suspension was stirred at 25 °C for 46 h during which it slowly dissolved. The reaction mixture was partitioned between 250 mL of Et_2O and 200 mL of 1:1 (v/v) water–$NaHCO_3$ (saturated). The aqueous phase was extracted with 200 mL of Et_2O, and the combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure to yield **54** as a white solid (6.70 g, 13.56 mmol, 82%). An analytical sample was recrystallized from CH_2Cl_2–heptane to give white warts: mp 154–155.5 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 2.38 (s, 3 H, $ArCH_3$), 3.85 (s, 3 H, OCH_3), 4.60 (s, 2 H, CH_2), 7.04 (s, 1 H, furan H), 7.15 (d, 1 H, ArH, J = 2.2 Hz), 7.65 (d, 1 H, ArH, J = 2.2 Hz); MS (70 eV, 190 °C) m/e M^+ (^{79}Br) 492 (22). Anal. Calcd for $C_{22}H_{22}Br_2O_3$: C, 53.47; H, 4.49. Found: C, 53.54; H, 4.48.

24,25-Dimethoxy-8,22-dimethyl-12,15,18,26-tetraoxatetracyclo[18.3.1.1^{2,5}.1^{6,10}]hexacosa-1(24),2,4,6,8,10(25),20,22-octaene (9). To a refluxing suspension of 974 mg (w/oil) of NaH (20.30 mmol) in 250 mL of dry THF was added dropwise under high dilution over 30 h a solution of 2.342 g (4.74 mmol) of dibromide **54** and 517 mg (4.87 mmol) of dry diethylene glycol in 215 mL of THF. Reflux was maintained an additional 41 h. The reaction mixture was cooled, the excess NaH was quenched with water, and the products were partitioned between 100 mL of Et_2O and 100 mL of water. The aqueous layer was extracted with 250 mL of Et_2O, and the combined organic phases were washed with 200 mL of ion-free water, dried ($MgSO_4$), and evaporated in vacuo. The residue was taken up in CH_2Cl_2 and chromatographed on silica gel. Concentration of the eluate with a retention volume between 146 and 173 mL provided a solid that was washed with pentane and dried in vacuo. The cycle, thus obtained, was a fine, white solid pure by ^1H NMR (661 mg, 1.51 mmol, 32%). An analytical sample was purified by recrystallization from CH_2Cl_2–heptane to give fine, fluffy, white needles: mp 147–148 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 2.30 (s, 3 H, $ArCH_3$), 3.50 (s, 3 H, OCH_3), 3.55–3.72 (m, 4 H, OCH_2), 4.55 (s, 2 H, $ArCH_2O$), 6.56 (s, 1 H, furan H), 7.00 (d, 1 H, ArH, J = 2.0 Hz), 7.16 (d, 1 H, ArH, J = 2.0 Hz); MS (70 eV, 190 °C) m/e M^+ 438 (100). Anal. Calcd for $C_{26}H_{30}O_6$: C, 71.21; H, 6.90. Found: C, 71.25; H, 6.86.

Crystal Structure Data. Compound **1** crystallized from CH_2Cl_2–CH_3OH–C_2H_5OH as colorless platelets in the monoclinic system $P2_1/c$. Unit cell dimensions are as follows: a = 13.936 (2) Å, b = 23.699 (3) Å, c = 18.599 (2) Å, β = 104.618 (4)°, V = 5944 Å^3, Z = 4. The crystal was examined on a modified Syntex P$\bar{1}$ diffractometer with Cu Kα radiation at 25 °C. The structure was determined by direct methods. Refinement of 208 parameters (4340 reflections with $I > 3\sigma(I)$) has an agreement value R currently at 0.097. Compound **2** crystallized from acetone–H_2O as very thin colorless platelets in the triclinic system P$\bar{1}$. Unit cell dimensions are as follows: a = 7.672 (1) Å, b = 9.243 (1) Å, c = 20.329 (3) Å, α = 100.151 (6)°, β = 94.383 (6)°, γ = 97.725 (6)°, V = 1403 Å^3, Z = 2. The crystal was examined on a modified Picker FACS-1 diffractometer with Mo Kα radiation at 25 °C. The structure was determined by direct methods. Refinement of 206 parameters (1905 reflections with $I > 3\sigma(I)$) has an agreement value currently at 0.075.

Compound **2**·$NaSbF_6$·CCl_4 crystallized from CCl_4–acetone as colorless multifaceted crystals in the monoclinic system $P2_1/n$. Unit cell dimensions are as follows: a = 13.5025 (6) Å, b = 15.1959 (7) Å, c = 18.9251 (8) Å, β = 92.411 (1)°, V = 3880 Å^3, Z = 4. The crystal was examined on a modified Picker FACS-1 diffractometer with Mo Kα radiation at 25 °C. The structure was determined by direct methods. Refinement of 318 parameters (4743 reflections with $I > 3\sigma(I)$) has an agreement value currently at 0.04.

Compound **4** crystallized from $CHCl_3$–C_2H_5OH as colorless parallelepipeds in the triclinic system P$\bar{1}$. Unit cell dimensions are as follows: a = 11.172 (4) Å, b = 11.895 (3) Å, c = 10.358 (3) Å, α = 111.71 (2)°, β = 93.08 (3)°, γ = 102.24 (3)°, V = 1236 Å^3, Z = 2. The crystal was examined on a Syntex P$\bar{1}$ diffractometer with Mo Kα radiation at 25 °C. The structure was determined by direct methods. Refinement of 343 parameters (3268 reflections with $I > 3\sigma(I)$) has an agreement value currently at 0.092.

Compound **6** crystallized from acetone–methanol as colorless needles in the monoclinic system $P2_1/a$. Unit cell dimensions are as follows: a = 7.304 (1) Å, b = 33.050 (5) Å, c = 11.068 (2) Å, β = 95.874 (5)°, V = 2658 Å^3, Z = 4. The crystal was examined on a modified Picker diffractometer with Mo Kα radiation at 25 °C. The structure was determined by direct methods. Refinement of 219 parameters (1925 reflections with $I > 2\sigma(I)$) has an agreement value currently at 0.11.

