Stereospecific and Regioselective Isocyanide Insertions into Siliranes and Reactions of the Resulting Iminosilacyclobutanes

Phuc T. Nguyen, Wylie S. Palmer, and K. A. Woerpel*

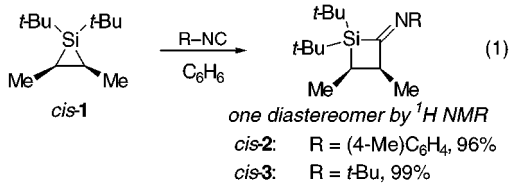
Department of Chemistry, University of California, Irvine, California 92697-2025

Received August 11, 1998

The insertions of *p*-tolyl and *tert*-butyl isocyanide into siliranes yielded iminosilacyclobutanes with stereospecific retention of configuration. Monosubstituted siliranes underwent insertion into the more substituted Si−C bond of the ring, although this regioselectivity was eroded as substitution increased on the silirane ring. The iminosilacyclobutane products tautomerized thermally or in the presence of a palladium catalyst to yield the thermodynamically more stable aminosilacyclobutenes. Ring-expansion reactions of iminosilacyclobutanes were promoted by acids: treatment with aqueous copper sulfate produced an oxasilacyclopentane in high yield, whereas with trifluoroacetic acid, oxasilacyclohexanes were formed.

Siliranes undergo a variety of ring-expansion reactions such as the two-atom insertions originally studied by Seyferth[1,2] and Ando.[3,4] A few single-atom insertions, including reactions with isocyanides,[5,6] oxygen,[7] sulfur,[8] and selenium,[9] have been reported, although the question of stereochemical control was not addressed systematically. In our own studies of the reactions of siliranes,[10−13] we found that these strained ring systems undergo a variety of stereospecific two-atom insertion reactions. In this paper, we detail our investigations of the stereospecific and regioselective one-atom insertions of isocyanides into siliranes. The stereospecificity of this reaction is not only important from a mechanistic perspective, but it also permits the stereocontrolled preparation of synthetically useful oxasilacyclopentane hemiacetals.[14,15]

Isocyanide Insertion. As with other carbon−carbon bond-forming reactions of siliranes,[11] the insertions of isocyanides, first reported by Weidenbruch,[5] proceed stereospecifically. Siliranes *cis*-**1** and *trans*-**1** react with a slight excess of *p*-tolyl isocyanide at 23 °C or *tert*-butyl isocyanide at 80 °C. After removal of volatile materials, analytically pure iminosilacyclobutanes **2** and **3**, respectively, were isolated in high yield (eqs 1 and 2). Analysis of ^{1}H NMR spectra indicated that the products of each reaction were formed as single stereoisomers. NOE difference measurements indicated that the products were formed with stereospecific retention of configuration about the C−Si bond.[16] The stereospecificity of these reactions indicates that homolysis or heterolysis of a C−Si bond prior to C−C bond formation is unlikely.[17]

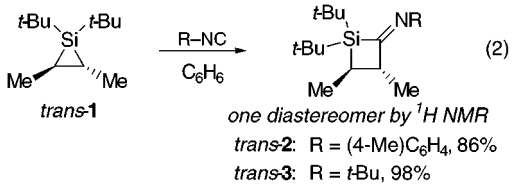


cis-**1**

one diastereomer by ^{1}H NMR

cis-**2**: R = (4-Me)C_6H_4, 96%

cis-**3**: R = *t*-Bu, 99%



trans-**1**

one diastereomer by ^{1}H NMR

trans-**2**: R = (4-Me)C_6H_4, 86%

trans-**3**: R = *t*-Bu, 98%

As with two-atom insertions,[11,12,15] the insertions of an isocyanide into monosubstituted siliranes proceed regioselectively into the more substituted C−Si bond (eq 3, Table 1). Only one regioisomer of the iminosilacyclobutane **5a** was detected using NMR spectroscopy upon reaction of silirane **4a** (R = *n*-Bu) with *tert*-butyl isocyanide (Table 1, entry 1). The regioselectivity decreased as the substituent on the silirane ring became sterically more demanding and the temperature required to effect insertion increased (entries 2 and 3). The erosion in regioselectivity reaches an extreme for geminally disubstituted siliranes, which undergo insertion of phenyl isocyanide into the less-substituted C−Si bond.[5]

Although we do not have any detailed information about the reaction mechanism, these reactions likely

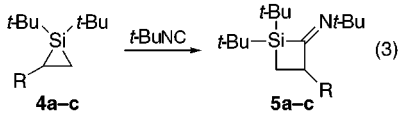
(1) Seyferth, D.; Duncan, D. P.; Shannon, M. L.; Goldman, E. W. *Organometallics* **1984**, *3*, 574−578.
(2) Seyferth, D.; Duncan, D. P.; Shannon, M. L. *Organometallics* **1984**, *3*, 579−583 and references therein.
(3) Saso, H.; Ando, W. *Chem. Lett.* **1988**, 1567−1570.
(4) Saso, H.; Ando, W.; Ueno, K. *Tetrahedron* **1989**, *45*, 1929−1940.
(5) Kroke, E.; Willms, S.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Tetrahedron Lett.* **1996**, *37*, 3675−3678.
(6) Brook, A. G.; Saxena, A. K.; Sawyer, J. F. *Organometallics* **1989**, *8*, 850−852.
(7) Saso, H.; Yoshida, H.; Ando, W. *Tetrahedron Lett.* **1988**, *29*, 4747−4750.
(8) Boudjouk, P.; Samaraweera, U. *Organometallics* **1990**, *9*, 2205−2206.
(9) Boudjouk, P.; Black, E.; Kumarathasan, R.; Samaraweera, U.; Castellino, S.; Oliver, J. P.; Kampf, J. W. *Organometallics* **1994**, *13*, 3715−3727.
(10) Bodnar, P. M.; Palmer, W. S.; Shaw, J. T.; Smitrovich, J. H.; Sonnenberg, J. D.; Presley, A. L.; Woerpel, K. A. *J. Am. Chem. Soc.* **1995**, *117*, 10575−10576.
(11) Bodnar, P. M.; Palmer, W. S.; Ridgway, B. H.; Shaw, J. T.; Smitrovich, J. H.; Woerpel, K. A. *J. Org. Chem.* **1997**, *62*, 4737−4745.
(12) Shaw, J. T.; Woerpel, K. A. *J. Org. Chem.* **1997**, *62*, 442−443.
(13) (a) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 1097−1099. (b) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 4824−4827.
(14) Shaw, J. T.; Woerpel, K. A. *J. Org. Chem.* **1997**, *62*, 6706−6707.
(15) Shaw, J. T.; Woerpel, K. A. *Tetrahedron* **1997**, *53*, 16597−16606.

(16) Empirically, the ^{29}Si NMR chemical shifts of **2** and **3** correlate to stereochemistry: the two cis products *cis*-**2** and *cis*-**3** have chemical shifts of 31.4 and 31.5 ppm, respectively, whereas the two trans products *trans*-**2** and *trans*-**3** have chemical shifts of 30.2 and 30.6 ppm, respectively.

