Synthesis of (Aminomethyl)silanes with the Use of an Easily Cleavable Carbon–Silicon Bond

D. Labrecque, K. T. Nwe, and T. H. Chan*

Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6

Received July 26, 1993®

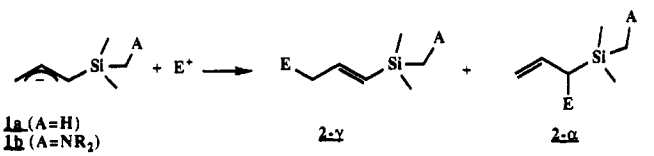
A number of (chloromethyl)dimethylsilanes **8a–c** bearing a heterocyclic substituent $(ClCH_2)(CH_3)_2Si(C_4H_nX)$ (**a**, $n = 3$, X = O; **b**, $n = 3$, X = S; **c**, $n = 5$, X = O) were synthesized and aminated with morpholine to give (aminomethyl)silanes **9a–c** $(C_5H_{10}NO)(CH_3)_2Si(C_4H_nX)$ (**a**, $n = 3$, X = O; **b**, $n = 3$, X = S; **c**, $n = 5$, X = O). They were screened for their capacity to undergo nucleophilic substitution reactions using lithium aluminum hydride. The heterocyclic substituent on silane **9c** was easily replaced with hydride, alkyls, and the trimethylsilyl group. This series of reactions was successfully applied to the synthesis of the pentamethyldisilane **14** $(C_5H_{10}NO)(CH_3)_5Si_2$ and the acetylene (aminomethyl)silane **21** $(C_{13}H_{19}NSi)$ not readily available in pure form by other means.

Introduction

While much of the current interest in the use of organosilicon chemistry for organic synthesis[1] has been focused on silicon compounds bearing simple alkyl or aryl groups, there has been increasing recognition that organosilicon compounds with proximate functional groups may modulate the reactivity patterns.[2] Comparison between a methyl substituted and an α-aminomethyl substituted organosilicon compound is particularly illustrative. It has been well established[3] that the (trimethylsilyl)allyl anion (**1a**, A = H) reacts with an electrophile regioselectively at the γ-position to give the product **2**-γ with *E* stereochemistry at the double bond (Scheme 1).

On the other hand, various [(α-aminomethyl)dimethylsilyl]allyl anions (**1b**, A = NR_2) can react with electrophiles giving different regioselectivity[4] and stereochemistry at the double bond.[5] In cases where the amino moiety is chiral, asymmetric synthesis using chiral (α-aminomethyl)-organosilicon compounds can be achieved, very often with high stereoselectivity.[6] Another difference is that the carbon–silicon bond of compounds in which the silicon bears an α-aminomethyl group can be cleaved readily by oxidation,[7] first to the corresponding silanol and eventually to the carbinol.[8] A similarly methyl substituted organosilicon compound is likely inert under the same oxidation conditions. This ready oxidation of (α-aminomethyl)-silanes may well account for their bioactivity as monoamine oxidase inhibitors.[9]

Scheme 1



(α-Aminomethyl)silanes **4** are usually synthesized by nucleophilic displacement of the corresponding (α-chloromethyl)silanes **3** with amines (Scheme 2).[4,10] This approach is quite adequate except in the cases where the precursor is not readily available or when the group R is reactive toward amines and/or amine hydrochloride salts.

Because of our interest in this area, we have examined an alternate approach to the synthesis of (α-aminomethyl)-silanes which involved the preparation of (chloromethyl)-silane **5**, from chloro(chloromethyl)dimethylsilane, containing a leaving group Y. This group was chosen for its inertness toward amines so that the displacement of the chlorine can take place to give **6**. Finally, the group Y itself is displaced by a nucleophile R to give **4** (Scheme 2). Even though the synthesis is somewhat roundabout, it does provide the desired (α-aminomethyl)silanes in good overall yield, and permit the synthesis of compounds with a reactive R group.

Results and Discussion

The group Y examined included 2-furyl, 2-thienyl, and 4,5-dihydro-2-furyl.[11] Thus, compounds **8a–c** were prepared by the reactions of **7** with the appropriate organolithium reagents.[12] In all cases, they were found to react with amines to give the corresponding **9a–c** in good yields. Morpholine was chosen as the representative amine, but other amines can be used as well.

Nucleophilic displacement of the Y group depends on the nature of Y as well as that of the nucleophile. Using

• Abstract published in *Advance ACS Abstracts*, December 1, 1993.

(1) Colvin, E. *Silicon Reagents for Organic Synthesis*; Academic Press: New York, 1988.