Compound **6**·$NaSbF_6$ crystallized from CH_2Cl_2–benzene as colorless parallelepipeds in the monoclinic system $P2_1/c$. Unit cell dimensions are as follows: a = 17.737 (2) Å, b = 11.366 (1) Å, c = 18.290 (2) Å, β = 117.208 (3)°, V = 3266 Å^3, Z = 4. The crystal was examined on a modified Picker FACS-1 diffractometer, with Mo Kα radiation at 25 °C. The structure was determined by direct methods. Refinement of 276 parameters (3120 reflections with $I > 3\sigma(I)$) has an agreement value currently at 0.05.

Further crystallographic details will be published elsewhere.

Acetylsilane *O*-Silylcyanohydrins as Precursors to α-Silyl Ketones and β-Siloxy-*N*,*N*-bissilylenamines

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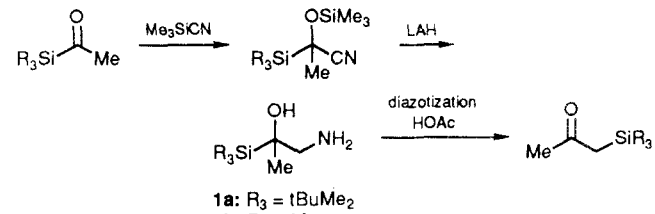
Reduction of acetylsilane *O*-silylcyanohydrins gave β-amino-α-hydroxysilanes, which were diazotized to give α-silyl ketones. The addition of organolithium reagents to the cyanohydrins was accompanied by sequential C → N and O → N silyl group migrations. Silylation of the resulting lithium enolates afforded β-siloxy-*N*,*N*-bissilylenamines.

Introduction

We have previously shown[1] that certain α,β-dihydroxysilanes undergo a proton-induced silapinacol rearrangement to afford α-(*tert*-butyldimethylsilyl) aldehydes and ketones, species that are synthetically useful as vinyl cation equivalents.[2] The less-hindered, but much more economical trimethylsilyl analogues, however, are unstable to the acidic conditions necessary for their formation,[1,3] and alternative approaches to these species were sought.

Scheme I

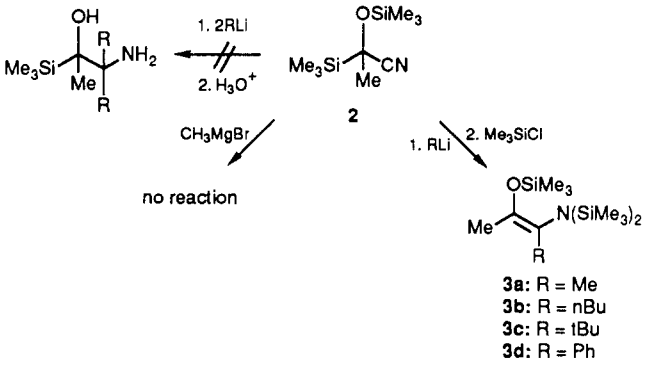


1a: R_3 = $tBuMe_2$
1b: R_3 = Me_3

(1) Cunico, R. F. *Tetrahedron Lett.* **1986**, *27*, 4269.
(2) (a) Colvin, E. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988. (b) Hudrlick, P. F.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 6251.

0022-3263/90/1955-4634$02.50/0

Scheme II



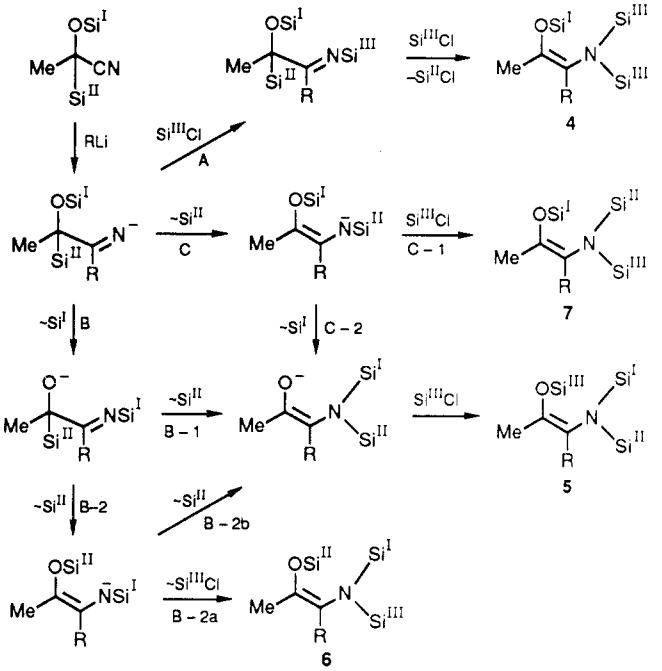
Within this context, it appeared that β-amino-α-hydroxysilanes might serve as appropriate α-silyl ketone precursors in a Tiffeneau–Demjanov reaction[4] requiring only mildly acidic conditions for rearrangement to occur via diazotization (Scheme I).

Results and Discussion

Parent members of this new class of compounds (**1a,b**) were prepared by reduction of the *O*-(trimethylsilyl)-cyanohydrins of acetylsilanes, and diazotization conditions were then indeed found (see Experimental Section) that allowed the conversion of **1a**, and more significantly **1b**, into the corresponding α-silyl ketones. Encouraged by these preliminary results, we investigated the protocols of Scheme II in an attempt to construct a series of substituted β-amino-α-hydroxysilanes. Although Grignard reagents are reported to add in high yield to *O*-(trimethylsilyl)-cyanohydrins of aldehydes,[5] **2** was found to be unreactive toward methylmagnesium bromide. Attention then turned to the report[6] that *O*-(trimethylsilyl)cyanohydrins undergo addition of 2 equiv of organolithium reagents to afford β,β-disubstituted-β-amino alcohols. Treatment of **2** in this manner did not lead to the desired product after hydrolysis, but if trimethylsilylation was carried out followed by an anhydrous workup, compounds of rearranged structure (**3**) were obtained in synthetically useful yields (60–90%).[7] All attempts to inhibit rearrangement by operating at low temperatures failed, and essentially identical results were obtained whether slightly in excess of 1 or 2 equiv of organolithium reagent were used. Only one stereoisomer has been found for each of the products **3a–d**, and these were originally assigned *Z* stereochemistry on the basis of mechanistic considerations (see below). Subsequent ROESY[8] experiments on **3a** confirmed this assignment; the two groups of allylic protons display a 20–25% NOE relative to each other, while trimethylsilyl group absorptions were not enhanced upon methyl group irradiations.