(17) These results are in contrast to the one- or two-atom insertions of sulfur into silacyclopropanes **1**, which are not stereospecific. Radical intermediates were suggested for those transformations (ref 9).

10.1021/jo9816257 CCC: $18.00
Published on Web 02/27/1999

Table 1. Regioseletive Insertion Reactions of Silacyclopropanes 4 (eq 3)[a]



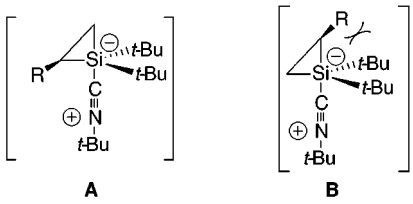
(3)

4a–c 5a–c

entry	reactant	temperature (°C)	yield[b] %	regio-selectivity[c]	^{29}Si NMR (δ)
1	**4a:** R = *n*-Bu	91	94	>95 : 5	34.4
2	**4b:** R = *i*-Pr	121	98	92 : 8	32.3
3	**4c:** R = *t*-Bu	127	97	86 : 14	29.6

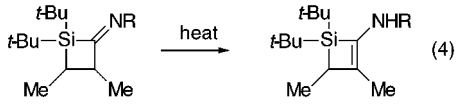
[a] Conditions: 1.0–1.3 equiv *tert*-butyl isocyanide, C_6H_6 as solvent. [b] Yields are for isolated products. [c] By ^{1}H NMR spectroscopy.

proceed through pentacoordinate siliconate intermediates formed by attack of the isocyanide on the silirane. The favored regioselectivity demonstrated in eq 3 and Table 1 is consistent with this analysis. Of the two possible pathways, the one leading via siliconate intermediate **A** to observed products avoids destabilizing interactions between the axially disposed alkyl substituent and the *tert*-butyl groups (as found in intermediate **B**). A similar argument has been used to explain the regioselectivity of formamide insertion.[12] As the size of the alkyl substituent R on the ring increases, interaction between the incoming isocyanide and the alkyl substituent becomes increasingly unfavorable, thereby leading to diminished regioselectivity.



Tautomerization of Iminosilacyclobutanes. The iminosilacyclobutanes obtained from isocyanide insertion into siliranes tautomerize thermally as well as in the presence of a palladium catalyst (eq 4, Table 2). When

Table 2. Rearrangement of Iminosilacyclobutanes 2 and 3 to Aminosilacyclobutenes 6 and 7 (eq 4)



(4)

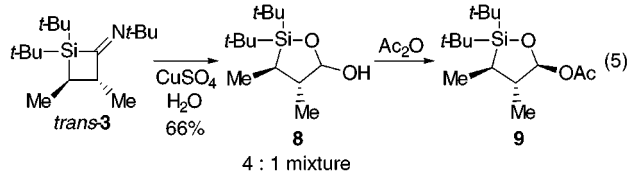
2: R = (4-Me)C_6H_4 **6**: R = (4-Me)C_6H_4
3: R = *t*-Bu **7**: R = *t*-Bu
(*cis* or *trans*)

entry	silacyclobutane	temp (°C)	time	product (% yield)[c]
1[a]	*cis*-**2**; R = (4-Me)C_6H_4	95	10 h	**6** (94)
2	*cis*-**2**; R = (4-Me)C_6H_4	169	15 h	**6** (100)
3	*trans*-**2**; R = (4-Me)C_6H_4	181	8 days[b]	**6** (98)
4	*cis*-**3**; R = *t*-Bu	77	12 h	**7** (89)
5	*trans*-**3**; R = *t*-Bu	119	19 h	**7** (89)

[a] 2 mol% of $PdCl_2(PPh_3)_2$ was employed. [b] Proceeded to 95 % completion as determined by ^{1}H NMR spectroscopy. [c] Yields are for isolated products.

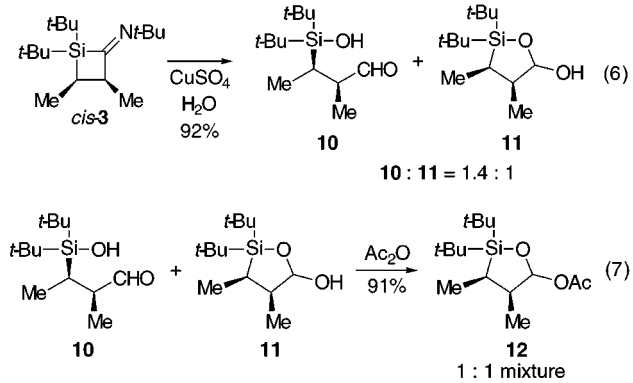
cis-**2** was heated (95 °C) with 2 mol % of $PdCl_2(PPh_3)_2$ in a sealed NMR tube, tautomerization to give the aminosilacyclobutene **6** was observed (entry 1). This tautomerization must be facilitated by the palladium catalyst, since higher temperatures (169 °C) were required without the catalyst (entry 2). The thermal tautomerization of *tert*-butylimines occurred at lower temperatures than for their aryl analogues (compare entries 3 and 4). The driving force behind the tautomerization may be the relief of allylic strain[18] associated with the imino substituent[19] and the *tert*-butyl silicon groups.[20]

Ring-Expansion Reactions. In the course of efforts to obtain ketones from imines **3** by hydrolysis, we discovered two unexpected ring-expansion processes. When *trans*-**3** was treated with an aqueous solution of $CuSO_4$,[21,22] hemiacetal **8**[15] was obtained as a 4:1 mixture of anomers[23] in 66% yield (eq 5). The hemiacetal **8** could be



(5)

acylated to give the acetate **9**. The trans relative stereochemistry between the methyl groups of the starting material *trans*-**3** was preserved in the product **8**. Similarly, treatment of *cis*-**3** with aqueous $CuSO_4$ provided the siloxy aldehyde **10** and the cis hemiacetal **11** (as a 3:1 mixture of anomers[23]) in 92% combined yield (eq 6). As with the trans dimethyl system, this reaction preserved the stereochemistry of the starting material.[24] The mixture of **10** and **11** was acylated[15] to give the acetate **12** (91% yield) as a 1:1 mixture of anomers (eq 7).[23]



(6)

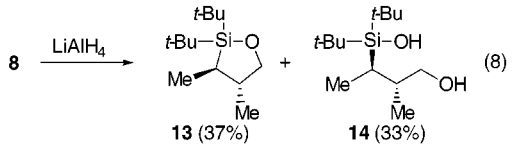
(7)

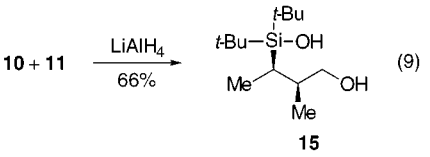
The oxasilacyclopentane acetates **9** and **12** derived from iminosilacyclobutanes are useful intermediates for stereoselective synthesis. Oxonium ions formed from