(2) Chan, T. H.; Koumaglo, K.; Horvath, R. F.; Wang, D.; Wei, Z. Y.; Yi, G. L.; Li, J. S. In *Silicon Chemistry*; Corey, T. J., Corey, E. R., Gaspar, P. P., Eds.; Ellis Hardwood Ltd.: Chichester, U.K., 1988; Chapter 5.

(3) Corriu, R.; Masse, J. *J. Organomet. Chem.* **1973**, 57, C5. Corriu, R. J. P.; Masse, J.; Samate, D. *Ibid.* **1975**, *93*, 71.

(4) Chan, T. H.; Horvath, R. F. *J. Org. Chem.* **1989**, *54*, 317.

(5) Labrecque, D.; Chan, T. H. *Tetrahedron Lett.* **1992**, *33*, 7997.

(6) Chan, T. H.; Pellon, P. *J. Am. Chem. Soc.* **1989**, *111*, 8737. Lamothe, S.; Chan, T. H. *Tetrahedron Lett.* **1991**, *32*, 1847. Lamothe, S.; Cook, K. L.; Chan, T. H. *Can. J. Chem.* **1992**, *70*, 1734. Chan, T. H.; Nwe, K. T. *J. Org. Chem.* **1992**, *57*, 6107. Hartley, R. C.; Lamothe, S.; Chan, T. H. *Tetrahedron Lett.* **1993**, *34*, 1449.

(7) Tamao, K.; Kakui, T.; Kumada, M. *J. Am. Chem. Soc.* **1978**, *100*, 2268.

(8) Chan, T. H.; Chen, L. M.; Wang, D. *J. Chem. Soc., Chem. Commun.* **1988**, 1280. Chan, T. H.; Chen, L. M.; Wang, D.; Li, L. H. *Can. J. Chem.* **1993**, *71*, 60.

(9) Silverman, R. B.; Banick, G. M. *J. Am. Chem. Soc.* **1987**, *109*, 2219.

(10) Sato, Y.; Toyo'oka, T.; Aoyama, T.; Shirai, H. *J. Org. Chem.* **1976**, *22*, 3559.

(11) Lukevics, E.; Borisova, L.; Gevorgian, G. *J. Organomet. Chem.* **1989**, *368*, 19; **1990**, *393*, 57; **1992**, *441*, 381.

(12) The 2-thienyllithium was either bought from Aldrich or made from *n*-butyllithium and thiophene. The 2-furyllithium and (dihydro-2-furyl)lithium were made following the procedures described by: Chadwick, D. J.; Willbe, C. *J. Chem. Soc., Perkin Trans. 1* **1977**, 887.

0276-7333/94/2313-0332$04.50/0

Scheme 2

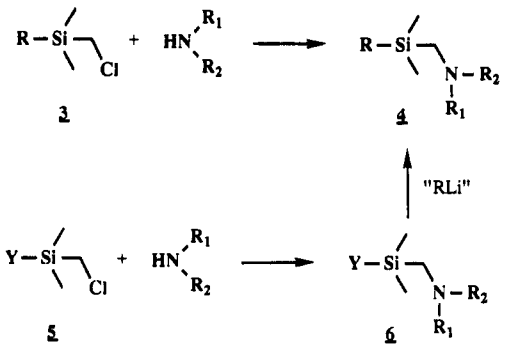
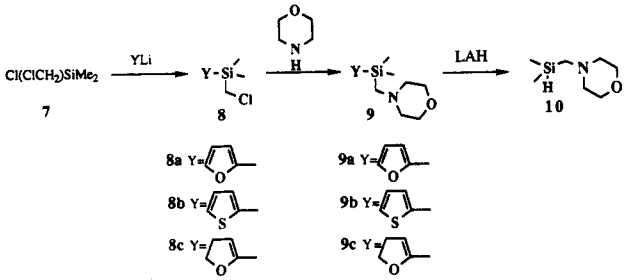


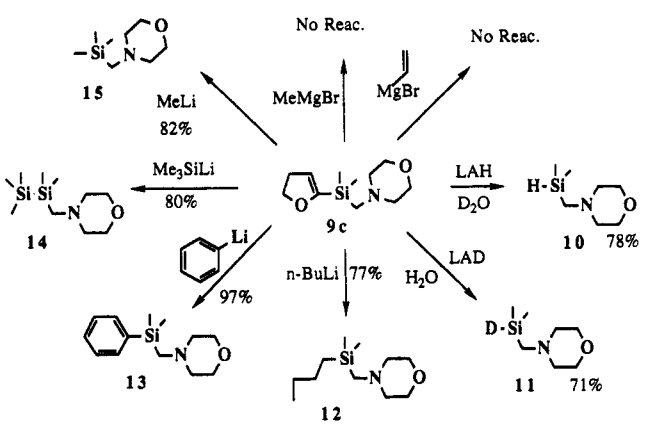
Table 1. Yields (%), for the Formation of Silane 10 and Intermediates, Based on Silane Starting Material