Since both the overall rearrangement and the β-siloxy-*N,N*-bissilylenamine products are novel,[9] some details of this transformation were investigated. A priori, this system presents an array of mechanistic possibilities. As Scheme III indicates, routes leading to four distribution patterns within **3** for the original O (Si^I), C (Si^{II}), and derivatizing (Si^{III}) silyl functions may be reasonably postulated (**4–7**). Route A assumes that silylation of an (unrearranged) imino anion is followed by structural rearrangement via allylic silyl group exchange, analogous to a known, but much slower, rearrangement of α-(trimethylsilyl) *N*-alkylimines.[10] Route B is suggested on the basis of relative anion stability, although bond strength considerations are in opposition;[11] if realized, routes B-1 and B-2 are then seen as possibilities. The former is unprecedented, while the latter represents a modified Brook rearrangement[12] to a 1-azaallyl anion, which could proceed to product by routes B-2a or B-2b. Finally, as an alternative to the above, the initial adduct may rearrange along pathway C (C-1, C-2). Support for this last direction comes from reports[13] that aryl-substituted α-(trimethylsilyl) *N*-lithioimines undergo a rapid 1,3 (C → N) silyl group rearrangement identical with the step initiating route C.

Scheme III



In an attempt to select among these possibilities, we have employed a series of acetylsilane cyanohydrins containing different silyl groups at O and C in the alkylation–silylation sequence, and these results are summarized in Table I. Again, only one stereoisomer each of the resulting β-siloxy-*N,N*-bissilylenamines (**12–17**) was obtained, and these are assumed to have *Z* configuration by analogy to **3a**. The ^1H NMR spectra of **12–17** are in the main unremarkable, and the location of silyl groups at

(3) Larson, G. L.; Hernandez, D.; Montes de Lopez-Cepero, I.; Torres, L. E. *J. Org. Chem.* **1985**, *50*, 5260. Also see ref 2a.

(4) (a) Smith, P. A. S.; Baer, D. R. *Org. React.* **1961**, *11*, 157. (b) Weller, T.; Seebach, D.; Davis, R. E.; Laird, B. B. *Helv. Chim. Acta* **1981**, *64*, 736.

(5) Gill, M.; Kiefel, M. J.; Lally, D. A. *Tetrahedron Lett.* **1986**, *27*, 1933.

(6) Amoureux, R.; Axiotis, G. P. *Synthesis* **1981**, 270.

(7) In one instance (RLi = PhLi), the product (**3d**) was accompanied by 1-(trimethylsiloxy)-1-(trimethylsilyl)-1-phenylethane. This probably arises by phenyllithium attack at the *O*-silyl group, cyanide ion expulsion to form acylsilane, and attack at the carbonyl group by a second equivalent of phenyllithium. The other organolithium reagents employed may have competitively formed small amounts of similar byproducts, but this aspect of the reaction was not explored.

(8) Bax, A.; Davis, D. G. *J. Magn. Reson.* **1985**, *63*, 207.

(9) To our knowledge, the closest extant analogue is a β-methoxy-*N,N*-bissilylenamine: Corriu, R. J. P.; Moreau, J. J. E.; Pataud-Sat, M. *Organometallics* **1985**, *4*, 623. β-Alkoxy-*N,N*-dialkylenamines have been reported: Barluenga, J.; Aznar, F.; Liz, R. *Synthesis* **1984**, 304.

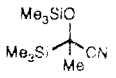
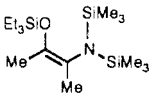
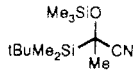
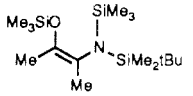
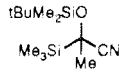
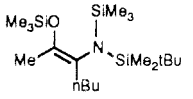
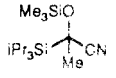
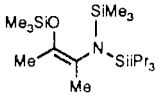
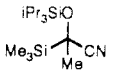
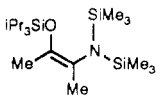
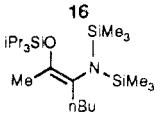
(10) $Me_2C(SiMe_3)CH{=}NR + Me_3SiBr \rightarrow Me_2C{=}CHN(SiMe_3)R$: Belavin, I. Yu.; Fedoseeva, N. A.; Baukov, Yu. I.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1973**, *43*, 443; **1974**, *44*, 569.

(11) Walsh (Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246) lists *D*(Si–O) = 128 and *D*(Si–N) = 100 kcal/mol.

(12) (a) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. (b) For parallel behavior of an allylsilane–(allyloxy)silane anion, see: Hosomi, A.; Hashimoto, H.; Sakurai, H. *J. Org. Chem.* **1978**, *43*, 2551.

(13) (a) Konakahara, T.; Sato, K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1241. (b) Konakahara, T.; Kurosaki, Y. *J. Chem. Res., Synop.* **1989**, 130.