(18) Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841−1860.
(19) The stereochemistry about the imine is not known. Weidenbruch, in his studies of this reaction (ref 5), demonstrated by X-ray crystallography that an iminosilacyclobutane possessed the (*Z*)-stereochemistry.
(20) We have examined the relative energies of the imine form and enamine form computationally using ab initio methods (the Spartan program from Wavefunction, Inc., Irvine, CA was employed). These calculations indicate that the relative energies between the two forms depends on the level of substitution on the silicon and nitrogen atoms as well as the substitution on the two ring carbons. Therefore, we conclude that the driving force behind the tautomerization is steric in origin.
(21) Attanasi, O.; Gasperoni, S. *Gazz. Chim. Ital.* **1978**, *108*, 137−138.
(22) Okano, K.; Morimoto, T.; Sekiya, M. *J. Chem. Soc., Chem. Commun.* **1985**, 119−120.
(23) Product ratios were determined using ^{1}H NMR spectroscopy.
(24) A minor amount (4%) of the hemiacetal **8** was detected by ^{1}H NMR spectroscopy and gas chromatography. This small amount of *trans*-dimethyl compound is most likely due to the presence of *trans*-2-butene as an impurity in commercially available *cis*-2-butene, from which silacyclopropane *cis*-**1** was made. The typical purity of *cis*-**1** is ≥95%.

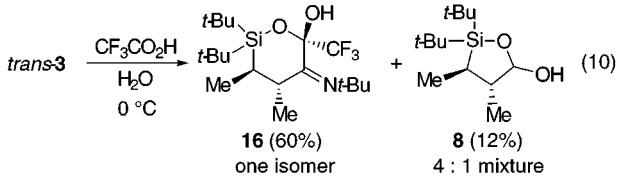
acetate **9** in the presence of Lewis acids undergo highly stereoselective reactions with allylsilanes and silyl enol ethers.[14,15] Although *trans*-dimethyl acetate **9** was previously prepared by insertion of a formamide into *trans*-**1**,[12] its *cis*-dimethyl analogue **12** could not be obtained by that method. The insertion of isocyanides reported here provides a high-yielding synthesis of *cis*-acetate **12**, an important intermediate for our ongoing investigations into nucleophilic additions to five-membered ring oxonium ions.[14]

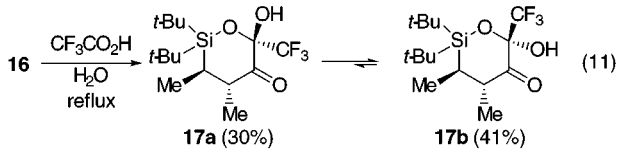
The stereochemistries of the hydrolysis products **8** and **10**−**12** were determined by spectroscopic methods and by chemical correlation. The structures of trans acetal **8** and its derived acetate **9** have been proven unambiguously.[15] The cis relative configuration of the methyl groups of acetate **12** was suggested by NOE difference experiments. Correlation between the cis and trans products was made by studying their reduction products, which decreased the number of stereocenters to consider. Reduction of **8** (eq 8) afforded the oxasilacyclopentane **13** (37%) and the diol **14** (33%). Diol **14** was found to form small amounts of oxasilacyclopentane **13** upon standing over several days. Reduction of the mixture of cis isomers **10** and **11** yielded the diol **15** (66%), which was clearly a diastereomer of **14**. Therefore, the relative stereochemistry of compounds **8**, **10**, and **11** can be assigned with confidence.



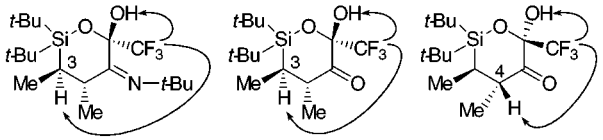


The use of aqueous CF_3CO_2H to hydrolyze imine *trans*-**3** instead resulted in two-atom insertion of the carbonyl group of the acid into a C−Si bond of silacyclobutane *trans*-**3**. When *trans*-**3** was treated with CF_3CO_2H and water, imine **16** (60%) was isolated as a single stereoisomer along with the hemiacetal **8** (12%, eq 10). Hydrolysis of **16** at higher temperatures provided the ketones **17a** and **17b** (71% combined yield) along with recovered **16** (15%, eq 11). Although **17a** was formed as the major stereoisomer under kinetically controlled reaction conditions, **17b** was favored as the thermodynamic product (10:1).[23]

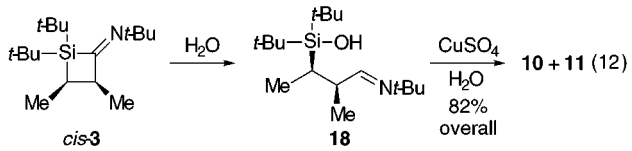




The structures and stereochemistries of the oxasilacyclohexanes **16** and **17** were determined by spectroscopic methods. The connectivities of these compounds were indicated by chemical shift data and coupling patterns as well as the Si−O stretch in the infrared spectrum (about 1170 and 820 cm^{-1}). This assignment was further supported by the presence of ketone carbonyl groups in the ^{13}C NMR spectra of **17a** and **17b** (202.8 and 208.8 ppm, respectively). The *trans*-dimethyl configuration was elucidated using NOE spectroscopy for products **16** and **17**, but the stereochemistry at the ketal center could not be determined using this technique. The assignment of stereochemistry at the ketal stereocenter was made possible using $^1H\{^{19}F\}$ NOE difference spectroscopy.[25] Irradiation of the CF_3 group in **16** and **17a** showed small NOE correlations to the C-3 methine proton and large NOE correlations to the hydroxyl proton, indicating that both compounds have the same relative stereochemistry.[26] Irradiation of the CF_3 group in **17b** showed an NOE correlation to the C-4 methine proton, demonstrating that **17b** differs in stereochemistry from **17a** at the acetal stereocenter.



A control experiment provided valuable information about the mechanism of the $CuSO_4$ hydrolysis reactions of iminosilacyclobutanes. Upon treatment with H_2O, *cis*-**3** underwent hydrolysis of a C−Si bond to provide imine **18** (eq 12). The structure of **18** was confirmed using IR, ^1H, and ^{13}C NMR spectroscopies, and using COSY and HMQC experiments.[27] Subjection of **18** to aqueous $CuSO_4$ resulted in imine hydrolysis, providing aldehyde **10** and oxasilacyclopentane **11** in 82% overall yield (eq 12). Because these products are the same ones obtained from hydrolysis of *cis*-**3** with aqueous $CuSO_4$ (eq 6), imine **18** is a viable intermediate in the hydrolysis of *cis*-**3**.



