30.8	41.0		3.9
4b, X = Me, Y = Cl	34.5	26.9	31.3	40.7	5.4	
7a, X = H, Y = Me	34.6	20.6	31.6	42.0		−4.2
7b, X = Me, Y = H	34.3	19.9	31.6	41.2	−1.2	
8a, X = OMe, Y = Me	33.9	23.3	31.4	41.8	50.0	−1.0
8b, X = Me, Y = OMe	34.4	22.9	31.8	41.2	1.1	49.7
9a, X = OEt, Y = Me	34.0	23.7	31.3	41.8	CH_2, 58.0 CH_3, 18.5	−0.3
9b, X = Me, Y = OEt	34.4	23.5	31.6	41.2	1.6	CH_2, 57.8 CH_3, 18.5
10a, X = *i*-PrO, Y = Me	34.0	24.1	31.3	41.8	CH, 64.5 CH_3, 25.7	0.9
10b, X = Me, Y = *i*-PrO	34.3	24.1	31.6	41.2	2.2	CH, 64.4 CH_3, 25.7
13a, X = OH, Y = Me	34.0	25.7	31.4	41.4		1.7
13b, X = Me, Y = OH	34.5	25.7	31.6	41.3	3.2	
15a, X = Ph, Y = Me	34.3	21.3	31.2	41.8	α, 140.1[b] o, 127.2 m, 133.1 p, 128.1	1.5
15b, X = Me, Y = Ph	34.6	22.7	31.7	41.4	0.2	α, 140.6[b] o, 127.3 m, 133.1 p, 128.2
16a, X = F, Y = Me	33.7 (0.9 Hz)[c]	24.7 (11.8 Hz)[c]	31.1	41.6		0.3 (15.6 Hz)[c]
16b, X = Me, Y = F	34.1 (3.0 Hz)[c]	24.2 (11.3 Hz)[c]	31.8	41.0		2.0 (16.3 Hz)[c]
bicyclo[3.2.1]octane[d]	35.8	33.4	29.4	40.1		
exo-3-methylbicyclo[3.2.1]octane[d]	35.7	42.6	29.6	39.8		22.8
endo-3-methylbicyclo[3.2.1]octane[d]	34.5	40.3	31.1	35.7	24.5	

[a] Assignments may be reversed. [b] Aromatic carbons; α, directly attached to Si. [c] Coupling constant; doublet. [d] Data from ref 32.

pure **7a** was chlorinated, and the resulting chlorosilane was directly reduced with LAH to give a 15:85 ratio of **7a**:**7b** in 71% overall yield after distillation. In another reaction, **4a**:**4b** (60:40) was reduced to a 40:60 mixture of **7a**:**7b** in 90% yield. The predominant inversion of stereochemistry by LAH parallels the stereochemical results found for acyclic silanes,[4b,19] silacyclohexanes,[7] and silacyclopentanes.[4d]

The parent compound **1** was also obtained in 93% yield by LAH reduction of dichlorosilane **2**.

Physical and Spectroscopic Properties of 3-Silabicyclooctanes. Previous reports described the gas-phase molecular structures of **1** and **7b**[8a] and the crystal molecular structure of **13b**.[8b] These studies established unequivocal isomer assignments for **7** and **13**. Correlation with other properties of individual isomers, especially NMR spectral data, allowed assignments of isomers for additional members of the 3-methyl-3-silabicyclooctane family.

The 60-MHz ^1H NMR spectra for the silabicyclooctanes showed several characteristic features. The bridgehead hydrogens gave broad multiplets centered at 2.5 ppm, characteristic of bicyclic molecular systems.[31] Hydrogens directly bonded to silicon in **1** and **7** appeared as multiplets at 3.6–4.0 ppm. For pure **7a** (*endo*-H) the peak center was at 3.92 ppm and for **7b** at 3.82 ppm. These relative shifts are consistent with the detailed NMR study of **1** by Carleer and Anteunis, who had assigned the *exo*-H bonded to silicon upfield of the *endo*-H in the 300-MHz spectrum.[9b] The *exo*-methyl group in the isomeric pairs **4**, **7**–**10**, **13**, **15**, and **16** absorbed upfield from the *endo*-methyl substituent. The shift differences ranged from 0.12 ppm in **16** to 0.31 ppm for **15**; these differences in each pair enabled measurements of isomer ratios by intergration.

The ^{13}C NMR spectral data are presented in Table I. Peak assignments were relatively straightforward due to the molecular symmetry. In addition, comparisons could be made with the three hydrocarbon analogues shown in the table.[32] The bridging carbon C-8 was identified by its relative intensity, which was about one-half that of the other ring carbons. Selective hydrogen decoupling easily distinguished the bridgehead carbons since the attached hydrogens were distinct from other ring hydrogens in the ^1H NMR spectra. Each carbon showed the appropriate multiplicity in off-resonance experiments. The α-carbons C-2 and -4 showed the greatest variation in chemical shift with differing substitution at silicon. The two- and three-bond ^{13}C–^{19}F coupling constants observed for fluorosilanes **16** further differentiated C-2,4 and C-1,5 from the other ring carbons. For the 3-methylsilane isomers, the *exo*-Me group generally absorbed upfield of the *endo*-Me group; this paralleled the hydrocarbon analogue[32] (Table I). The only exception was the isomers of methylphenylsilane **15**.