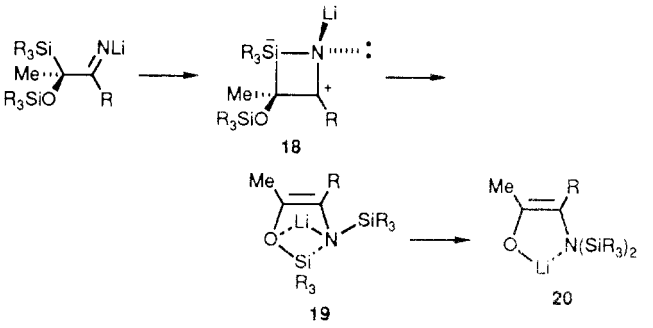
Table I. Alkylation/Silylation of Various Acetylsilane O-Silylcyanohydrins

cyanohydrin	RLi	chloro-silane	product	yield (%)
 2	MeLi	Et_3SiCl	 12	88
 8	MeLi	Me_3SiCl	 13	79
 9	MeLi	Me_3SiCl	13	80
9	nBuLi	Me_3SiCl	 14	72
 10	MeLi	Me_3SiCl	 15	81
 11	MeLi	Me_3SiCl	 16	80
11	nBuLi	Me_3SiCl	 17	37

either the O or N terminus could be deduced from a combination of integration and chemical shift data (OSiMe absorptions were found at lower field than those of NSiMe). In the case of both **13** and **14**, the methyl groups of the *tert*-butyldimethylsilyl function were diastereotopic, a phenomenon we tentatively attribute to slow nitrogen inversion in these compounds relative to the NMR time scale.[14] Similar behavior was displayed by the isopropyl moieties of **15**. Although accidental chemical shift equivalence of these methyl (and methyne) absorptions occurred in the ^1H NMR spectrum, the ^{13}C NMR spectrum displayed separate absorptions for the methyl groups.

With regard to the mechanism by which enamine products arise, the following conclusions may be drawn from the results of Table I: (a) in all instances, the *C*-silyl group of the starting cyanohydrin is emplaced at nitrogen in the product; (b) except for the (most highly hindered[15]) triisopropylsilyl group (in **11**), original *O*-silyl groups are also transferred to nitrogen; (c) thus in every such instance silylative derivitization is occurring at enolate oxygen, a conclusion confirmed by the structure of **12**. The example of **11** aside, these observations are immediately incompatible with structures **4**, **6**, and **7** arising from routes A, B-2a, and C-1, of Scheme III. Bearing in mind the caveat of a possible change in mechanism, the ability of **11** to undergo C → N silyl group rearrangement without accompanying *O*-silyl group migration mitigates against route B in general, and taken together with the fact that **10** rearranges to give **15**, rigorously excludes option B-2b. The evidence of "silyl group following" thus indicates pathway C for an explanation of results. The reaction normally proceeds via C-2 to **5** but is diverted (C-1) to **7** if the *O*-silyl moiety is too crowded for efficient transfer to nitrogen. If this rearrangement is viewed (Scheme IV) as proceeding through a four-membered cyclic transition state (**18**) isoelectronic with the intermediate postulated for the well-studied thermal rearrangement of α-silyl ketones,[16] intramolecular Li–O complexation accompanying C → N silyl group migration may determine its stereochemical outcome. At any rate, such complexation must be involved in promoting Li/Si exchange within **19** and in stabilizing the resulting *Z* enolate **20**. The conversion of amide ion to enolate anion that accompanies the 1, 4 (O → N) silyl group migration serves as an additional counterbalance to the contrathermodynamic component[11] of this rearrangement.

Scheme IV



Experimental Section

General Comments. Methyllithium (MeLi, 1.5 M in ether, LiBr complex), *n*-butyllithium (nBuLi, 2.4 M in hexane), and *tert*-butyllithium (tBuLi, 2.7 M in pentane) were obtained commercially and standardized. Unless indicated otherwise, Kugelrohr distillation (oven temperature given) was used to purify reaction products, and analytical and spectral samples were obtained by preparative VPC. VPC analyses utilized a 2 ft × 0.25 in. 20% SE-30 column. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl immediately prior to use. All reactions were carried out under nitrogen atmosphere. IR spectra were determined on neat films. ^1H and ^{13}C NMR spectra were recorded by using $CDCl_3$ solutions and a Brucker WP 200SY FT spectrometer.

1-Amino-2-(*tert*-butyldimethylsilyl)-2-propanol (1a). A mixture of 2.5 g (9.7 mmol) of **8** and 0.95 g of (25 mmol) of $LiAlH_4$ in 50 mL of ether was refluxed for 16 h. At 0 °C, 2 mL of 15% NaOH was added dropwise, followed by 3 mL of H_2O. The white suspension was filtered through Celite, and the filtrate was dried ($MgSO_4$) and distilled to give 1.6 g (86%) of **1a**, oven temperature 38 °C (0.5 mmHg), which VPC showed contained 10% of a low-boiling component. IR: 3360 br, 1570 br, 1249, 835 cm^{-1}. ^1H NMR: δ, 0.01 (s, 6 H), 0.96 (s, 9 H), 1.21 (s, 3 H), 2.58 (br s, 3 H), 2.73 and 2.98 (AB pattern, J = 13 Hz, 2 H). Anal. Calcd for $C_9H_{23}NOSi$: C, 57.08; H, 12.24. Found: C, 57.12; H, 12.16.

1-Amino-2-(trimethylsilyl)-2-propanol (1b). A solution of 0.53 g (2.5 mmol) of **2** in 5 mL of ether was slowly added to 0.40 g (10 mmol) of $LiAlH_4$ in 20 mL of ether. After 1 h at reflux, water was added very slowly (0.5 mL over 4 h) until the initially gray solid turned completely white. The use of NaOH in the hydrolysis step led to much lower yields. The suspension was filtered through Celite, and the filtrate was dried and evacuated to give 0.38 g of a slightly colored semisolid. Sublimation (50 °C, 2 mmHg, 0 °C cold finger) gave 0.34 g (94%) of **1b** as soft white crystals, mp 33–34.5 °C. IR: 3360 br, 1580 br, 1248, 840 cm^{-1}. ^1H NMR: δ 0.01 (s, 9 H), 1.07 (s, 3 H), 1.61 (br s, 3 H), 2.59 and 2.80 (AB pattern, J = 13 Hz, 2 H). ^{13}C NMR: δ −4.0, 21.6, 48.8, 64.8. Anal.

(14) Data indicating the pyramidal nature of some enamines are given by Brown, K. L.; Damon, L.; Dunitz, J. D.; Eschenmoser, A.; Hobi, R.; Kratky, C. *Helv. Chim. Acta* **1978**, *61*, 3108.

(15) Cartledge, F. A. *Organometallics* **1983**, *2*, 425.

(16) Kwart, H.; Barnette, W. E. *J. Am. Chem. Soc.* **1977**, *99*, 614.

Calcd for $C_6H_{17}NOSi$: C, 48.93; H, 11.63; N, 9.51. Found: C, 49.12; H, 11.88; N, 9.46.