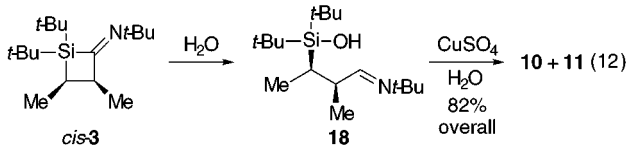
The observation of imine **18** suggests that the mechanisms for reactions of iminosilacyclobutanes involve nucleophilic attack at the silicon atom rather than at the imine carbon atom. This common motif would explain both hydrolysis and incorporation of CF_3CO_2H. Hydrolysis of the imine *cis*-**3** upon treatment with aqueous $CuSO_4$ (eq 6) involves attack of water at the silicon atom to form

(25) For recent examples of the use of $^1H\{^{19}F\}$ NOE difference spectroscopy, see (a) Huber, E. W.; Kane, J. M.; Dalton, C. R. *J. Fluorine Chem.* **1997**, *82*, 47−50. (b) McCarthy, J. R.; Huber, E. W.; Le, T.-B.; Laskovics, F. M.; Matthews, D. P. *Tetrahedron* **1996**, *52*, 45−58.

(26) Homonuclear NOE experiments on **16** reveal a large NOE between the *tert*-butyl imino group and the C-4 methine and the hydroxyl group. These data are consistent with a conformation with both methyl groups and the trifluoromethyl group in axial positions, presumably to alleviate allylic strain.

(27) Attempted purification of imine **18** by chromatography over SiO_2 provided **10** and **11** in 66% overall yield from *cis*-**3**.

C. Subsequent protonolysis of the C−Si bond would provide imine **18**, which would hydrolyze to form observed products **10** and **11** under acidic conditions. A similar mechanism would apply for hydrolysis of *trans*-**3** (eq 5). The incorporation of CF_3CO_2H into *trans*-**3** (eq 10) can also be explained by proposing nucleophilic attack at the silicon atom of an iminosilacyclobutane. In this case, attack of CF_3CO_2H onto *trans*-**3** would form pentacoordinate siliconate **D**. Migration of the nucleophilic C−Si bond to the protonated carbonyl group would lead to the carbonyl insertion product **16**.



Conclusion. Siliranes undergo one-atom insertion reactions with isocyanides under mild conditions to provide iminosilacyclobutanes in a stereospecific and regioselective manner. A hydrolysis reaction of the resulting silacyclobutanes maintains the relative stereochemistry between the ring substituents, thus providing a stereocontrolled route to oxasilacyclopentane acetates. The preparation of the *cis*-dimethyl acetate **12** using this method suggests broader use of silirane chemistry in organic synthesis.

Experimental Section

General. General experimental details are provided as Supporting Information. Microanalyses were performed by Atlantic Microlab, Atlanta, GA, or by Microlytics, South Deerfield, MA. NMR tube experiments were carried out with 5 mm Wilmad J. Young tubes, using C_6D_6 (distilled from CaH_2 then sodium/benzophenone ketyl) as solvent. Analytical gas−liquid chromatography (GLC) was performed on a Hewlett-Packard 5890 Level 4 chromatograph, equipped with split-mode capillary injection system and a flame ionization detector. Fused silica capillary columns (30 × 0.32 mm) wall coated with DB-1 (J & W Scientific) were used with helium as the carrier gas. All reactions were carried out under a stream of nitrogen in glassware that had been flame-dried. Commercially available *tert*-butyl isocyanide (Acros) was used. 4-Tolyl isocyanide was prepared from 4-methylaniline using an improved Hofmann carbylamine procedure.[28] Siliranes *cis*-**1**, *trans*-**1**, **4a**,[11] **4b**, and **4c** were prepared according to the method of Boudjouk.[29] Siliranes, silacyclobutanes, and silacyclobutenes were stored and handled in an Innovative Technologies nitrogen atmosphere drybox. Solvents were dried and distilled prior to use.

1,1-Di-*tert*-butyl-2-(4-tolylimino)-*cis*-3,4-dimethylsilacyclobutane (*cis*-2). Silirane *cis*-**1** (0.21 g, 1.1 mmol) and 4-tolyl isocyanide (0.13 g, 1.1 mmol) were dissolved in 6 mL of benzene. The reaction mixture immediately turned red and was stirred for 15 min at ambient temperature before concentrating in vacuo to give *cis*-**2** as a dark red liquid (0.32 g, 96%): IR (thin film) 2858, 1635, 1503, 1470, 819 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz) δ 6.93 (d, J = 7.8, 2H), 6.82 (d, J = 8.2, 2H), 3.11 (m, 1H), 2.08 (s, 3H), 1.82 (m, 1H), 1.27 (d, J = 7.4, 3H), 1.16 (d, J = 8.2, 3H), 0.97 (s, 9H), 0.81 (s, 9H); ^{13}C NMR (C_6D_6, 125 MHz) δ 198.0, 153.6, 133.5, 129.5, 119.9, 50.3, 29.2, 28.8, 21.1, 20.9, 19.8, 18.7, 12.4, 11.5; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ 31.4; HRMS (CI/isobutane) calcd for $C_{20}H_{33}NSi$ (M^+) 315.2382, found 315.2387. Anal. Calcd for $C_{20}H_{33}NSi$: C, 76.12; H, 10.54; N, 4.44. Found: C, 75.86; H, 10.68; N, 4.39.

1,1-Di-*tert*-butyl-2-(4-tolylimino)-*trans*-3,4-dimethylsilacyclobutane (*trans*-2). Prepared in a similar manner as *cis*-**2**. The product *trans*-**2** was purified further by recrystallization from hexanes to give 273 mg (86%) of a light-yellow solid: mp = 65−67 °C; IR (KBr) 2858, 1640, 1502, 1466, 820 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz) δ 6.93 (d, J = 7.9, 2H), 6.84 (d, J = 8.2, 2H), 2.54 (m, 1H), 2.08 (s, 3H), 1.35 (d, J = 6.5, 3H), 1.26 (d, J = 7.1, 3H), 1.22 (m, 1H), 1.06 (s, 9H), 0.72 (s, 9H); ^{13}C NMR (C_6D_6, 125 MHz) δ 195.6, 153.6, 133.6, 129.5, 120.0, 56.8, 29.3, 28.5, 25.2, 20.9, 20.7, 20.3, 16.8, 15.6; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ 30.2; HRMS (CI/isobutane) calcd for $C_{20}H_{33}NSi$ (M^+) 315.2382, found 315.2389. Anal. Calcd for $C_{20}H_{33}NSi$: C, 76.12; H, 10.54; N, 4.44. Found: C, 75.97; H, 10.64; N, 4.37.

1,1-Di-*tert*-butyl-2-(*N*-*tert*-butylimino)-*cis*-3,4-dimethylsilacyclobutane (*cis*-3). Prepared in a similar manner as *cis*-**2**, except that the reaction mixture was heated at 80−85 °C for 2 h. The product was isolated as a clear liquid (1.18 g, 99%): IR (thin film) 2859, 1632, 1471, 816 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz) δ 2.99 (m, 1H), 1.79 (m, 1H), 1.23 (s, 9H), 1.17 (d, J = 7.7, 3H), 1.15 (d, J = 8.4, 3H), 1.09 (s, 9H), 1.02 (s, 9H); ^{13}C NMR (C_6D_6, 125 MHz) δ 183.9, 56.5, 50.4, 30.2, 29.9, 29.1, 22.0, 20.6, 18.5, 13.4, 12.3; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ 31.5; HRMS (CI/isobutane) calcd for $C_{17}H_{35}NSi$ (M^+) 281.2539, found 281.2534. Anal. Calcd for $C_{17}H_{35}NSi$: C, 72.52; H, 12.53; N, 4.97. Found: C, 72.46; H, 12.74; N, 4.89.