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(31) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon: Oxford, UK, 1969, pp 230–231.

(32) Lippmaa, E.; Pehk, T.; Belikova, N. A.; Bobleva, A. A.; Kalinichenko, A. N.; Ordubadi, M. D.; Plate, A. F. *Org. Magn. Reson.* **1976**, *8*, 74.

The ^{19}F NMR chemical shifts for the fluorosilanes were 159.4 and 157.9 ppm upfield of $CFCl_3$ for **16a** and **16b**, respectively. The two- and three-bond ^{13}C–^{19}F coupling constants are shown in Table I. The three-bond coupling constant to C-1,5 in *exo*-fluoride **16b** was three times greater than for **16a**. Roberts and co-workers have shown that such three-bond couplings were strongly dependent on molecular geometry in various 2-fluoronorbornanes;[33] the greater coupling of the *exo*-F to the bridgehead carbons was expected.

The ^{29}Si NMR chemical shifts (relative to Me_4Si) for **1**, **7a**, and **7b** were −43.0, −20.76, and −20.74 ppm, respectively. These data were previously compared with data for 2-silanorbornanes.[3a,34] The chemical shifts of ^{29}Si nuclei have been shown to be sensitive to steric interactions in the same manner as ^{13}C nuclei,[35] and the near equivalence in the shifts for the isomers of **7** is notable in this respect.

Gas chromatography provided another means for distinguishing isomers in the 3-methylsilane series. The isomers were separable on a polar stationary phase; Carbowax 20M and FFAP were used, but the latter was generally more effective. In all cases, the isomer with *exo*-Me groups had shorter retention times; this pattern should prove useful for new members in this series. The isomer ratios measured by this technique were always in excellent agreement with those from ^1H NMR spectral integration.

Mass spectral data were obtained at 70 eV (peaks > m/e 35 recorded) for **1**, **7a**,**b**, **8**, **14**, **15a**,**b**, and **16**. A relatively abundant molecular ion (M) was observed for these compounds except phenylmethysilane **15b** and the isomers of phenylsilane **14**. Loss of three-carbon species appeared to be an important fragmentation pathway for the silabicyclooctanes in general, similar to 2-silanorbornanes.[3a]

The most notable feature in these mass spectral studies was the dramatic change in the fragmentation pattern for the isomers of **7**. Silane **7a**, with an *endo*-H, gave a base peak resulting from loss of H_2; **7b** gave an M − 2 peak of low intensity. The M − 2 peak was also the base peak in the spectrum of **1**. The loss of a hydrogen atom from silicon was confirmed by the spectra of the deuterium analogues of **7**, prepared by LAD reduction of chlorosilane **4**. The source of the second hydrogen is not known, but a 1,4-interaction with the *endo*-hydrogens of the bimethylene bridge is an interesting possibility.[36] We are unaware of any other molecular system where simple loss of H_2 is as dominant.[37] Cyclic silanes containing a Si–H bond often give an M − 2 peak, but these are normally of low to moderate intensity.[38–40] The uniqueness of this particular fragmentation is highlighted by the fact that peaks corresponding to M − 2 were not observed for the 2-silanorbornyl analogues of **1** and **7**.[1,3a]

The isomers of **15** also gave different fragmentation patterns. For the *endo*-phenyl isomer, loss of C_6H_6 (M − 78) predominated while other peaks were of relatively low intensity and the molecular ion was not observed. For **15b** loss of C_6H_6 was still important, but the base peak was at M − 43 and a molecular ion of significant intensity was present.

The isomers of phenylsilane **14** presented a gauge of the relative importance of the two fragmentation pathways: loss of H_2 vs. loss of C_6H_6. Both isomers gave identical spectra, however, and the loss of C_6H_6 prevailed. The molecular ion was of low intensity, and the peak at M − 2 was not observed. Loss of fragments of lower mass than C_6H_6 were barely observable.