R	8	9	10
2-furyl (**a**)	87[a]	85[a]	23[a]
2-thienyl (**b**)	83[a]	84[a]	68,[b] 42[a]
4,5-dihydro-2-furyl (**c**)	89[a]	94[a]	73[c]

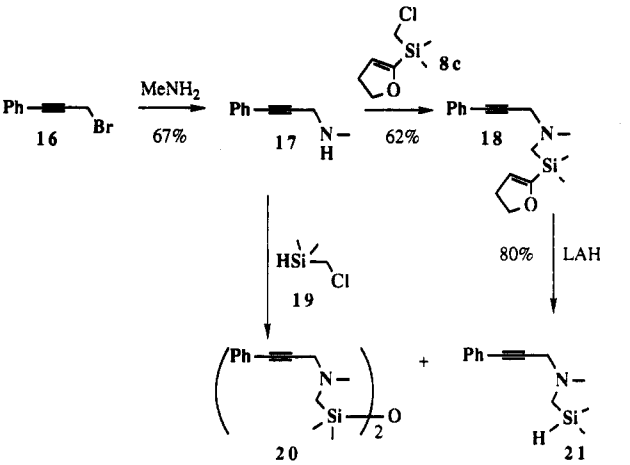
[a] The products were purified by Kugelrohr distillation under vacuum. [b] Crude product. [c] The product was pure as shown by ^{1}H NMR.

Scheme 3



lithium aluminum hydride as the common nucleophile, it was possible to evaluate the effectiveness of different Y groups for the synthesis of (aminomethyl)silanes **10**. The results are compared in Table 1. Conversion of **9a** to **10** required heating of the reagents in THF in a sealed tube at 150 °C, and the yield was relatively low (23%). Reductions of **9b** and **9c** to **10** could be carried out under milder reaction temperatures, and with better yields. The 4,5-dihydro-2-furyl group seemed to be the best leaving group of the three, requiring the mildest reaction conditions, and giving the best overall yield from **7** to **10**. Use of lithium aluminum deuteride gave the corresponding deuteriosilane **11**. Other nucleophiles can be used as well (Scheme 3). For example, organolithiums were found to be very effective in displacing the heterocyclic substituent on compound **9c**, giving a variety of (aminomethyl)silanes **12–15**. On the other hand, Grignard reagents were found not to displace the 4,5-dihydro-2-furyl group (Scheme 3).

Scheme 4



Equally effective is the displacement of the 4,5-dihydro-2-furyl group of **9c** using (trimethylsilyl)lithium as the nucleophile. Compound **14** was obtained in good yield. This illustrates one of the advantages of the present synthetic approach. The alternative approach (Scheme 2) was less versatile and less convenient since (chloromethyl)pentamethyldisilane was not readily available.[13]

The usefulness of the present synthetic approach was also demonstrated by the synthesis of compound **21**, needed for another project. Direct reaction of (chloromethyl)dimethylsilane **19** with the amine **17** gave a mixture of products including the desired compound **21** and the disiloxane **20**. Because of the sensitivity of **21** to air oxidation, it was difficult to perform chromatography to obtain pure **21**. Similarly, displacement of (chloromethyl)-dimethylethoxysilane with amine **17** gave the disiloxane **20** as well. On the other hand, reaction of the amine **17** with **8c** gave the compound **18** in 62% yield. Reduction of **18** with lithium aluminum hydride in THF gave the silane **21** in 80% yield (Scheme 4). Since **21** was the only compound obtained, purification by chromatography was not necessary.

Conclusion

A number of α-aminosilanes have been synthesized by the use of amphiphilic group Y via Scheme 2. This approach can be used for the syntheses of reactive hydrosilanes.

Experimental Section

Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Hexanes and ethyl acetate were distilled from calcium hydride. NMR spectra were recorded on a Varian Gemini 200 or Varian XL-200 (^{1}H at 200 MHz, ^{13}C at 50 MHz) or Varian XL-300 (^{1}H at 300 MHz, ^{13}C at 75 MHz) or a JEOL-270 (^{1}H at 270 MHz, ^{13}C at 68 MHz). ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances relative to tetramethylsilane (δ 0 ppm). Low and high resolution electron impact mass spectra were recorded on a Kratos MS 25RFA spectrometer operating at 70 eV. IR spectra were recorded on a Analet FT, A25–18 or on a BOMEM Michelson Series between NaCl plates (neat liquids or solutions).