1,1-Di-*tert*-butyl-2-(*N*-*tert*-butylimino)-*trans*-3,4-dimethylsilacyclobutane (*trans*-3). Prepared in a similar manner as *cis*-**2**, except that the reaction mixture was heated at 80−85 °C for 2 h. The product was isolated as a clear liquid (519 mg, 98%): IR (thin film) 2861, 1637, 1471, 818 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.30 (m, 1H), 1.32 (d, J = 7.4, 3H), 1.21 (s, 9H), 1.15 (s, 10H), 1.11 (d, J = 6.6, 3H), 1.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 184.1, 56.5, 55.0, 29.8, 29.4, 28.8, 25.7, 21.5, 21.1, 17.8, 15.1; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ 30.6; HRMS (CI/isobutane) calcd for $C_{17}H_{35}NSi$ (M^+) 281.2539, found 281.2536. Anal. Calcd for $C_{17}H_{35}NSi$: C, 72.52; H, 12.53; N, 4.97. Found: C, 72.26; H, 12.76; N, 4.89.

1,1-Di-*tert*-butyl-2-(2-propyl)silirane (4b). This compound was prepared according to the method of Boudjouk.[29] Purification by bulb-to-bulb distillation (60−70 °C/0.05 Torr) afforded **4b** as a very air-sensitive colorless liquid (0.93 g, 73%): bp 60−70 °C (0.05 Torr); IR (thin film) 2954, 1473, 1363, 824 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz) δ 1.60 (m, 1H), 1.19 (d, J = 6.3, 3H), 1.10 (s, 9H), 1.08 (d, J = 6.6, 3H), 1.02 (s, 9H), 0.81 (dd, J = 12.1, 10.8, 1H), 0.60 (apar-td, J = 11.4, 9.2, 1H), 0.18 (dd, J = 10.6, 9.2, 1H); ^{13}C NMR (C_6D_6, 125 MHz) δ 31.3, 30.9, 30.0, 26.3, 24.9, 19.1, 18.2, 3.1; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ −47.7; HRMS (EI) m/z calcd for $C_{13}H_{28}Si$ (M^+): 212.1960, found 212.1964. Anal. Calcd for $C_{13}H_{28}Si$: C, 73.50; H, 13.28. Found:[30] C, 72.59; H, 13.23.

1,1-Di-*tert*-butyl-2-(*tert*-butyl)silirane (4c). This compound was prepared according to the method of Boudjouk.[29] Purification by bulb-to-bulb distillation (84−88 °C/0.05 Torr) afforded **4c** as an air-sensitive colorless liquid (3.45 g, 81%): IR (thin film) 2949, 1471, 1362, 822 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz) δ 1.15 (s, 9H), 1.11 (s, 9H), 1.04 (s, 9H), 0.91 (t, J = 12.6, 1H), 0.70 (dd, J = 12.5, 10.4, 1H), 0.40 (dd, J = 12.6, 10.3, 1H); ^{13}C NMR (C_6D_6, 125 MHz) δ 32.3, 31.8, 31.3, 30.7, 30.3, 18.9, 18.5, −0.2; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ −43.0; HRMS (EI) m/z calcd for $C_{14}H_{30}Si$ (M^+): 226.2117, found 226.2121. Anal. Calcd for $C_{14}H_{30}Si$: C, 74.25; H, 13.35. Found:[30] C, 72.94; H, 13.76.

1,1-Di-*tert*-butyl-2-(*N*-*tert*-butylimino)-3-(*n*-butyl)silacyclobutane (5a). Prepared in a similar manner as *cis*-**2**, except that the reaction mixture was heated at 91 °C for 4 h. The product was isolated as a clear liquid (115 mg, 94%): IR (thin film) 2858, 1638, 1468, 818 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz) δ 2.62 (m, 1H), 2.19 (m, 1H), 1.49 (m, 1H), 1.31 (m, 4H), 1.24 (s, 9H), 1.23 (dd, J = 15.1, 11.2, 1H), 1.04 (s, 9H), 1.03 (s, 9H), 0.92 (t, J = 6.4, 3H), 0.69 (dd, J = 15.0, 8.6, 1H); ^{13}C

(28) Weber, W. P.; Gokel, G. W. *Tetrahedron Lett.* **1972**, 1637−1640.
(29) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355−1356.

(30) Repeated attempts to obtain satisfactory elemental analysis were unsuccessful. Silicon carbide formation could prevent proper analyses.

NMR (C_6D_6, 125 MHz) δ 182.9, 56.8, 52.0, 34.7, 30.2, 29.6, 29.00, 28.96, 23.3, 21.0, 19.8, 14.6, 11.9 ($^1J_{Si-C}$ = 45.3); ^{29}Si NMR (C_6D_6, 99.3 MHz) δ 34.4; HRMS (CI/isobutane) calcd for $C_{19}H_{39}NSi$ (M^+) 309.2852, found 309.2855. Anal. Calcd for $C_{19}H_{39}NSi$: C, 73.71; H, 12.70; N, 4.52. Found: C, 73.46; H, 12.89; N, 4.59.

1,1-Di-*tert*-butyl-2-(*N*-*tert*-butylimino)-3-(2-propyl)silacyclobutane (5b). Prepared in a similar manner as *cis*-**2**, except that the reaction mixture was heated at 121 °C for 9 h. The product was isolated as a 92:8 mixture of regioisomers (as determined by ^{1}H NMR spectroscopy) as a clear liquid (0.24 g, 98%). The structure of the minor isomer was assigned using GCMS: IR (thin film) 2961, 1636, 1467, 819 cm^{-1}. Major regioisomer: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.63 (dt, J = 10.6, 4.5, 1H), 2.33 (m, 1H), 1.23 (s, 9H), 1.10 (s, 18H), 0.98 (m, 2H), 0.90 (d, J = 6.9, 3H), 0.77 (d, J = 6.8, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 184.9, 56.8, 56.7, 29.9, 29.8, 29.0, 28.9, 22.2, 20.4, 19.6, 16.6, 5.0; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ 32.3; HRMS (EI/GC-MS) calcd for $C_{18}H_{37}NSi$ (M^+) 295.2695, found 295.2704. Anal. Calcd for $C_{18}H_{37}NSi$: C, 73.14; H, 12.62; N, 4.74. Found:[30] C, 72.57; H, 13.02; N, 4.29. Minor regioisomer: HRMS (CI/isobutane) calcd for $C_{18}H_{37}NSi$ (M^+) 295.2695, found 295.2694.