Experimental Section

General Comments. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. ^1H NMR spectra (60 MHz) were recorded on a Varian A-60A spectrometer in CCl_4 solution; Me_4Si, or, for methylsilanes, $CHCl_3$ (7.25 ppm) were used as internal standards. ^{13}C (15 MHz) and ^{19}F (56 MHz) NMR spectra were recorded on a JEOL FX-60Q spectrometer in $CDCl_3$ solution using 10-mm tubes; Me_4Si ($CFCl_3$ for ^{19}F NMR spectra) was used as an internal standard. All chemical shifts are reported as δ (ppm). GC–MS were obtained from a Finnigan Model 4000 spectrometer at 70 eV. Preparative GC were performed on a Hewlett-Packard F&M Model 700 or F&M Model 770 instrument. The following GC columns were used: column A, 6 ft × $^1/_4$ in., 5% QF-1 on Chromosorb W; column B, 6 ft × $^1/_4$ in., 10% Carbowax 20M on Chromosorb W; column C, 12 ft × $^1/_4$ in., Carbowax 20M on Chromosorb W; column D, 8 ft × $^1/_2$ in., 5% Carbowax 20M on Chromosorb W. Analytical GC were performed on a Hewlett-Packard Model 5710A (flame ionization) chromatograph interfaced with a Model 3380A integrator; reported retention times were obtained on a 6 ft × $^1/_8$ in. column of 8% FFAP on Chromosorb G. Capillary melting points were determined by using a Thomas-Hoover Uni-melt apparatus; melting points and boiling points are uncorrected.

All reactions and manipulations involving organosilicons and/or air-sensitive materials were run in dried glassware (oven dried at 115 °C overnight and/or flame dried) under a nitrogen atmosphere. Diethyl ether and THF were fractionally distilled from Na/K/benzophenone under nitrogen directly before use. Diglyme was stirred over LAH at 50 °C for 2 h and then distilled at reduced pressure. Reagent alcohols were used directly or distilled from the appropriate magnesium alkoxide. Other solvents were reagent grade and used directly. Trichloromethylsilane and silicon tetrachloride were fractionally distilled under nitrogen from calcium hydride directly before use. Trichlorophenylsilane (Aldrich) was used directly.

3,3-Dichloro-3-silabicyclo[3.2.1]octane (2). Dibromide **3** (12.8 g, 50 mmol) in 30 mL of ether was added dropwise over 20 min to a magnetically stirred mixture of Mg turnings (2.6 g, 0.11 mol) in 40 mL of ether, which had been previously stirred with four drops of ethylene dibromide. The exothermic reaction was moderated by periodic cooling with an ice water bath. The reaction mixture was stirred for 3 h at room temperature, and the resulting two-phase organometallic mixture (light gray upper layer, gray-black lower layer) was added dropwise to $SiCl_4$ (6.4 mL, 9.4 g, 55 mmol) in 200 mL of ether over 2.5 h. This mixture was filtered through a filter stick (gas dispersion tube) and concentrated by distillation. Fractional distillation of the residue (7-cm Vigreux column) gave 1.9 g (20%) of **2**: bp 44–45 °C (1.0 mm); ^1H NMR 2.5 (m, 2 H), 1.0–2.0 (m, 10 H). An analytical sample was collected by preparative GC as for **4** below. Anal. Calcd. for $C_7H_{12}Cl_2Si$: C, 43.08; H, 6.20. Found: C, 42.77; H, 6.30.

3-Chloro-3-methyl-3-silabicyclo[3.2.1]octane (4). A mixture of Mg powder (Baker) (10.6 g, 0.44 mol) in 250 mL of THF and 0.5 mL of ethylene dibromide was mechanically stirred for 1.5 h in a 3000-mL 3-necked flask fitted with an addition funnel and a Claisen adaptor with a thermometer and condenser attached. About 2 mL of neat *cis*-1,3-bis(bromomethyl)cyclopentane (**3**) from a preweighed portion (51.2 g, 0.20 mol) was added directly to the

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(34) Please note the error in representation of the 3-silabicyclooctanes on p 1628 of ref 3a; a correction appears in: *J. Org. Chem.* **1982**, *47*, 5427.

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(40) Silacyclohexanes: ref 39b.

reaction mixture, and the remainder was added to the addition funnel which contained trichloromethylsilane (31.8 g, 0.21 mol) in 450 mL of THF. About 50 mL of the chlorosilane/**3** solution was added over 5 min. After the solution was stirred vigorously for 5 min, initiation of the reaction occurred as indicated by a steady increase in temperature from 20 to 40 °C. An additional 500 mL of THF was added to the reaction mixture over 5–10 min, and the remaining chlorosilane/**3** solution was added dropwise over 2 h to maintain the temperature at ca. 40 °C. The mixture was stirred for 24 h, after which 1000 mL of THF was removed by distillation. To the cooled, black residue was added 700 mL of ether, and the mixture was vigorously stirred overnight. The supernatant was separated from the white solid by pressure filtration through a filter stick (gas dispersion tube), washing with additional ether, into a 3-necked flask attached to a distillation apparatus. Most of the solvents were removed by simple distillation, and the residue was pressure filtered as above, washing with pentane, into a 100-mL flask. After concentration by distillation, fractional distillation (7-cm Vigreux column) under reduced pressure gave 18.2 g (52%) of **4** as a clear, colorless liquid which fumed in air: bp 53–55 °C (2.6 mm); ^{1}H NMR δ 2.5 (m, 2 H), 1.2–2.0 (m, 6 H), 1.0–1.2 (m, 4 H), 0.55 and 0.36 (two s, 3 H). An analytical sample was collected by preparative GC using column A with a column temperature of 120 °C and a 100 mL/min flow rate. Anal. Calcd for $C_8H_{15}ClSi$: C, 54.99; H, 8.65. Found: C, 55.16; H, 8.65.