(1) (Chloromethyl)dimethyl(2-furyl)silane (8a). Under argon, 2-furyllithium (0.0136 mol, solution in 20 mL of ether: TMEDA)[11] was transferred at −78 °C to a solution containing (chloromethyl)dimethylchlorosilane (1.5 g, 0.011 mol) in anhy-

(13) Inoue, S.; Sato, Y. *Organometallics* **1989**, *8*, 1237. Kobayashi, T.; Pannell, K.H. *Organometallics* **1991**, *10*, 1960 and references cited therein.

drous ether. The solution was slowly warmed to room temperature, and 20 mL of water was added. The reaction mixture was extracted using 20 mL of hexanes. The organic layer was dried over anhydrous $MgSO_4$ and the solvents were evaporated under reduced pressure. Kugelrohr vacuum distillation (60–70 °C, 0.05 mmHg) gave 1.6 g (87%) of a clear liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (dd, J = 1.7, 0.5 Hz, 1H), 6.75 (dd, J = 3.3, 0.5 Hz, 1H), 6.42 (dd, J = 3.3,1.7 Hz, 1H), 2.96 (s, 2H), 0.42 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 147.2, 121.3, 108.5, 29.4, -5.0. IR (film): 3115, 2963, 1550, 1395, 1254, 1110, 749–600 cm^{-1}. Exact mass calcd for $C_7H_{11}OSiCl$: 174.0268. Found: 174.0270. MS (EI): m/e 176 (4%), 174 (12%), 125 (100%).

(2) (Chloromethyl)dimethyl(2-thienyl)silane (8b). Under argon, 2-thienyllithium (31 mL, 1.0 M in THF) was added to 40 mL of anhydrous THF containing chloro(chloromethyl)dimethylsilane (4.0 g, 0.028 mol) maintained at -78 °C. The reaction mixture was then slowly warmed to room temperature. The reaction mixture was extracted using 20 mL of hexanes. The organic layer was dried over anhydrous $MgSO_4$, and the solvents were evaporated under reduced pressure. Kugelrohr vacuum distillation (80–85 °C, 0.05 mmHg) gave 4.4 g (83%) of a clear liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.66 (d, J = 4.6 Hz, 1H), 7.36 (d, J = 3.4 Hz, 1H), 7.23 (dd, J = 3.4, 4.6 Hz, 1H), 2.96 (s, 2H), 0.48 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 135.3, 131.4, 128.3, 30.6, -3.4. IR (film): 3103, 2960–25, 1684, 1497, 1402, 1254, 1215, 995, 823 cm^{-1}. Exact mass calcd for $C_7H_{11}SSiCl$: 190.0039. Found: 190.0036. MS (EI) m/e 192 (5%), 190 (11%), 141 (100%), 83 (2%), 97(10%).

(3) (Chloromethyl)(4,5-dihydro-2-furyl)dimethylsilane (8c). (4,5-Dihydrofuryl)lithium (0.035 mol in 20 mL of ether: TMEDA) was obtained by adding, at -78 °C, *tert*-butyllithium (1.7 M in pentane, 22 mL, 0.038 mol) to a solution containing 20 mL of anhydrous ether, 4 mL of TMEDA (distilled over CaH_2), and 4,5-dihydrofuran (5 mL, 0.07 mol). This solution was warmed to room temperature and stirred for 20 min.

The temperature of the (dihydrofuryl)lithium solution was lowered to -78 °C, and chloro(chloromethyl)dimethylsilane (5.0 g, 0.035 mol) was then slowly added to it. The reaction mixture was warmed to room temperature, and 20 mL of water was added. The reaction mixture was extracted using 20 mL of hexanes, and the organic layer was dried over anhydrous $MgSO_4$. The solvents were evaporated under reduced pressure and Kugelrhor vacuum distillation of the residue (62–65 °C, 0.05 mmHg) gave 5.5 g (89%) of a clear liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ 5.30 (t, J = 2.7 Hz, 1H), 4.26 (t, J = 9.5 Hz, 2H), 2.87 (s, 2H), 2.59 (dt, J = 2.5, 9.5 Hz, 2H), 0.26 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 158.6, 113.2, 70.3, 30.6, 28.91, -5.5. IR (film): 2964–2866, 1596, 1394, 1252, 1096, 927, 815 cm^{-1}. Exact mass calcd for $C_7H_{13}OSiCl$: 176.0424. Found: 176.0419. MS (EI) m/e 178 (10%), 176 (28%), 127 (48%), 107 (14%), 97 (100%).