1,1-Di-*tert*-butyl-2-(*N*-*tert*-butylimino)-3-(*tert*-butyl)silacyclobutane (5c). Prepared in a similar manner as *cis*-**2**, except that the reaction mixture was heated at 127 °C for 4 h. The product was isolated as an 86:14 mixture of regioisomers (as determined by ^{1}H NMR spectroscopy) as a clear liquid (140 mg, 97%). The structure of the minor isomer was assigned using GCMS and ^{1}H NMR spectroscopy. IR (thin film) 2962, 1634, 1358, 1472, 818 cm^{-1}. Major regioisomer: ^{1}H NMR (C_6D_6, 500 MHz) δ 2.53 (t, J = 11.1, 1H), 1.23 (s, 9H), 1.17 (s, 9H), 1.040 (s, 9H), 1.037 (s, 9H), 0.98 (m, 2H); ^{13}C NMR (C_6D_6, 125 MHz) δ 181.8, 61.2, 57.2, 36.3, 29.9, 29.3, 29.1, 28.2, 22.1, 19.6, 8.6; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ 29.6; HRMS (CI/isobutane) calcd for $C_{19}H_{39}NSi$ (M^+) 309.2852, found 309.2857. Anal. Calcd for $C_{19}H_{39}NSi$: C, 73.71; H, 12.70; N, 4.52. Found: C, 73.53; H, 12.67; N, 4.73. Minor Regioisomer: ^{1}H NMR (C_6D_6, 500 MHz) δ 3.14 (dd, J = 15.6, 10.6, 1H), 2.61 (dd, J = 15.5, 14.1, 1H), 1.92 (dd, J = 14.1, 10.6, 1H), 1.29 (s, 9H), 1.19 (s, 9H), 1.15 (s, 9H), 1.03 (s, 9H); HRMS (CI/isobutane) calcd for $C_{19}H_{39}NSi$ (M^+) 309.2852, found 309.2853.

1,1-Di-*tert*-butyl-2-[*N*-(4-tolyl)amino]-3,4-dimethylsilacyclobut-2-ene (6). Catalyzed Tautomerization of *cis*-2. To a bomb were added *cis*-**2** (50 mg, 0.16 mmol), $PdCl_2(PPh_3)_2$ (2.6 mg, 3.7×10^{-3} mmol), and 1.2 mL of benzene. The vessel was sealed and placed in an 85 °C oil bath for 24 h. The reaction mixture was cooled and concentrated in vacuo, and then the product was dissolved in hexanes (5 mL) and decanted from the insoluble inorganic material. Concentration in vacuo gave **6** (47 mg, 94%) as a red viscous oil: IR (thin film) 3405, 2858, 1607, 1520, 1471, 818 cm^{-1}; ^{1}H NMR (C_6D_6, 500 MHz) δ 6.94 (d, J = 8.1, 2H), 6.65 (d, J = 8.4, 2H), 5.22 (br-s, 1H), 2.14 (s, 3H), 1.81 (qd, J = 7.4, 1.1, 1H), 1.51 (d, J = 1.2, 3H), 1.31 (d, J = 7.4, 3H), 1.22 (s, 9H), 1.14 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.0, 137.2, 129.5, 129.3, 127.3, 113.6, 29.5, 28.8, 24.1, 21.1, 20.8, 20.4, 15.1, 11.8; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ 17.8; HRMS (CI/isobutane) calcd for $C_{20}H_{33}NSi$ (M^+) 315.2382, found 315.2384. Anal. Calcd for $C_{20}H_{33}NSi$: C, 76.12; H, 10.54; N, 4.44. Found: C, 75.94; H, 10.27; N, 4.21.

1,1-Di-*tert*-butyl-2-(*N*-*tert*-butylamino)-3,4-dimethylsilacyclobut-2-ene (7). Representative Procedure for the Thermal Tautomerization of Iminosilacyclobutanes 2 and 3. To a bomb were added *cis*-**3** (71 mg, 0.23 mmol) and 1.4 mL of benzene. The vessel was sealed and placed in a 169 °C oil bath for 20 h. The reaction mixture was cooled and concentrated in vacuo to give **7** (71 mg, 100%) as a yellow liquid: IR (thin film) 3444, 2859, 1472, 819 cm^{-1}; ^{1}H NMR (C_6D_6, 500 MHz) δ 2.88 (br-s, 1H), 1.71 (q, J = 7.5, 1H), 1.51 (d, J = 1.0, 3H), 1.30 (d, J = 7.4, 3H), 1.24 (s, 9H), 1.17 (s, 9H), 1.12 (s, 9H); ^{13}C NMR (C_6D_6, 125 MHz) δ 142.5, 129.3, 50.5, 30.8, 29.8, 29.4, 24.1, 21.6, 21.5, 15.7, 11.1; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ 16.6; HRMS (CI/isobutane) calcd for $C_{17}H_{35}NSi$ (M^+) 281.2539, found 281.2533. Anal. Calcd for $C_{17}H_{35}NSi$: C, 72.52; H, 12.53; N, 4.97. Found:[30] C, 70.92; H, 12.40; N, 4.21.

Synthesis of Cis Aldehyde 10 and Cis Hemiacetal Epimers 11 (eq 6). Representative Procedure for the Hydrolysis of Iminosilacyclobutanes. To a 0 °C solution of *cis*-**3** (0.24 g, 0.85 mmol) in 5.0 mL of THF was added 2.0 mL of $CuSO_4$ (saturated aqueous solution) dropwise, and the mixture was stirred overnight at ambient temperature. The reaction mixture was partitioned between 10 mL of water and 15 mL of ether. The ether layer was concentrated in vacuo, dissolved in 10 mL of CH_2Cl_2, dried over Na_2SO_4, and concentrated in vacuo. Purification by column chromatography (10:90 EtOAc:hexanes) yielded 0.19 g (92%) of a clear liquid of **10** and **11** as a 1.4:1 mixture (as determined by ^{1}H NMR spectroscopy).[24] Analytical data were obtained for the mixture of **10** and **11**; resonances from the ^{1}H NMR spectrum can be assigned to a particular isomer: IR (thin film) 3384, 2859, 1715, 1471, 822, cm^{-1}; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 207.6, 102.2, 48.9, 43.6, 28.8, 28.5, 28.1,[31] 21.6, 21.4, 21.3, 21.2, 20.2, 18.5, 14.0, 13.6, 12.4, 11.5; HRMS (CI/NH_3) calcd for $C_{13}H_{27}O_2Si$ (M^+ − H) 243.1780, found 243.1780; Cis aldehyde (**10**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.66 (d, J = 2.5, 1H), 2.66 (m, 1H), 2.37 (br-s, 1H), 1.53 (m, 1H) 1.24 (d, J = 7.0, 3H) 1.16 (d, J = 7.9, 3H), 1.08 (s, 9H), 1.047 (s, 9H). Major hemiacetal epimer (**11**): Hemiacetal **11** was determined to be a 3.3:1 ratio of epimers by ^{1}H NMR spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.05 (d, J = 7.0, 1H), 4.37 (br-s, 1H), 2.01 (m, 1H), 1.53 (m, 1H), 1.09 (s, 12H), 1.050 (s, 9H), 1.02 (d, J = 7.2, 3H).