Diazotization of 1a. A solution of 0.30 g of **1a** (90% pure, 1.4 mmol) in 6 mL of acetic acid was treated at once with 0.24 g (3.5 mmol) of sodium nitrite. After 10 min at 25 °C, the mixture was poured into water–pentane and the organic layer washed ($NaHCO_3$) and dried ($MgSO_4$). Distillation gave 0.21 g of **1-(*tert*-butyldimethylsilyl)-2-propanone**, bp 40–42 °C (100 mmHg), which VPC indicated was 80% pure (70% yield). IR: 1692, 1230 cm^{-1}. ^1H NMR: δ 0.06 (s, 6 H), 0.88 (s, 9 H), 2.09 (s, 3 H), 2.21 (s, 2 H). Anal. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70. Found: C, 62.75, H, 11.77.

Diazotization of 1b. Application to **1b** of the procedure used to diazotize **1a** afforded no ketone. The following approach proved successful. A mixture of 0.34 g (2.3 mmol) of sublimed **1b** in 5.0 mL of chloroform and containing 1 g of 3A molecular sieves was stirred 5 min at 25 °C. Glacial acetic acid (0.13 mL, 2.3 mmol) was added followed by isoamyl nitrite (0.27 g, 2.3 mmol), and the mixture was heated to 55 °C for 10 min. The mixture was cooled in ice, and the yield of **1-(trimethylsilyl)-2-propanone**[17] was determined by VPC at 40 °C (the reaction solution was compared to a standard solution of authentic ketone using known volume aliquots). The yield of ketone product was quantitative. Allowing the original reaction mixture to stand at 25 °C resulted in progressive loss of ketone, and the simultaneous appearance of (isoamyloxy)trimethylsilane, presumably due to acid-catalyzed transsilylation.

Cyanotriisopropylsilane. A mixture of chlorotriisopropylsilane (5.78 g, 30 mmol), 18-crown-6 ether (0.4 g), potassium cyanide 6.5 g, 100 mmol), and 20 mL of CH_2Cl_2 was refluxed for 67 h.[18] The cooled solution (25 °C) was filtered under N_2 pressure (glass frit), solvent was removed, and the residue was short-path distilled to give 4.0 g of product, bp 76–78 °C (6 mmHg), which VPC (125 °C) showed consisted of 88% cyanotriisopropylsilane and 12% chlorotriisopropylsilane. IR: 2945 s, 2888 m, 2863 s, 2173 w, 1464 m, 1388 w, 1370 w, 884 m, 687 m, 666 m cm^{-1}. ^1H NMR: δ 1.05–1.3, m. ^{13}C NMR: δ 10.4, 18.1, 124.5. Anal. Calcd for $C_{10}H_{21}NSi$: C, 65.50; H, 11.54; N, 7.64. Found: C, 65.36; H, 11.84; N, 7.50.

General Procedure for O-Silylcyanohydrins. 2-(Trimethylsiloxy)-2-(trimethylsilyl)propanenitrile (2). A mixture of 14.2 g (123 mmol) of acetyltrimethylsilane[19] and 13.4 g (135 mmol) of cyanotrimethylsilane in 150 mL of CH_2Cl_2 was cooled to −78 °C, and 0.22 mL (1.14 mmol) of trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf)[20] in 15 mL of CH_2Cl_2 was added dropwise. After 2 h at −78 °C, pyridine (20 drops) was added and the mixture was stirred an additional 5 min. The solution was then poured into saturated aqueous $NaHCO_3$, and the organic phase was dried ($MgSO_4$) and concentrated. Short-path distillation gave 23.1 g (87%) of **2**, bp 55–56 °C (5 mmHg). IR: 2965 m, 2940 w, 2905 w, 2210 w, 1445 w, 1410 w, 1370 w, 1255 s, 1140 m, 1090 s, 975 s, 845 vs, 755 m, 725 w, 695 w cm^{-1}. ^1H NMR: δ 0.14 (s, 9 H), 0.20 (s, 9 H), 1.51 (s, 3 H). ^{13}C NMR: δ −5.0 ($SiCH_3$), 1.4 ($OSiCH_3$), 23.5 (CH_3), 61.1 (*C*CN), 122.9 (CN). Anal. Calcd for $C_9H_{21}NOSi_2$: C, 50.18; H, 9.82. Found: C, 50.31; H, 9.87.

2-(*tert*-Butyldimethylsilyl)-2-(trimethylsiloxy)propanenitrile (8). From acetyl-*tert*-butyldimethylsilane[21] (5.0 g, 32 mmol), cyanotrimethylsilane (4.1 g, 41 mmol), Me_3SiOTf (0.67 g, 0.058 mL, 0.3 mmol), and 10 drops of pyridine there was obtained 5.1 g (62%) of **8**, bp 90–93 °C (6 mmHg). IR: 2210 w, 1255 s cm^{-1}. ^1H NMR: δ 0.09 (s, 3 H), 0.11 (s, 3 H), 0.20 (s, 9 H), 0.99 (s, 9 H), 1.59 (s, 3 H). Anal. Calcd for $C_{12}H_{27}NOSi_2$: C, 55.97; H, 10.57. Found: C, 55.92; H, 10.66.

2-(*tert*-Butyldimethylsiloxy)-2-(trimethylsilyl)propanenitrile (9). From acetyltrimethylsilane (3.0 g, 26 mmol), *tert*-butylcyanodimethylsilane (4.0 g, 29 mmol), Me_3SiOTf (0.10 mL, 0.52 mmol), and 10 drops of pyridine there was obtained 5.0 g (75%) of **8**, bp 90–94 °C (8 mmHg). IR: 2210 w, 1255 s cm^{-1}. ^1H NMR: δ 0.15 (s, 9 H), 0.19 (s, 3 H), 0.22 (s, 3 H), 0.85 (s, 9 H), 1.51, s, 3 H. ^{13}C NMR: δ −4.9 ($SiCH_3$), −3.9 ($OSiCH_3$), −2.9 ($OSiCH_3$), 18.1 (*C*CH_3), 23.4 (CH_3), 25.5 (C*C*H_3), 61.2 (*C*CN), 122.9 (CN). Anal. Calcd for $C_{12}H_{27}NOSi_2$: C, 55.97; H, 10.57; N, 5.44. Found: C, 56.04; H, 10.67; N, 5.46.