(4) *N*-[(Dimethyl(2-furyl)silyl)methyl]morpholine (9a). (Chloromethyl)dimethyl(2-furyl)silane (**8a**) (1.0 g, 5.7 mmol) was heated with morpholine (1.25 g, 14.36 mmol) neat at 80 °C for 24 h. During this time a precipitate formed, indicating that the reaction went to completion. The reaction mixture was extracted with ether and water. The ether layer was dried with $MgSO_4$ and then evaporated. The residue was distilled on Kugelrohr under reduced pressure (80–90 °C, 0.05 mmHg), giving 1.1 g (85%) of a clear liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.65 (dd, J = 0.6, 1.7 Hz, 1H), 6.68 (dd, J = 0.6, 3.2 Hz, 1H), 6.38 (dd, J = 1.7, 3.2 Hz, 1H), 3.62 (m, 4H), 2.36 (m, 4H), 2.13 (s, 2H), 0.32 (s, 6H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 158.5, 146.8, 120.4, 109.5, 67.1, 57.2, 49.5, -3.3. IR (film): 3112, 2958–2853, 1545, 1362, 1250, 1117 cm^{-1}. Exact mass calcd for $C_{11}H_{19}O_2NSi$: 225.1185. Found: 225.1186. MS (EI): m/e 225 (12%), 210 (1%), 139 (1%), 125 (11%), 100 (100%).

(5) *N*-[(Dimethyl(2-thienyl)silyl)methyl]morpholine (9b). (Chloromethyl)dimethyl(2-thienyl)silane (**8b**) (2.0 g, 11 mmol) was heated with morpholine (2.3 g, 26 mmol) in the same manner as described for **9a** and distilled on Kugelrohr under reduced pressure (90 °C, 0.05 mmHg), giving 2.1 g (84%) of a clear liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (dd, J = 0.8, 4.7 Hz, 1H), 7.33 (dd, J = 0.8, 2.3 Hz, 1H), 7.20 (dd, J = 3.3, 4.7 Hz, 1H), 3.67 (m, 4H), 2.40 (m, 4H), 2.17 (s, 2H), 0.40 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.9, 134.5, 130.8, 128.1, 67.1, 57.3, 50.6, -1.5. IR (film): 3103, 2956–2793, 1407, 1250, 1118, 1008 cm^{-1}. Exact mass calcd for $C_{11}H_{19}NOSSi$: 241.0957. Found: 241.0961. MS (EI): m/e 241 (11%), 226 (1%), 198 (1%), 184 (3%), 144 (2%), 141 (12%), 100 (100%).

(6) *N*-[(Dimethyl(4,5-dihydro-2-furyl)silyl)methyl]morpholine (9c). The (chloromethyl)dimethyl(4,5-dihydro-2-furyl)-silane (**8c**) (1.0 g, 5.7 mmol) was reacted with morpholine (1.4 g, 16.1 mmol) neat at room temperature for 48 h, during which time a white precipitate formed. The reaction mixture was extracted with ether and water. The ether layer was dried with $MgSO_4$ and then evaporated, and the residue was distilled (Kugelrohr) under reduced pressure (88–90 °C, at 0.05 mmHg), giving 1.2 g (94%) of a clear liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ 5.25 (t, J = 2.5 Hz, 1H), 4.25 (t, J = 9.5 Hz, 2H), 3.65 (m, 4H), 2.57 (td, J = 9.5, 2.5 Hz, 2H), 2.39 (m, 4H), 2.03 (s, 2H), 0.18 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 160.8, 111.8, 70.1, 66.8, 56.9, 48.7, 30.5, -4.0. IR (film): 2956–2690, 1594, 1450, 1250, 1118, 1093, 928 cm^{-1}. Exact mass calcd for $C_{11}H_{21}O_2NSi$: 227.1342. Found: 227.1341. MS (EI): m/e 227 (11%), 141 (6%), 100 (100%).

(7) *N*-[(Dimethylsilyl)methyl]morpholine (10). (a) From Product 9a. *N*-[(Dimethyl(2-furyl)silyl)methyl]morpholine (**9a**) (1.9 g, 8.4 mmol) was dissolved in 2.0 mL of THF, lithium aluminum hydride (0.32 g, 8.4 mmol) was added, and THF was evaporated; next the reaction mixture was heated at 150 °C in a sealed tube with stirring for 48 h. The reaction mixture was then added to 1 mL NH_4Cl saturated with ice and worked up. Evaporation and Kugelrohr distillation (40 °C, 0.05 mmHg) gave 0.3 g (23%) of a clear liquid.