Hemiacetal Epimers 8. These compounds were prepared from iminosilacyclobutane *trans*-**3** using the procedure described for the synthesis of **10** and **11**. The products were formed in 66% isolated yield. The spectral data for this compound matched the reported values.[15]

1-Oxa-*cis*-3,4-dimethyl-5-acetoxy-2,2-di-*tert*-butylsilacyclopentane (12). To a stirred solution of hemiacetal **10** and aldehyde **11** (0.16 g, 0.65 mmol) in 10 mL of CH_2Cl_2 were added triethylamine (2 mL, 14 mmol), acetic anhydride (1 mL, 11 mmol), and a few crystals of (dimethylamino)pyridine. The reaction mixture was stirred at ambient temperature for 20 h, concentrated in vacuo, and directly purified by flash chromatography (10:90 EtOAc:hexanes) to afford **12** (0.17 g, 91%) as a clear liquid. This material was determined to be a 1:1 mixture of epimers by ^{1}H NMR spectroscopy.[24] IR and combustion analysis data were obtained for the mixture of diastereomers: IR (thin film) 2935, 1753, 1474, 1364, 1234, 822 cm^{-1}. Anal. Calcd for $C_{15}H_{30}O_3Si$: C, 62.89; H, 10.56. Found: C, 62.81; H, 10.50. Epimer A: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.94 (d, J = 4.4, 1H), 2.25 (m, 1H), 2.05 (s, 3H), 1.65 (m, 1H), 1.13 (d, J = 8.1, 3H), 1.10 (s, 9H), 1.06 (s, 9H), 1.01 (d, J = 7.4, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.3, 101.7, 42.0, 28.5, 28.2, 21.4, 21.0, 20.4, 17.6, 12.7, 11.2; ^{29}Si NMR ($CDCl_3$, 99.3 MHz) δ 32.4; HRMS (EI-GC) calcd for $C_{13}H_{26}OSi$ ($M^+ - C_2H_4O_2$) 226.1753, found 226.1755. Epimer B: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.18 (d, J = 4.3, 1H), 2.38 (m, 1H), 2.04 (s, 3H), 1.36 (m, 1H), 1.20 (d, J = 8.0, 3H), 1.11 (s, 9H), 1.01 (s, 9H), 0.98 (d, J = 7.1, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.4, 99.6, 40.1, 28.7, 28.0, 21.24, 21.19, 20.8, 17.4, 12.2, 10.9; ^{29}Si NMR ($CDCl_3$, 99.3 MHz) δ 36.5; (EI-GC) calcd for $C_{13}H_{26}OSi$ ($M^+ - C_2H_4O_2$) 226.1753, found 226.1753.

Representative Procedure for the Lithium Aluminum Hydride Reduction of Hemiacetals. Reduction of 8 To Provide 13 and 14 (eq 8). To a 0 °C solution of hemiacetal **8** (160 mg, 0.67 mmol) in 6.0 mL of THF was added $LiAlH_4$ (74 mg, 1.9 mmol). The reaction mixture was stirred at 0 °C for 2 h, then quenched with 25 mL of water, and extracted with ether (2 × 25 mL). The combined organic layers were concentrated in vacuo, dissolved in 15 mL of CH_2Cl_2, dried over Na_2SO_4, concentrated in vacuo, and purified by column chromatography (30:70 EtOAc:hexanes) to yield **13** (61 mg, 37%) as a clear liquid and **14** (50 mg, 33%) as a white solid. **3,4-*trans*-Dimethyl-2,2-di-*tert*-butyl-1-oxa-2-silacyclopentane (13).** IR (thin film) 2932, 1472, 1033, 822, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.07 (dd, J = 9.3, 6.7, 1H), 3.24 (dd, J = 11.1, 9.3, 1H), 1.85 (m, 1H), 1.21 (d, J = 7.5, 3H), 1.05 (s,

(31) Two carbons are overlapping.

9H), 1.03 (s, 9H), 0.93 (d, $J = 6.4$, 3H), 0.80 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 74.3, 41.2, 27.93, 27.86, 25.1, 21.3, 21.1, 15.4, 12.6; ^{29}Si NMR ($CDCl_3$, 99.3 MHz) δ 28.7; HRMS (CI/isobutane) calcd for $C_{13}H_{28}OSi$ (M^+) 228.1909, found 228.1912. Anal. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35. Found: C, 68.34; H, 12.11. ***trans*-2-Methyl-3-di-*tert*-butylhydroxysilyl-butan-1-ol (14).** mp = 99−100 °C; IR (thin film) 3260, 2858, 1474, 1016, 820, 670 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.67 (dd, $J = 10.4$, 4.3, 1H), 3.41 (dd, $J = 10.4$, 7.1, 1H), 2.66 (br-s, 1H), 2.00 (m, 1H), 1.65 (br-s, 1H), 1.19 (m, 1H), 1.11 (d, $J = 7.7$, 3H), 1.08 (s, 9H), 1.04 (s, 9H), 0.95 (d, $J = 7.0$, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 68.9, 36.5, 28.9, 28.5, 21.9, 21.3, 20.8, 15.9, 12.9; ^{29}Si NMR ($CDCl_3$, 99.3 MHz) δ 10.5; HRMS (CI/NH_3) calcd for $C_{13}H_{31}O_2Si$ ($M^+ + H$) 247.2093, found 247.2094. Anal. Calcd for $C_{13}H_{30}O_2Si$: C, 63.35; H, 12.27. Found: C, 63.45; H, 12.25.

***cis*-2-Methyl-3-di-*tert*-butylhydroxysilyl-butan-1-ol (15).** Prepared in a similar manner as **13** and **14**. Purification by column chromatography (20:80 EtOAc:hexanes) yielded **15** (54 mg, 66%) as a white solid: mp = 88−89 °C; IR (KBr) 3281, 2858, 1468, 1030, 824, 658 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 5.17 (s, 1H), 4.39 (t, $J = 4.8$, 1H), 3.50 (dt, $J = 9.8$, 4.7, 1H), 3.23 (ddd, $J = 10.1$, 7.3, 5.0, 1H), 1.83 (m, 1H), 1.07 (m, 1H), 1.01 (d, $J = 7.9$, 3H), 1.00 (s, 9H), 0.97 (d, $J = 6.8$, 3H), 0.96 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 65.8, 36.8, 28.9, 28.1, 22.7, 21.8, 21.4, 17.0, 12.1; ^{29}Si NMR ($CDCl_3$, 99.3 MHz) δ 10.8; HRMS (CI/isobutane) calcd for $C_{13}H_{30}O_2Si$ ($M^+ + H$) 247.2093, found 247.2100. Anal. Calcd for $C_{13}H_{30}O_2Si$: C, 63.35; H, 12.27. Found: C, 63.44; H, 12.35.