2-(Triisopropylsilyl)-2-(trimethylsiloxy)propanenitrile (10). A mixture of ethyl vinyl ether (6.4 mL, 67 mmol) in 50 mL of THF was treated dropwise at −78 °C with 73 mmol of tBuLi. The solution was slowly warmed to −5 °C, and, after 30 min, recooled to −78 °C. Chlorotriisopropylsilane (12.9 g, 67 mmol) in 10 mL of ether was added dropwise and the mixture was then stirred at 25 °C overnight. Hydrolysis with ammonium chloride solution was followed by drying of the organic phase ($MgSO_4$). Short-path distillation gave 15.3 g (95%) of 1-ethoxy-1-(triisopropylsilyl)ethene, bp 64–68 °C (1 mmHg), which VPC showed was over 95% pure. IR: 1580 m, 1210 s, 1054 s cm^{-1}. ^1H NMR: δ 1.9–2.2 (m, 21 H), 2.25 (t, J = 7 Hz, 3 H), 3.66 (q, J = 7 Hz, 2 H), 4.24 (s, 1 H), 4.67 (s, 1 H). ^{13}C NMR: δ 10.7 (SiCH), 14.6 (CH_2CH_3), 18.3 ($CHCH_3$), 61.4 (CH_2), 95.6 (=CH_2), 166.4 (=C). Anal. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35. Found: C, 68.30; H, 12.49.

The above product (13.7 g, 60 mmol), 20 mL of ether, and 20 mL of 3 N HCl were stirred at 25 °C for 3 h. Workup gave 11.4 g (95%) of acetyltriisopropylsilane,[22] which VPC indicated was over 95% pure.

As described for **2**, 6.0 g (30 mmol) of acetyltriisopropylsilane, 4.0 g (40 mmol) of cyanotrimethylsilane, 0.067 g (0.3 mmol) of Me_3SiOTf, and 10 drops of pyridine gave 8.5 g (94%) of **10**, bp 100–102 °C (1 mmHg), which VPC showed was over 95% pure. IR: 2215 w, 1252 s cm^{-1}. ^1H NMR: δ 0.22 (s, 9 H), 1.16 (d, J = 7 Hz, 18 H), 1.31 (m, 3 H), 1.71 (s, 3 H). ^{13}C NMR: δ 1.8, 10.9, 19.0, 26.3, 62.0, 124.0. Anal. Calcd for $C_{15}H_{33}NOSi_2$: C, 60.13; H, 11.10; N, 4.68. Found: C, 60.00; H, 11.10; N, 4.48.

2-(Triisopropylsiloxy)-2-(trimethylsilyl)propanenitrile (11). From acetyltrimethylsilane (2.0 g, 14 mmol), cyanotriisopropylsilane (3.2 g, 88% pure, 15 mmol), Me_3SiOTf (0.10 mL, 0.52 mmol), and 5 drops of pyridine there was obtained 3.4 g (80%) of **11**, bp 104–106 °C (0.7 mmHg). IR: 2210 w, 1250 s cm^{-1}. ^1H NMR: δ 0.19 (s, 9 H), 1.08 (m, 21 H), 1.59 (s, 3 H). ^{13}C NMR: δ −4.5 ($SiCH_3$), 12.9 (CH), 18.1 ($CHCH_3$), 23.5 (CH_3), 61.8 (*C*CN), 123.0 (CN). Anal. Calcd for $C_{15}H_{33}NOSi_2$: C, 60.13; H, 11.10; N, 4.68. Found: C, 60.27; H, 11.08; N, 4.55.

General Procedure for Organolithium Additions to O-Silylcyanohydrins. (*Z*)-2-[*N*,*N*-Bis(trimethylsilyl)-amino]-3-(trimethylsiloxy)-2-butene (3a). Methyllithium (2.2 mmol) was added to a solution of **2** (0.43 g, 2.0 mmol) in 5 mL of ether at 25 °C. After 2 h, chlorotrimethylsilane (Me_3SiCl) (0.24 g, 2.2 mmol) was added. After an additional 2 h, volatiles were removed under vacuum (5 mmHg) and 30 mL of pentane was added. The mixture was filtered through a glass frit under N_2, and the filtrate was concentrated and distilled to give 0.60 g of **3a**, oven temperature 70 °C (25 mmHg), which VPC (135 °C) showed to be 92% pure (90% yield). IR: 2960 m, 2920 w, 2900 w, 1666 w, 1445 w, 1385 w, 1250 s, 1200 s, 1118 m, 1007 m, 942 s, 896 m, 840 s, 755 w, 680 w cm^{-1}. ^1H NMR: δ 0.04 (s, 18 H), 0.16 (s, 9 H), 1.59 (q, J = 0.9 Hz, 3 H), 1.78 (q, J = 0.9 Hz, 3 H). ^{13}C NMR: δ 1.8 ($OSiCH_3$), 2.3 ($NSiCH_3$), 18.4 and 22.6 (=CCH_3), 118.9 (=CN),[23] 138.4 (=CO).[23] Anal. Calcd for $C_{13}H_{33}NOSi_2$: C, 51.42; H, 10.95; N, 4.61. Found: C, 51.67; H, 10.98; N, 4.75.