(b) From Product 9b. *N*-[(Dimethyl(2-thienyl)silyl)methyl]-morpholine (**9b**) (0.48 g, 2.0 mmol) was dissolved in 10.0 mL of THF, a solution of lithium aluminum hydride (1 M in THF, 1.0 mL, 1.0 mmol) was added, and the reaction mixture was heated at 60 °C with stirring in a sealed tube for 10 h. The reaction mixture was then added to NH_4Cl saturated with ice; workup and evaporation gave 0.21 g (68%) of a crude yellow liquid which upon Kugelrohr distillation (40 °C, 0.05 mmHg) gave 0.13 g (42%) of pure **10**.

(c) From Product 9c. *N*-[(Dimethyl(4,5-dihydro-2-furyl)-silyl)methyl]morpholine (**9c**) (0.1g, 0.44 mmol) was dissolved in 2.0 mL of THF, lithium aluminum hydride (1 M in THF, 0.22 mL, 0.2 mmol) was added, and the reaction mixture was left stirring at room temperature for 6 h. The reaction mixture was then added to 1 mL of NH_4Cl saturated with ice; workup and evaporation of the solvents gave the silane **10**, 0.051 g (73%), as a pure clear liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ 3.99 (n, J = 3.6 Hz, 1H), 3.69 (m, 4H), 2.43 (m, 4H), 2.00 (d, J = 3.6 Hz, 2H), 0.12 (d, J = 3.6 Hz, 6H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 67.1, 57.1, 49.1, -4.7. IR (film): 2957–2793, 2119, 1449, 1288, 1250, 1119, 890 cm^{-1}. Exact mass calcd for $C_7H_{17}ONSi$: 159.1079. Found: 159.1099. MS (EI): m/e 159 (10%), 144 (3%), 100 (100%), 86 (4%).

(8) *N*-[(Deuteriodimethylsilyl)methyl]morpholine (11). *N*-[(Dimethyl(4,5-dihydro-2-furyl)silyl)methyl]morpholine (**9c**) (0.1g, 0.44 mmol) was reacted with lithium aluminum deuteride. Workup and evaporation of the solvents gave 0.05 g (71%) of the silane **11**.

^{1}H NMR (200 MHz, $CDCl_3$): δ 3.67 (m, 4H), 2.40 (m, 4H), 1.9 (s, J = 3.6 Hz, 2H), 0.10 (s, J = 3.6 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 67.0, 57.0, 49.0, -4.8.

(9) General Procedure for the Reaction of Organolithium with *N*-[(Dimethyl(4,5-dihydro-2-furyl)silyl)methyl]morpholine (9c). Under argon, *N*-[(dimethyl(4,5-dihydro-2-furyl)-silyl)methyl]morpholine (**9c**) was dissolved in 1 mL of anhydrous THF or ether. The organolithium in solution was transferred to the flask containing **9c** at 0 °C and the reaction mixture was then

warmed to room temperature and left stirring for 6 h, before water was added and the organic layer worked up.

(a) *N*-[(*n*-Butyldimethylsilyl)methyl]morpholine (12). A solution of *n*-butyllithium (2.5 M in hexanes, 0.36 mL, 0.88 mmol) was reacted with **9c** (0.1 g, 0.44 mmol) in THF in the manner described above to give 0.08 g (84%) of pure product, upon workup and evaporation of the solvents.

^{1}H NMR (200 MHz, $CDCl_3$): δ 3.64 (m, 4H), 2.85 (s, 2H), 2.35 (m, 4H), 1.25 (m, 4H), 0.85 (m, 3H), 0.5 (m, 2H), 0 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 67.0, 57.3, 50.0, 26.5, 25.9, 15.1, 13.7, -3.0. IR (film): 2962–2735, 1451, 1282, 1248, 1120 cm^{-1}. Exact mass calcd for $C_{11}H_{25}ONSi$: 215.1705. Found: 215.1707. MS (EI): *m/e* 215 (7%), 158 (20%), 100 (100%).

(b) *N*-[(Dimethylphenylsilyl)methyl]morpholine (13). A solution of phenyllithium (1.8 M in cyclohexane ether solution, 0.88 mL, 0.88 mmol) was reacted with **9c** (0.1 g, 0.44 mmol) in THF in the manner described previously to give 0.18 g of a crude mixture, upon workup and evaporation of the solvents. This yellow oil was purified by flash chromatography by first eluting the biphenyl side product with hexanes and then eluting out of the column the desired product using ether as eluent. A quantity of 0.10 g of **13** (97%) was obtained as a clear oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.55 (m, 2H), 7.35 (m, 3H), 3.65 (m, 4H), 2.35 (m, 4H), 2.15 (s, 2H), 0.45 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 67.0, 57.3, 50.0, 26.5, 25.9, 15.1, 13.7, -3.0. IR (film): 2968–2736, 1591, 1450, 1282, 1249, 1117 cm^{-1}. Exact mass calcd for $C_{13}H_{22}ONSi$: 235.1392. Found: 235.1396. MS (EI): *m/e* 235 (6%), 135 (11%), 100 (100%).