In two reactions, the bromo analogue (**6**) of **4** was collected: bp 84–85 °C (5.5 mm); ^{1}H NMR (both isomers) δ 2.5 (m, 2 H), 1.4–2.1 (m, 6 H), 1.1–1.4 (m, 4 H), 0.70 and 0.50 (two s, 3 H); ^{13}C NMR (both isomers) δ 40.9 and 40.6, 34.9 and 34.3, 31.2 and 30.8, 27.5 and 26.7, 6.4 and 5.1.

3-Chloro-3-phenyl-3-silabicyclo[3.2.1]octane (5). The reaction of trichlorophenylsilane with **3** under the conditions described for the preparation of **4** gave **5** as a mixture of isomers in 50% yield: bp 107–108 °C (0.25 mm); ^{1}H NMR δ 7.2–7.8 (m, 5 H), 2.6 (m, 2 H), 1.2–2.2 (m, 10 H).

3-Methoxy-3-methyl-3-silabicyclo[3.2.1]octane (8). A sodium methoxide solution was prepared from Na (1.2 g, 0.050 mol) and methanol (20 mL, 16.0 g, 0.5 mol) in 100 mL of ether. Chlorosilane **4** (8.8 g, 50 mmol) in 50 mL of ether was added to this solution over 5 min with magnetic stirring; the resulting white suspension was stirred for 1 h and then poured onto 125 mL of ice water overlaid with 100 mL of pentane. The layers were separated, and the organic layer was washed with 100 mL of water and 100 mL of salt solution. The dried (Na_2SO_4) organic fraction was evaporated under a stream of nitrogen from a warm water bath. Residual solvents were removed under reduced pressure to give 8.4 g (99%) of **8**; ^{1}H and ^{13}C NMR spectra and GC analyses indicated pure product. Distillation under reduced pressure gave 7.8 g (92%) of **8**: bp 53–54 °C (3.3 mm); ^{1}H NMR δ 3.39 (s, *endo*-OMe) and 3.30 (s, *exo*-OMe) (3 H), 2.5 (m, 2 H), 1.0–2.0 (m, 6 H), 0.6–1.0 (m, 4 H), 0.22 and 0.02 (two s, 3 H); MS, m/e (relative intensity) 170 (15), 155 (100), 127 (71), 59 (56), 43 (20); the MS spectra of both isomer were identical. The two isomers were separable by preparative GC using column C with a column temperature of 100 °C and a 60 mL/min flow rate or using column D with a column temperature of 90 °C and a 22 mL/min flow rate. The isomers were analytically separable at a column temperature of 90 °C and a 30 mL/min flow rate. Retention times: **8a**, 7.4 min; **8b**, 10.3 min. An analytical sample was collected by preparative GC using column B with a column temperature of 120 °C and a 100 mL/min flow rate. Anal. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65. Found: C, 63.26; H, 10.74.

3-Ethoxy-3-methyl-3-silabicyclo[3.2.1]octane (9) was prepared from sodium ethoxide and **4** according to the procedure for **8** in 82% yield: bp 54 °C (2.7 mm); ^{1}H NMR δ 3.3–3.9 (overlapping q's, 2 H), 2.5 (m, 2 H), 1.0–2.0 (br m, 9 H), 0.7–1.0 (m, 4 H), 0.20 and 0.04 (two s, 3 H). An analytical sample was collected by preparative GC as for **8**. The two isomers were analytically separable at a column temperature of 100 °C and a 25 mL/min flow rate. Retention times: **9a**, 11.0 min; **9b**, 15.4 min. Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.94. Found: C, 64.96; H, 10.78.

3-Isopropoxy-3-methyl-3-silabicyclo[3.2.1]octane (10) was prepared in 90% yield using the procedure for **8**, except that 2 equiv of sodium isopropoxide was used, and the reaction mixture was stirred overnight: bp 63–65 °C (3.3 mm); ^{1}H NMR δ 3.7–4.2 (m, 1 H), 2.5 (m, 2 H), 1.0–2.0 (br m, 12 H), 0.7–1.0 (m, 4 H), 0.20 and 0.30 (two s, 3 H). The two isomers were analytically separable at a column temperature of 110 °C and a 30 mL/min flow rate. Retention times: **10a**, 7.5 min; **10b**, 10.1 min. The isomers were separable by preparative GC using column D with a column temperature of 110 °C and a 22 mL/min flow rate. An analytical sample was collected as for **8**. Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.78; H, 11.32.

