Novel 4-(Trimethylsilyl)aminoalkanes and 4-(Trimethylsilyl)aminoalk-2-enes, via a 1,5-Hydride Shift, in the Reaction of α-Unsaturated Silanes with Aminomethylbenzotriazoles

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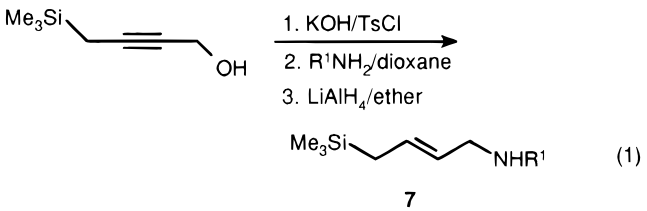
1-[(Dialkylamino)methyl]benzotriazoles react with allyl- and propargyltrimethylsilanes in the presence of aluminum chloride to give, as major products, the unexpected 4-(trimethylsilyl)aminoalkanes and 4-(trimethylsilyl)aminoalk-2-enes, respectively. The products thus obtained are unusual and could be explained by a 1,5-hydride shift occurring in the formation of the initial (and expected) carbocation intermediate. When such a migration is not possible, the resulting products in the reaction are the usual homoallylamines or α-allenylamines. To our knowledge 4-(trimethylsilyl)aminoalkanes and 4-(trimethylsilyl)-aminoalk-2-enes have not been previously reported.

Introduction

Allyltrimethylsilane[1−5] and propargyltrimethylsilane[6−8] react with iminium salts generated in situ from secondary amines and formaldehyde, to furnish homoallylamines and α-allenylamines, respectively. On the other hand, 1-[1-(dialkylamino)alkyl]benzotriazoles are versatile iminium-ion synthetic equivalents and consequently excellent aminomethylation reagents.[9−12]

In solution, 1-[1-(dialkylamino)alkyl]benzotriazoles exist in equilibrium with a small concentration of benzotriazole anion and the corresponding iminium cation, as shown by the intermolecular isomerization between the 1- and 2-substituted isomers.[11,13,14] Allyl- and propargyltrimethylsilanes were thus expected to react with such benzotriazole derivatives, to give tertiary homoallylamines and α-allenylamines, respectively (Scheme 1). Instead, two new classes of organosilanes were found: 4-(trimethylsilyl)aminoalkanes **4** were obtained by starting from allyltrimethylsilane, while propargyltrimethylsilane afforded 4-(trimethylsilyl)aminoalk-2-enes **7**.

To our knowledge, there are no previous reports of similar compounds, which may be useful intermediates in organic synthesis. The silylated amines Me_3SiCH_2-$CH{=}CH(CH_2)_nNHR$ ($n = 2-4$) are known in the literature, as they have been used for the preparation of nitrogen-containing heterocycles[1,2] via an aminomethylation−desilylation process. However, 4-silylaminoalk-2-enes ($n = 1$) are scarce; they could be obtained from a sequence leading to the propargylic amine[7] and then by partial reduction with $LiAlH_4$ (eq 1).[15] Complete



(1)

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hydrogenation of the propargylic amine would afford the saturated amines[15] $Me_3Si(CH_2)_4NHR^1$ (**4**).

The novel organosilanes were isolated and characterized, and we report herein several examples, along with mechanistic aspects of the synthesis.