(c) *N*-[(Pentamethyldisilyl)methyl]morpholine (14). A solution of (trimethylsilyl)lithium (1.78 mmol in HMPA) prepared by an established method[14] was reacted with **9c** (0.2 g, 0.88 mmol) in the manner described previously. The reaction mixture was worked up with a saturated ammonium chloride solution and then water and brine. The organic phase was separated. The solvents were evaporated, giving 2.9 g of impure clear oil which was distilled under vacuum (Kugelrohr, 110–120 °C, 0.05 mmHg) and then purified by flash chromatography using an hexanes: ether (85:15) eluent mixture to give 0.16 g (80%) of disilane **14**.

^{1}H NMR (200 MHz, $CDCl_3$): δ 3.65 (m, 4H), 2.35 (m, 4H), 1.95 (s, 2H), 0.05 (s, 6H), 0.01 (s, 9H), ^{13}C NMR (50 MHz, $CDCl_3$): δ 67.2, 57.3, 50.0, -2.1, -3.7. IR (film): 2954–2734, 1451, 1295, 1246, 1120 cm^{-1}. Exact mass calcd for $C_{10}H_{25}ONSi_2$: 231.1475. Found: 231.1487. MS (EI): *m/e* 231 (3%), 216 (6%), 158 (57%), 100 (100%), 73 (16%).

(d) *N*-[(Trimethylsilyl)methyl]morpholine (15). A solution of methyllithium (1.4 M in hexanes, 0.37 mL, 0.53 mmol) was reacted with **9c** (0.1 g, 0.44 mmol) in ether in the manner described previously to give 0.062 g (82%) of pure **15** upon workup and evaporation of the solvents.

^{1}H NMR (200 MHz, $CDCl_3$): δ 3.65 (m, 4H), 2.35 (m, 4H), 1.87 (s, 2H), 0.03 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 67.1, 57.3, 51.2, -1.3. IR (film): 2957–2736, 1451, 1296, 1248, 1120 cm^{-1}. Exact mass calcd for $C_8H_{19}ONSi$: 173.1236. Found: 173.1237. MS (EI): *m/e* 173 (14%), 158 (9%), 116 (8%), 100 (100%), 73 (21%).

(10) Phenylpropargyl Bromide (16). To a solution of phenylpropargyl alcohol (1.30 g, 0.01 mol) in 20 mL of anhydrous ether and 0.08 mL of pyridine at 0 °C was added dropwise a solution of PBr_3 (0.78 mL, 0.08 mol) in 10 mL of ether. After the addition, the reaction mixture was refluxed at 45 °C for 3 h. It was then cooled and poured into 30 mL of water and the organic layer was separated. The aqueous layer was extracted with ether, and the combined ether layer was washed with 10% $NaHCO_3$ solution and water and dried ($MgSO_4$). Removal of the solvent gave a quantitative yield of **4**. Reported yield = 70%.[15]

^{1}H NMR ($CDCl_3$): δ 7.20-7.50 (m, 5H), 4.16 (s,1H). ^{13}C NMR ($CDCl_3$): δ 131.83, 128.83, 128.29, 122.09, 86.68, 84.19, 15.28. IR (film): 3050, 2220, 1598, 1489, 1203, 754, 669, 591 cm^{-1}.

(11) *N*-Methyl-*N*-(phenylpropargyl)amine (17). To a 33% solution of *N*-methylamine in EtOH (12 mL, 0.08 mol) at 0 °C was added dropwise a solution (2.0 g, 0.01 mol) of **16** in 5 mL of absolute EtOH, and the reaction mixture was stirred at room temperature for 1 h, after the addition. The solvent was evaporated from the reaction mixture, extracted with ether, and washed with water. Ether was removed to give a crude mixture of di- and monopropargylated amine in a 1:4 ratio. Kugelrohr distillation of the mixture afforded 1.0 g (67% yield) of **17**, bp 80–90 °C, 0.05 mmHg. Some of the product seemed to polymerize on distillation.