3-Methoxy-3-phenyl-3-silabicyclo[3.2.1]octane (11) was prepared from **5** and 2 equiv of sodium methoxide as for **10**: bp 80–84 °C (0.15 mm); ^{1}H NMR (both isomers) δ 7.2–7.8 (m, 5 H), 3.40 and 3.20 (two s, 3 H), 2.6 (m, 2 H), 0.9–2.0 (m, 10 H); ^{13}C NMR (both isomers) δ 137.3 and 137.2, 133.4 and 133.1, 129.3 and 129.0, 127.5 and 127.4, 50.8 and 50.2, 41.9 and 41.6, 34.3 and 34.0, 31.5 and 31.4, 21.9 and 20.6. An analytical sample was collected by preparative GC using column A with a column temperature of 170 °C and a 100 mL/min flow rate. Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67. Found: C, 72.15; H, 8.78.

3-Silabicyclo[3.2.1]octane (1) was prepared from **2** by LAH reduction as described for **7** below. Evaporation of the solvent after workup gave 93% of the product as a semisolid mass which was further purified by sublimation at 60 °C (10 mm): mp 98–100 °C; ^{1}H NMR δ 3.6–4.0 (m, 2 H), 2.5 (m, 2 H), 1.1–2.0 (m, 6 H), 0.8–1.1 (m, 4 H); MS, *m/e* (relative intensity) 126 (30), 125 (21), 124 (100), 111 (43), 97 (88), 83 (75), 55 (53), 43 (90). An analytical sample was collected by two successive sublimations. Anal. Calcd for $C_7H_{14}Si$: C, 66.58; H, 11.17. Found: C, 66.35; H, 11.17.

3-Methyl-3-silabicyclo[3.2.1]octane (7) from the LAH Reduction of 4. Chlorosilane **4a**:**4b** (60:40) (5.7 g, 33 mmol) in 40 mL of ether was added dropwise over 10 min to a magnetically stirred mixture of LAH (2.3 g, 61 mmol) in 200 mL of ether at room temperature. The mixture was stirred for 1 h and slowly poured onto 800 mL of 20% H_2SO_4 and ice overlaid with 150 mL of pentane. This mixture was stirred for 15 min, and the layers were separated. The organic layer was washed with two 100-mL portions of water, 100 mL of 5% sodium bicarbonate, and 100 mL of salt solution. The dried (Na_2SO_4) organic layer was evaporated under a stream of nitrogen from a warm water bath to give **7a**:**7b** (40:60) quantitatively. Distillation under reduced pressure gave 4.2 g (91%) of product: bp 50–51 °C (10 mm); ^{1}H NMR (both isomers) δ 3.6–4.2 (m, 1 H), 2.5 (m, 2 H), 1.2–2.1 (m, 6 H), 0.6–1.2 (m, 4 H), 0.29 (d, J = 4.3 Hz) and 0.11 (d, J = 3.7 Hz) (3 H); MS *m/e* (relative intensity) (**7a**) 140 (15), 139 (18), 138 (100), 125 (36), 111 (30), 97 (90), 43 (95), (**7b**) 140 (60), 139 (28), 138 (8), 125 (60), 111 (40), 97 (100), 43, (62). The isomers were analytically separable at a column temperature of 75 °C and a 25 mL/min flow rate. Retention times: **7a**, 6.2 min; **7b**, 7.0 min. An analytical sample was collected by preparative GC using column A with a column temperature of 90 °C and a 100 mL/min flow rate. Anal. Calcd for $C_8H_{16}Si$: C, 68.49; H, 11.50. Found: C, 68.17; H, 11.55.

LAH Reduction of an Isomeric Mixture of 8 in Ether. A magnetically stirred mixture of **8a**:**8b** (58:42) (0.76 g, 4.5 mmol) and LAH (0.22 g, 5.8 mmol) in 15 mL of ether was heated at reflux for 48 h. GC analysis at this time showed only a small amount of unreacted **8a**. The reaction mixture was poured onto 200 mL of 10% H_2SO_4 and ice overlaid with 100 mL of pentane. The layers were separated, and the organic layer was washed with 100 mL of water and then with 100 mL of salt solution. The dried (Na_2SO_4) organic layer was evaporated under a stream of nitrogen from a warm water bath to give 0.6 g (95%) of **7a**:**7b** (55:45).

LAH Reduction of an Isomeric Mixture of 8 in Diglyme. A similar reduction was performed as that run in ether (above) except that 15 mL of diglyme was used as the solvent. GC analysis showed the reaction to be complete after stirring overnight at room temperature. Workup as above gave **7a**:**7b** (55:45) in 83% yield.