(*Z*)-3-[*N*,*N*-Bis(trimethylsilyl)amino]-2-(trimethylsiloxy)-2-heptene (3b). The reaction of 0.43 g (2.0 mmol) of **2** and 0.9 mL (2.2 mmol) of nBuLi, initially at −78 °C, then at −20 °C for 0.5 h, was followed by addition of 0.24 g (2.2 mmol) of Me_3SiCl. There was obtained 0.65 g of **3b**, oven temperature 55–60 °C (20 mmHg), which VPC (150°) indicated was 85% pure (80% yield). No reaction occurred when **2** and nBuLi were mixed at −78 °C followed by chlorotrimethylsilane derivatization (−78 °C) 15 min later. IR: 1657 w, 1261 s, 1249 s cm^{-1}. ^1H NMR: δ 0.07 (s, 18 H), 0.17 (s, 9 H), 0.89 (t, 3 H), 1.3 (m, 4 H), 1.80 (s, 3 H), 1.9 (m, 2 H). ^{13}C NMR: δ 1.9 ($OSiCH_3$), 2.7 ($NSiCH_3$), 14.0 (CH_3), 18.4

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(=CCH_3), 23.3 (CH_2), 29.8 (CH_2), 35.5 (CH_2), 123.5 (=CN), 137.7 (=CO). Anal. Calcd for $C_{16}H_{39}NOSi_3$: C, 55.58; H, 11.37; N, 4.05. Found: C, 55.69; H, 11.28; N, 4.11.

(*Z*)-3-[*N*,*N*-Bis(trimethylsilyl)amino]-4,4-dimethyl-2-(trimethylsiloxy)-2-pentene (3c). The reaction of 0.43 g (2.0 mmol) of **2** and 2.4 mmol of tBuLi, initially at −78 °C, then 1 h at −20 °C, was derivatized at 25 °C with 0.27 g (2.5 mmol) of Me_3SiCl. There was obtained 0.58 g of material, oven temperature 80–85 °C (1 mmHg), which VPC (160 °C) indicated was 72% pure (60% yield). IR: 1624 w, 1260 s, 1247 s, 1238 s cm^{-1}. ^1H NMR: δ 0.09 (s, 18 H), 0.21 (s, 9 H), 1.13 (s, 9 H), 1.97 (s, 3 H). ^{13}C NMR: δ 2.4 ($OSiCH_3$), 3.3 ($NSiCH_3$), 20.4 (CH_3), 31.4 [$C(CH_3)$], 34.2 [$C(CH_3)$], 130.1 (=CN), 142.1 (=CO). Anal. Calcd for $C_{16}H_{39}NOSi_3$: C, 55.58; H, 11.37; N, 4.05. Found: C, 54.92; H, 11.71; N, 3.88.

(*Z*)-1-[*N*,*N*-Bis(trimethylsilyl)amino]-1-phenyl-2-(trimethylsiloxy)propene (3d). A solution of phenyllithium prepared from 0.41 g (2.6 mmol) of bromobenzene and 0.04 g (5.7 mmol) of Li wire (1% Na) in ether was transferred to an ether solution of 0.43 g (2.0 mmol) of **2** at −78 °C. Derivatization was carried out at 25 °C using 0.33 g (3.0 mmol) of Me_3SiCl and the mixture was stirred overnight. Workup gave 0.8 g of material, oven temperature 90–95 °C (3 mmHg), which VPC (170 °C) showed to consist of two major components. The first of these to elute (30% yield) was identified as 1-phenyl-1-(trimethylsiloxy)-1-(trimethylsilyl)ethane.[24] ^1H NMR: δ −0.12 (s, 9 H), 0.07 (s, 9 H), 1.80 (s, 3 H), 7.08–7.63 (m, 5 H). ^{13}C NMR: δ −4.5 ($SiCH_3$), 2.7 ($OSiCH_3$), 24.0 (CCH_3), 73.1 (CCH_3), 124.8–127.2–127.4–128.7 (Ph). Anal. Calcd for $C_{14}H_{26}OSi_2$: C, 63.09; H, 9.83. Found: C, 63.01; H, 9.91.

The second component to elute was **3d** (65% yield). IR: 1632 w, 1254 s cm^{-1}. ^1H NMR: δ 0.03 (s, 18 H), 0.28 (s, 9 H), 1.95 (s, 3 H), 7.1–7.3 (m, 5 H). ^{13}C NMR: δ 1.9 ($OSiCH_3$), 2.4 ($NSiCH_3$), 20.5 (CH_3), 125.8–126.3–127.2–130.0–141.4–142.7 (Ph and C=C). Anal. Calcd for $C_{18}H_{35}NOSi_3$: C, 59.11; H, 9.65; N, 3.83. Found: C, 59.42; H, 9.81; N, 3.78.

(*Z*)-2-[*N*,*N*-Bis(trimethylsilyl)amino]-3-(triethylsiloxy)-2-butene (12). From 0.43 g (2.0 mmol) of **2**, 2.2 mmol of MeLi, and 0.33 g (2.2 mmol) of chlorotriethylsilane there was obtained 0.61 g (88%) of **12**, oven temperature 70 °C (1 mmHg). IR: 1664 w, 1248 s cm^{-1}. ^1H NMR: δ 0.04 (s, 18 H), 0.66 (q, 6 H), 0.97 (t, 9 H), 1.61 (s, 3 H), 1.81 (s, 3 H). ^{13}C NMR: δ 2.3 ($SiCH_3$), 6.4 and 7.0 ($SiCH_2CH_3$), 18.3 and 22.8 (=CCH_3), 117.4 (=CN), 138.5 (=CO). Anal. Calcd for $C_{16}H_{39}NOSi_3$: C, 55.58; H, 11.37; N, 4.05. Found: C, 55.58; H, 11.40; N, 3.98.

(*Z*)-2-[*N*-(*tert*-Butyldimethylsilyl)-*N*-(trimethylsilyl)amino]-3-(trimethylsiloxy)-2-butene (13). From 0.52 g (2.0 mmol) of **8**, 2.2 mmol of MeLi, and 2.2 mmol of Me_3SiCl there was obtained 0.64 g of **13**, oven temperature 80–83 °C (7 mmHg), which VPC (160 °C) showed to be 85% pure (79% yield). IR: 1662 w, 1265 s, 1252 s cm^{-1}. ^1H NMR: δ −0.02 (s, 3 H), 0.05 (s, 9 H), 0.08 (s, 3 H), 0.18 (s, 9 H), 0.87 (s, 9 H), 1.64 (q, J = 1 Hz, 3 H), 1.78 (q, J = 1 Hz, 3 H). ^{13}C NMR: δ −3.1 and −1.2 [Si(CH_3)$_2$tBu], 2.0 ($OSiCH_3$), 3.0 ($NSiCH_3$), 18.3 and 22.8 (=CCH_3), 19.6 [$C(CH_3)_3$], 27.6 [$C(CH_3)_3$], 117.6 (=CN). 138.8 (=CO). Anal. Calcd for $C_{16}H_{38}NOSi_3$: C, 55.58; H, 11.37; N, 4.05. Found: C, 55.54; H, 11.03; N, 4.13.