3,4-*trans*-Dimethyl-5-(*tert*-butylimino)-6-(α-hydroxy-β-trifluoromethyl)-2,2-di-*tert*-butyl-1-oxa-2-silacyclohexane (16). To a solution of *trans*-**3** (110 mg, 0.40 mmol) in 1.5 mL of dry THF were added trifluoroacetic acid (5−7 drops) and 0.5 mL of water. The reaction mixture was stirred for 30 min and then was made basic with excess K_2CO_3. Water (5 mL) was added, and the mixture was extracted with ether (20 mL). The organic layer was washed with 15 mL of sat aqueous NaCl solution and concentrated in vacuo. The resulting material was dissolved in 15 mL of CH_2Cl_2, dried over Na_2SO_4, concentrated in vacuo, and purified by column chromatography (10:90 EtOAc:hexanes) to yield **16** (94 mg, 60%) as a clear liquid and hemiacetal **8** (12 mg, 12%) as a white solid. The *trans*-methyl stereochemistry of **16** was determined by homonuclear NOE spectroscopy, and the stereochemistry about the epimeric center was determined using $^1H(^{19}F)$ difference NOE spectroscopy: IR (KBr) 3448, 2974, 1664, 1164, 823 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.89 (br-s, 1H), 2.74 (m, 1H), 1.33 (m, 1H), 1.13 (d, $J = 7.2$, 3H), 1.10 (s, 9H), 1.07 (s, 9H), 1.00 (s, 9H), 0.93 (d, $J = 7.5$, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.1, 122.7 ($^1J_{C-F} = 287.0$), 92.6 ($^2J_{C-F} = 33.5$), 57.7, 38.9, 30.3, 28.4, 28.3, 21.6, 21.4, 20.9, 20.5, 15.9; ^{19}F NMR (C_6D_6, 376.3 MHz) δ -80.5; ^{29}Si NMR ($CDCl_3$, 99.3 MHz) δ 9.8; HRMS (CI/isobutane) calcd for $C_{19}H_{36}NO_2F_3Si$ (M^+) 395.2469, found 395.2469. Anal. Calcd for $C_{19}H_{36}NO_2F_3Si$: C, 57.69; H, 9.17; N, 3.54. Found: C, 57.95; H, 9.11; N, 3.55.

Trifluoroacetic Acid Hydrolysis of Iminooxasilacyclohexane 16 To Provide 17a,b. To a solution of **16** (110 mg, 0.27 mmol) in 6 mL of THF were added trifluoroacetic acid (0.5 mL, 6.5 mmol) and 0.5 mL of water, and the mixture was heated at reflux for 30 min. The reaction mixture was cooled and neutralized with excess K_2CO_3. Water was added (5 mL), and the mixture was extracted with ether (15 mL). The organic layer was concentrated in vacuo, dissolved in CH_2Cl_2 (15 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification by column chromatography (10:90 EtOAc:hexanes) gave **17a** (35 mg, 38%) as a white solid, **17b** (28 mg, 30%) as a clear oil, and recovered starting material **16** (16 mg, 15%). The ketooxasilacyclohexanes equilibrated to a 1:10 (**17a**:**17b**) ratio in $CDCl_3$ solution after several days. The *trans*-methyl stereochemistry of **17a** and **17b** was determined by homonuclear NOE spectroscopy, and the stereochemistry about the epimeric carbon center required the use of $^1H(^{19}F)$ difference NOE spectroscopy. **17a**: mp = 99−104 °C; IR (KBr) 3385, 2966, 2864, 1729, 1204, 1112, 894 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz) δ 3.10 (br-s, 1H), 2.98 (m, 1H), 1.17 (m, 1H), 1.01 (s, 9H), 0.96 (d, $J = 6.5$, 3H), 0.88 (s, 9H), 0.85 (d, $J = 7.5$, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 202.8, 122.6 ($^1J_{C-F} = 286.0$), 92.9 ($^2J_{C-F} = 31.0$), 43.0, 28.2, 27.5, 25.5, 21.9, 20.7, 13.9, 13.2; ^{19}F NMR (C_6D_6, 376.3 MHz) δ -81.7; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ 12.2; HRMS (CI/isobutane) calcd for $C_{15}H_{27}O_3F_3Si$ (M^+) 340.1682, found 340.1691. **17b**: IR (thin film) 3473, 2939, 1728, 1475, 1181, 930, 823 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz) δ 4.83 (br-s, 1H), 3.02 (m, 1H), 1.07 (s, 9H), 0.96 (m, 1H), 0.92 (d, $J = 6.3$, 3H), 0.87 (d, $J = 7.1$, 3H), 0.85 (s, 9H); ^{13}C NMR (C_6D_6, 125 MHz) δ 208.8, 122.5 ($^1J_{C-F} = 287.7$), 94.2 ($^2J_{C-F} = 33.4$), 94.2, 44.8, 27.9, 27.4, 24.8, 22.1, 20.5, 13.5, 12.5; ^{19}F NMR (C_6D_6, 376.3 MHz) δ -81.4; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ 13.5; HRMS (CI/isobutane) calcd for $C_{15}H_{27}O_3F_3Si$ (M^+) 340.1682, found 340.1685. Anal. Calcd for $C_{15}H_{27}O_3F_3Si$: C, 52.92; H, 7.99. Found: C, 53.21; H, 8.01.

Imine 18. To a 0 °C solution of *cis*-**3** (221 mg, 0.79 mmol) in THF (6 mL) was added water (1 mL). The reaction mixture was stirred for 3 h at 0 °C, brine (10 mL) was added, and the mixture was extracted with ether (2 × 10 mL). The organic phases were concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (20 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo to give **18** as a clear liquid: IR (thin film) 3355, 2967, 1666, 1473, 821 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.55 (d, $J = 4.9$, 1H), 6.40 (br-s, 1H), 2.86 (m, 1H), 1.30 (m, 1H), 1.23 (d, $J = 7.1$, 3H), 1.20 (s, 9H), 1.11 (d, $J = 7.8$, 3H), 1.05 (s, 9H), 1.02 (s, 9H); ^{13}C NMR (C_6D_6, 125 MHz) δ 166.3, 56.9, 40.4, 29.5, 29.4, 28.7, 24.9, 21.85, 21.78, 17.7, 13.0. Hydrolysis according to representative procedure for the hydrolysis of iminosilacyclobutanes provided a mixture of **10**, **11** (as a 3:1 mixture of anomers) along with 10% of **8** (as a 4:1 mixture of anomers) in 82% isolated yield.

Acknowledgment. This research was supported by the National Institutes of Health (General Medical Sciences). K.A.W. thanks the American Cancer Society, the Research Corporation, Glaxo-Wellcome, and the Camille and Henry Dreyfus Foundation for awards to support research. We thank Dr. Jiejun Wu for assistance with the ^1H-{^{19}F} NOE difference experiments, and Dr. John Greaves and Dr. John Mudd for mass spectrometric data.

Supporting Information Available: ^1H and ^{13}C NMR spectra for **4b**, **4c**, **5b**, **7**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO9816257