Preparation of 7b by Selective LAH Reduction of an Isomeric Mixture of 8. A solution of **8a**:**8b** (55:45) (9.4 g, 55 mmol) in 35 mL of ether was added dropwise over 20 min to a magnetically stirred mixture of LAH (1.9 g, 50 mmol) in 100 mL of ether cooled to 0 °C. The mixture was stirred for 2 h while it was allowed to warm to 10 °C and then stirred at 10 °C for 2 h; GC analysis at this point indicated nearly complete reduction of **8b**. The reaction mixture was cooled to 0 °C, and excess hydride was decomposed by the dropwise addition of 8.3 mL of saturated potassium sodium tartrate solution over 2.5 h; the resulting mixture was stirred overnight at room temperature. The white solid was removed by suction filtration, and the filtrate was dried (Na_2SO_4) and concentrated under a stream of nitrogen from a warm water bath. The residue was fractionally distilled (15 cm column packed with glass helices) using an air-cooled condenser. Since pure **7b** is a solid, the distillation head was gently warmed with an air gun to dislodge any solid that formed. This gave 3.0 g of **7b**, bp 54–55 °C (11 mm), which contained traces of **8a**. This product was further purified by passage through 100 g of silica gel, eluting with 200 mL of pentane, which removed all methoxysilane impurities. (An alternative purification involved sublimation at 50–70 °C (15 mm).) This product was >95% isomerically pure. The second fraction from the distillation was collected at 55–70 °C (11 mm) to give 1.9 g of a 50:50 mixture of **8a**:**7b**. The fractionating column was removed, and **8a** was distilled, giving 2.6 g (>95% isomerically pure): bp 41–43 °C (1.3 mm).

Preparation of 7b by Selective Reduction of 8 (Isomeric Mixture) with Lithium Trimethoxyaluminum Hydride (LTAH). LTAH was prepared by the dropwise addition of methanol (15.2 mL, 12.0 g, 378 mmol) in 30 mL of ether to a magnetically stirred mixture of LAH (4.8 g, 126 mmol) in 180 mL of ether cooled in an ice water bath. A solution of **8a**:**8b** (33:67) (10.7 g, 63 mmol) in 30 mL of ether was added in one portion, and the resulting mixture was stirred at reflux for 24 h. The final GC assay showed **7b** and unreacted **8a**. The reaction mixture was slowly poured onto 500 mL of ice–salt water overlaid with 100 mL of pentane. The layers were separated, and the organic layer was washed twice with 100-mL portions of salt solution and dried (Na_2SO_4). Concentration and distillation gave 5.0 g of **7b**. Using this particular workup, a 50:50 mixture of unreacted **8a**:**8b** was collected; **8a** apparently underwent isomerization during the workup.

LAH Reduction of 8a to 7a. A magnetically stirred mixture of **8a** (3.7 g, 22 mmol) and LAH (1.0 g, 26 mmol) in 60 mL of ether was heated at reflux for 24 h. The cooled mixture was slowly poured onto 200 mL of 10% H_2SO_4 and ice overlaid with 100 mL of pentane. The layers were separated, and the organic layer was washed with 100 mL of 10% H_2SO_4, two 100-mL portions of water, 100 mL of 5% sodium bicarbonate, and 100 mL of salt solution. The dried (Na_2SO_4) organic layer was concentrated. Bulb-to-bulb distillation into a dry ice-cooled receiver at 1.0 mm (pot temperature of 20–30 °C) gave 2.1 g (71%) of **7a**.

Bis(3-methyl-3-silabicyclo[3.2.1]oct-3-yl) Ether (12). Chlorosilane 4 (1.0 g, 6 mmol) in 10 mL of 10% H_2SO_4 was magnetically stirred at 60 °C overnight. The resulting two-phase solution was neutralized by the addition of 8.5 mL of 3 M NaOH and extracted with 35 mL of pentane. The organic fraction was dried (Na_2SO_4) and concentrated on the rotary evaporator to give 1.0 g of **12**. This product was bulb-to-bulb distilled at 0.05 mm, pot temperature of 50–90 °C, with most of the material distilling at 60 °C: ^1H NMR δ 2.5 (m, 4 H), 1.1–2.1 (m, 12 H), 0.6–1.1 (m, 8 H), 0.28 and 0.03 (two s, 6 H); ^{13}C NMR δ 41.7 and 41.3, 34.7 and 34.3, 31.6 and 31.2, 26.2, 4.7 and 2.5. An analytical sample was collected by preparative GC using column A with a column temperature of 190 °C and a 70 mL/min flow rate. Anal. Calcd for $C_{16}H_{30}OSi$: C, 65.24; H, 10.25. Found: C, 65.02; H, 10.40.

3-Hydroxy-3-methyl-3-silabicyclo[3.2.1]octane (13) was prepared as described in ref 8b.