^{1}H NMR ($CDCl_3$): δ 7.20–7.50 (m, 5H), 3.61 (s, 2H), 2.54 (s, 3H), 1.48 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 131.40, 128.03, 127.78, 123.01, 87.22, 83.40, 40.52, 35.09. IR (film): 3300, 2793–2970, 1598, 1489, 1328, 1107, 756, 691 cm^{-1}. Exact mass calcd for $C_{10}H_{11}N$: 145.0891. Found: 145.0888. MS (EI): *m/e* 145 (27%), 144 (100%), 115 (46%), 68 (11%).

(12) Reaction of 17 with Different Silanes. (a) With Ethoxy(chloromethyl)dimethylsilane. A mixture of **17** (0.29 g, 2 mmol) and ethoxy(chloromethyl)dimethylsilane (0.15 g, 1 mmol) was kept in a sealed tube at room temperature for 6 h. Ether was added, the insoluble solid was filtered out, and the solvent was removed. ^{1}H NMR of the reaction mixture showed the formation of disiloxane **20**.

(b) With Chloromethyldimethylsilane. A mixture of **17** (0.29 g, 2 mmol) and (chloromethyl)dimethylsilane (0.1 g, 1 mmol) was kept in a sealed tube at room temperature for 6 h. Ether was added, the insoluble solid was filtered out, and the solvent was removed. ^{1}H NMR of the crude mixture showed that **21** and disiloxane **20** were formed in a 1:1 ratio.

(c) With (Chloromethyl)(4,5-dihydro-2-furyl)dimethylsilane. A mixture of **17** (0.29 g , 2 mmol) and (dihydrofuryl)-(chloromethyl)dimethylsilane (**8c**) (0.26 g, 1.5 mmol) was heated at 40 °C in a sealed tube for 2 days. Ether was added, the insoluble solid was filtered out, and the solvent was removed. Separation of the crude mixture by column chromatography (10% EtOAc + 3% NEt_3 in hexanes) gave 0.176 g (62%) of **18**. Some of the product seemed to decompose on the column.

^{1}H NMR ($CDCl_3$): δ 7.20–7.50 (m, 5H), 5.30 (t, *J* = 2.5 Hz, 1H), 4.26 (t, *J* = 9.5 Hz, 2H), 3.53 (s, 2H), 2.58 (dt, *J* = 2.5, 9.5 Hz, 2H), 2.37 (s, 3H), 2.20 (s, 2H), 0.23 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 160.73, 131.70, 128.20, 127.91, 123.35, 112.42, 85.66, 84.65, 70.44, 50.25, 46.06, 45.54, 30.73, -3.94. IR ($CHCl_3$): 3000–2782, 1596, 1445, 1325, 1253, 1092, 925 cm^{-1}; Exact mass calcd for $C_{17}H_{23}SiNO$: 285.1549. Found: 285.1553. MS (EI): *m/e* 285 (4%, M^+), 170 (18%), 158 (51%), 115 (100%).

(13) *N*-[(Dimethylsilyl)methyl]-*N*-methyl-*N*-(phenylpropargyl)amine (21). To a solution of **18** (0.028 g, 0.1 mmol) in 1 mL of dried THF was added a solution of LAH (0.008 g, 0.2 mmol) in 1 mL of THF, under argon, and the reaction mixture was stirred at room temperature overnight. Then it was poured onto 1 mL of saturated NH_4Cl solution containing some ice and extracted with ether. The organic layer was dried ($MgSO_4$) and the solvent removed to give 0.017 g (80%) of the silane **21**. The product is very sensitive to air and moisture and is easily converted to disiloxane.

^{1}H NMR ($CDCl_3$): δ 7.20–7.50 (m, 5H), 3.99 (n, *J* = 3.6 Hz, 1H), 3.53 (s, 2H), 2.39 (s, 3H), 2.14 (d, *J* = 3.6 Hz, 2H), 0.14 (d, *J* = 3.6 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 131.64, 128.25, 128.16, 127.88, 123.27, 85.55, 84.55, 50.09, 45.99, 45.18, -4.85. IR ($CHCl_3$): 2963, 2779, 2122, 1489, 1254, 1222, 908 cm^{-1}. Exact mass calcd for $C_{13}H_{19}SiN$: 217.1286. Found: 217.1284. MS (CI): *m/e* 218 (33%, MH^+), 202 (5%), 158 (70%), 115 (100%).

Acknowledgment. We thank the NSERC and FCAR for financial support of this research and M. Nadim Saadé for the low and high resolution mass spectra analysis.

Supplementary Material Available: Figures of ^{1}H and ^{13}C NMR spectra of new compounds (32 pages). Ordering information is given on any current masthead page.

OM930513X

(14) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063.
(15) Lai, T. Y. *Bull. Soc. Chim. Fr.* **1933**, *53*, 1533.