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The identical product was formed (80% yield) from 0.26 g (1.0 mmol) of **9**, 2.0 mmol of MeLi, and 0.25 g (2.3 mmol) of Me_3SiCl.

(*Z*)-3-[*N*-(*tert*-Butyldimethylsilyl)-*N*-(trimethylsilyl)amino]-2-(trimethylsiloxy)-2-heptene (14). A mixture of 0.26 g (1.0 mmol) of **9** and 3 mL of ether was treated with 0.84 g (2.0 mmol) of nBuLi at −78 °C. After being warmed momentarily to −20 °C, Me_3SiCl (0.25 g, 2.3 mmol) was added at −78 °C. The usual workup gave 0.27 g of material, oven temperature 60–65 °C (6 mmHg), which VPC (175 °C) showed to be an approximately 1:2 mixture of **9** and **14**. The latter had the following spectral properties. IR: 1655 w, 1253 s cm^{-1}. ^1H NMR: δ 0.06 (s, 3 H), 0.09 (s, 9 H), 0.10 (s, 3 H), 0.18 (s, 9 H), 0.88 (m, 12 H), 1.26 (m, 4 H), 1.81 (s, 3 H), 2.02 (m, 2 H). ^{13}C NMR: δ −2.2 and −0.3 [Si(CH_3)$_2$tBu], 2.2 ($OSiCH_3$), 3.6 ($NSiCH_3$), 14.0 (CH_3), 18.1 (=CCH_3), 19.8 [$C(CH_3)_3$], 23.3 (CH_2), 27.6 [$C(CH_3)_3$], 30.2 (CH_2), 35.8 (CH_2), 122.9 (=CN), 138.1 (=CO). Anal. Calcd for $C_{19}H_{45}NOSi_3$: C, 58.84; H, 11.69; N, 3.61. Found: C, 59.14; H, 11.72; N, 3.43.

(*Z*)-2-[*N*-(Triisopropylsilyl)-*N*-(trimethylsilyl)amino]-3-(trimethylsiloxy)-2-butene (15). A solution of 0.30 g (1.0 mmol) of **10** was treated at 25 °C with 1.1 mmol of MeLi. After stirring overnight, 0.12 g (1.1 mmol) of MeSiCl was added and stirring continued for 3 h. The usual workup gave 0.37 g of **15**, oven temperature 60–65 °C (1.5 mmHg), which VPC (190 °C) showed to be 85% pure (81% yield). IR: 1655 m, 1252 s cm^{-1}. ^1H NMR: δ 0.07 (s, 9 H), 0.17 (s, 9 H), 1.08 (s, 21 H), 1.17 (s, 3 H), 1.81 (s, 3 H). ^{13}C NMR: δ 2.1 ($OSiCH_3$), 3.1 ($NSiCH_3$), 14.4 ($CHCH_3$), 19.0 and 24.2 (=CCH_3), 19.3 and 19.6 ($CHCH_3$), 116.0 (=CN), 139.9 (=CO). Anal. Calcd for $C_{19}H_{45}NOSi_3$: C, 58.84; H, 11.70; N, 3.61. Found: C, 58.66; H, 11.91; N, 3.53.

(*Z*)-2-[*N*,*N*-Bis(trimethylsilyl)amino]-3-(triisopropylsiloxy)-2-butene (16). From 0.30 g (1.0 mmoL) of **11**, 2.2 mmol of MeLi, and 2.2 mmol of Me_3SiCl there was obtained 0.39 g of **16**, oven temperature 60–65 °C (3 mmHg), which VPC (155 °C) showed to be 80% pure (80% yield). IR: 1665 w, 1255 s cm^{-1}. ^1H NMR: δ 0.06 (s, 18 H), 1.07 (m, 21 H), 1.67 (s, 3 H), 1.78 (s, 3 H). ^{13}C NMR: δ 2.3 ($SiCH_3$), 13.3 (OSiCH), 18.1 [$CH(CH_3)_2$], 18.5 and 21.1 (=CCH_3), 121.0 (=CN), 142.9 (=CO). Anal. Calcd for $C_{19}H_{45}NOSi_3$: C, 58.84; H, 11.69; N, 3.61. Found: C, 58.69; H, 11.79; N, 3.52.

(*Z*)-3-[*N*,*N*-Bis(trimethylsilyl)amino]-2-(triisopropylsiloxy)-2-heptene (17). nBuLi (2.4 mmol) was added to **11** (0.30 g, 1.0 mmol) in 5 mL of ether at −78 °C. The solution was held at −20 °C for 2 h and derivatized with 0.24 g (2.2 mmol) of Me_3SiCl at −78 °C. The usual workup gave 0.23 g of distillate, oven temperature 55–60 °C (3 mmHg), which VPC (190 °C) indicated to contain two major components in a 3:7 ratio. The first of these was tentatively identified as 2-(triisopropylsiloxy)propionitrile from its ^1H NMR spectrum: δ 1.08 (m, 21 H), 1.57 (d, J = 7 Hz, 3 H), 4.63 (q, J = 7 Hz, 1 H). The major component was **17**. IR: 1658 w, 1252 s cm^{-1}. ^1H NMR: δ 0.08 (s, 18 H), 0.88 (t, 3 H), 1.06 (m, 21 H), 1.3 (m, 4 H), 1.80 (s, 2 H), 2.08 (m, 2 H). ^{13}C NMR: δ 2.6 ($NSiCH_3$), 13.4 (OSiCH), 14.1 (CH_3), 18.2 [$CH(CH_3)$], 18.9 (=CCH_3), 23.5 (CH_2), 29.5 (CH_2), 34.4 (CH_2), 125.4 (=CN), 142.2 (=CO). Anal. Calcd for $C_{22}H_{51}NOSi_3$: C, 61.46; H, 11.96; N, 3.26. Found: C, 61.66; H, 11.72; N, 3.19.

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