3-Phenyl-3-silabicyclo[3.2.1]octane (14). Methoxysilane 11 (2.6 g, 1.1 mmol) in 10 mL of ether was added in one portion to a magnetically stirred mixture of LAH (0.6 g, 16 mmol) in 80 mL of ether with no obvious exotherm. The reaction mixture was stirred at reflux for 24 h and then slowly poured onto 500 mL of 10% H_2SO_4 and ice overlaid with 125 mL of pentane. The layers were separated, and the organic fraction was washed with 100 mL of 10% H_2SO_4 and then with three 100-mL portions of water. The dried (Na_2SO_4) organic layer was concentrated on the rotary evaporator, and the crude product was purified by Kugelrohr distillation at 70–90 °C (0.25 mm) to give 2.0 g (90%) of **14** as a mixture of isomers: ^1H NMR δ 7.0–7.7 (m, 5 H), 4.3–4.7 (m, 1 H), 2.6 (m, 2 H), 0.8–2.0 (m, 10 H); ^{13}C NMR δ 137.1 and 136.0, 134.1 and 133.7, 128.8 and 128.5, 127.5 and 127.3, 42.1 and 41.5, 34.6 and 33.9, 31.6 and 31.3, 19.6 and 18.0; MS, *m/e* (relative intensity) 202 (8), 159 (5), 124 (100); the MS spectra for both isomers were identical. An analytical sample was collected by preparative GC using column A with a column temperature of 140 °C and a 70 mL/min flow rate. Anal. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.96. Found: C, 76.92; H, 9.03.

***exo*-3-Methyl-3-phenyl-3-silabicyclo[3.2.1]octane (15a).** Pure **8a** (1.21 g, 7.1 mmol) in 2 mL of ether was added dropwise over 5 min to a magnetically stirred solution of 25 mL of 0.6 M phenyllithium (15 mmol) in ether at 16 °C. The reaction mixture was stirred for 1 h at room temperature; GC analysis at this point showed the absence of starting material. The reaction mixture was slowly poured onto 100 mL of 10% H_2SO_4 and ice overlaid with 100 mL of pentane. After the mixture was stirred for 15 min, the layers were separated and the organic layer was washed with 100 mL of salt solution. The dried (Na_2SO_4) organic fraction was concentrated under a nitrogen purge from a warm water bath. The residue was bulb-to-bulb distilled into a dry ice cooled receiver at 0.05 mm, maximum pot temperature of 90 °C, to give 1.70 g (theory, 1.53 g) of a clear, colorless liquid whose ^{13}C NMR spectrum showed **15a** plus traces of a contaminant which only absorbed in the aromatic region. Pure **15a** was collected by preparative GC using column A with a column temperature of 135 °C and a 100 mL/min flow rate: ^1H NMR δ 7.2–7.7 (m, 5 H), 2.5 (m, 2 H), 0.8–1.9 (m, 10 H), 0.10 (s, 3 H); MS, *m/e* (relative intensity), 216 (nil), 201 (7), 173 (45), 138 (100), 43 (28). Anal. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32. Found: C, 77.56; H, 9.35.

***endo*-3-Methyl-3-phenyl-3-silabicyclo[3.2.1]octane (15b).** Silane **7a**:**7b** (22:78) (0.47 g, 3.7 mmol) was added in one portion to a magnetically stirred solution of 30 mL of 0.6 M phenyllithium (18 mmol) in ether at room temperature. The resulting milky suspension was heated at reflux for 2 h; a GC assay at this point indicated the absence of **7**. The cooled reaction mixture was slowly poured onto 100 mL of 10% H_2SO_4 and ice overlaid with 100 mL of pentane. The layers were separated, and the organic fraction, which contained some suspended material, was filtered and washed with 100 mL of 10% H_2SO_4, 100 mL of water, 100 mL of 5% sodium bicarbonate, and 100 mL of salt solution. The dried (Na_2SO_4) organic fraction was concentrated, and the residue was bulb-to-bulb distilled into a dry ice cooled receiver at 0.04 mm (maximum pot temperature of 100 °C) to give 0.93 g (theory, 0.80 g) of a clear, colorless liquid whose ^{13}C NMR spectrum showed **15** plus traces of a contaminant which only absorbed in the aromatic region. ^1H NMR and GC analyses showed a 17:83 ratio of **15a**:**15b**. Pure **15b** was collected by preparative GC using column A and the same conditions as for **15a**: ^1H NMR δ 7.1–7.6 (m, 5 H), 2.6 (m, 2H), 1.2–2.1 (m, 6 H), 0.9–1.2 (m, 4 H), 0.41 (s, 3 H); MS, *m/e* (relative intensity) 216 (18), 201 (39), 173 (100), 138 (93), 43 (39). The two isomers of **15** were analytically separable at a column temperature of 170 °C and a 30 mL/min flow rate. Retention times: **15a**, 11.3 min; **15b**, 14.7 min.

3-Fluoro-3-methyl-3-silabicyclo[3.2.1]octane (16). Gaseous BF_3 was bubbled, using a gas dispersion tube, through a magnetically stirred solution of **8** (50:50 isomer mixture) (1.7 g, 10 mmol) in 150 mL of pentane at 0 °C over 20 min. The reaction was complete (GC assay) after 10 min. Nitrogen was bubbled through the reaction mixture to remove excess BF_3, and the solution was evaporated under a stream of nitrogen from a warm water bath to give 1.6 g (100%) of the isomers of **16**, which showed only traces of impurities by NMR and GC analyses. This product was further purified by preparative GC using column B with a column temperature of 105 °C and a 100 mL/min flow rate: ^1H NMR δ 2.5 (m, 2 H), 0.8–2.1 (m, 10 H), 0.26 (d, J = 9.1 Hz), 0.14 (d, J = 7.7 Hz) (3 H); ^{19}F NMR (**16a**) δ 159.4, (**16b**) 157.9; MS, *m/e* (relative intensity) 158 (61), 143 (40), 116 (54), 89 (100), 63 (62), 47 (71), 43 (5); the MS spectra of both isomers were identical. The two isomers were analytically separable at a column temperature of 90 °C and a 30 mL/min flow rate. Retention times: **16a**, 8.4 min; **16b**, 9.4 min. A high-resolution mass spectrum was obtained: calcd 158.0927, found 158.0927 (parent molecular ion). Anal. Calcd for $C_8H_{15}FSi$: C, 60.70; H, 9.55. Found: C, 60.37; H, 9.06.

Free Radical Chlorination of 7. Preparation of the Isomers of 4. Silane **7a** (pure isomer) (1.4 g, 10 mmol) and benzoyl peroxide (25 mg) in 30 mL of CCl_4 was magnetically stirred at reflux for 8.5 h; ^1H NMR analysis only showed **4a** present. Most of the solvent was removed by slowly reducing the pressure to 40 mm and keeping the flask at 0–10 °C. This gave **4a**:**4b** (95:5) and some residual CCl$_4$. This material was directly reduced as described in the next experiment. In a separate experiment in which **4b** had been prepared from **7b** in an analogous fashion, distillation of the isomerically pure product caused isomerization and a 60:40 ratio of **4a**:**4b** was obtained.

LAH Reduction of Isomer-Enriched 4a to 7a and 7b. The crude product from the chlorination reaction of 1.4 g of **7a** was taken up in 40 mL of ether and added dropwise over 15 min to a magnetically stirred mixture of LAH (2.5 g, 66 mmol) in 125 mL of ether at 5 °C. After being stirred for 1 h at room temperature, the reaction mixture was slowly poured onto 400 mL of 10% H$_2$SO$_4$ and ice overlaid with 150 mL of pentane. The organic layer was separated and washed with 200 mL of 10% H$_2$SO$_4$, 200 mL of water, 200 mL of 5% sodium bicarbonate, and 200 mL of salt solution. The dried (Na$_2$SO$_4$) organic fraction was concentrated under a stream of nitrogen from a warm water bath, and the residue was bulb-to-bulb distilled under reduced pressure (10 mm) to give 1.0 g of **7a**:**7b** in a 15:85 ratio.

Chlorinations of 7 with Pd/C in Carbon Tetrachloride. One 5-mm NMR tube was charged with **7a** (pure isomer) in 0.5 mL of CCl$_4$; a similar tube was charged with **7a**:**7b** (20:80) in 0.5 mL of CCl$_4$. To each of these was added 10 mg of 30% Pd/C. The tubes became warm, and there was bubling in the reaction mixtures; a slow reaction occurred over the next 15 h. The latter reaction was complete at this time, and **4a**:**4b** were obtained in a 1:1 ratio. In the former reaction, after 15 h, a mixture of **7a** and **4a**:**4b** (70:30) in a 40:60 ratio was present. Heating at 65 °C for 1 h brought the reaction to completion, and **4a**:**4b** were obtained in a 60:40 ratio.

In a similar experiment, 5% Pd/C (10 mg), which had been freshly dried in vacuo at 140 °C, was added to **7a**:**7b** (15:85). An immediate reaction occurred, and within 15 min, only traces of 7 remained and **4a**:**4b** (25:75) was present. After 2 h, no starting material was observed and **4a**:**4b** was present in a 40:60 ratio; after 1.5 days the isomer ratio was 60:40.

Chlorination of 7 with Trityl Chloride. To a 5-mm NMR tube was added **7b** (39 mg, 0.34 mmol), freshly recrystallized trityl chloride (99 mg, 0.35 mmol), and 0.5 mL of benzene-d_6. A slow reaction took place at room temperature over 2 weeks to give **4a**:**4b** (60:40) and triphenylmethane. No other silicon-containing product was observed in the ^{1}H or ^{13}C NMR spectra of the final reaction mixture.

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Supplementary Material Available: Tables II and III, more detailed mass spectral data on compounds **1**, **7a**,**b**, **8**, **14**, **15a**,**b**, and **16** (4 pages). Ordering information is given on any current masthead page.