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Scheme 1

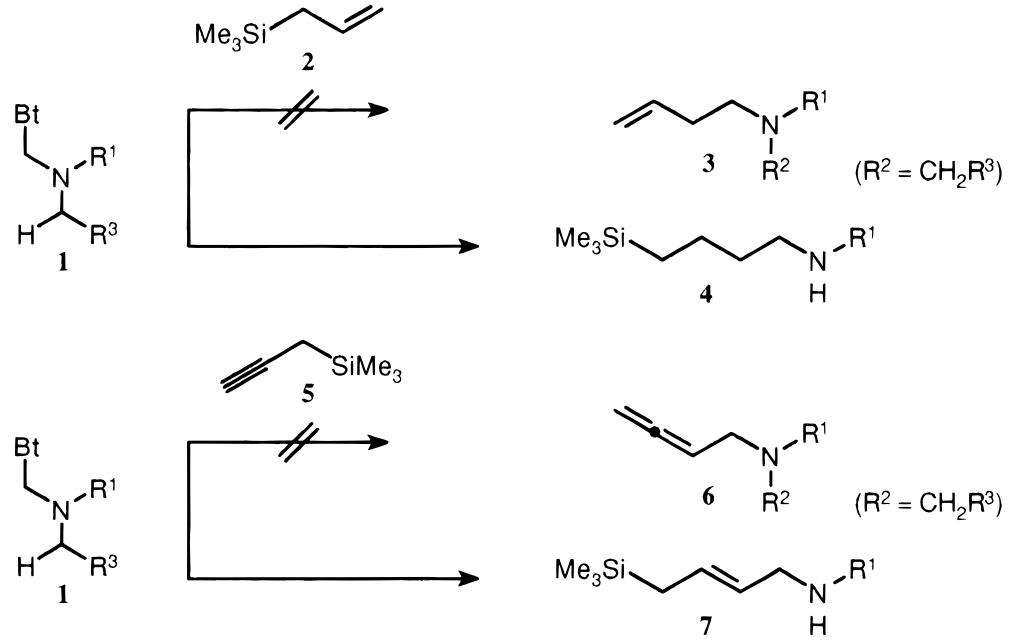

Table 1. Reaction of 1-[(Dialkylamino)methyl]benzotriazoles with Allyltrimethylsilane

	$BtCH_2NR^1R^2$ [a] (**1**)		$CH_2{=}CH(CH_2)_2$-NR^1R^2 (**3**), %	$Me_3Si(CH_2)_4$-NHR^1 (**4**), %
entry	R^1	R^2		
a	Et	Et		52
b	Pr^n	Pr^n		66
c	Pr^i	Pr^i		26
d	Bn	Bn	5	77[b]
e	$-(CH_2)_2O(CH_2)_2-$		33[c]	

[a] Conditions: 5 mmol of [(dialkylamino)methyl]benzotriazole, 20 mL of dichloromethane, 10 mmol of $AlCl_3$, 6 mmol of allyltrimethylsilane, 3 h at 40 °C. [b] Benzaldehyde, 60% yield. [c] Reaction carried out in the presence of $ZnCl_2$: 19%.

Table 2. Reaction of 1-[(Monoalkylamino)methyl]benzotriazoles with Allyltrimethylsilane

	$BtCH_2NR^1R^2$ [a] (**1**)			
entry	R^1	R^2	$CH_2{=}CH(CH_2)_2NR^1R^2$ (**3**), %	**10**, %
f	H	Bu^t	3	45
g	H	Bn	10	19

[a] Conditions: 5 mmol of [(monoalkylamino)methyl]benzotriazole, 20 mL of dichloromethane, 10 mmol of $AlCl_3$, 6 mmol of allyltrimethylsilane, 3 h at 40 °C.

Results and Discussion

A series of 1-[(dialkylamino)methyl]- and 1-[(monoalkylamino)methyl]benzotriazoles were tested in reactions with allyltrimethylsilane and propargyltrimethylsilane, as described in the Experimental Section. Aluminum chloride was found to be preferable to zinc chloride (entry e, Table 1). A 2:1 ratio of aluminum chloride to aminomethylbenzotriazole, as used in a similar aminomethylation,[12] was experimentally found to give better yields without affecting the distribution of products, as 1 equiv of Lewis acid is consumed for the generation of the iminium ion; moreover, nitrogen atoms of the benzotriazolyl ring are prone to complexation.

The reactions were each quenched with sodium hydroxide and the products separated by distillation or preparative gas chromatography, using a methodology previously described for similar reactions of silanes (allyl[3,16] and propargyl[7,8]).

Reactivity of Allyltrimethylsilane. The results of the reaction of benzotriazole derivatives **1a**−**e** with allyltrimethylsilane are presented in Table 1. The expected products were amines **3a**−**e**: of these, only **3d** and **3e** were isolated in yields of 5 and 33%, respectively. The generation of products of type **4** could be explained by nitrogen-assisted intramolecular migration of a hydride ion, as shown in Scheme 2. The variation of the yields in compounds **4** reflects the influence of the adjacent groups in the migratory capabilities of the hydrogen. When the amino moiety is morpholine, a 1,5-hydride shift is geometrically disallowed and the reaction product is the expected homoallylamine **3e**.

As a comparison, the two [(monomethylamino)methyl]-benzotriazoles **1f** and **1g** were reacted with allyltrimethylsilane under the same conditions, and the results are shown in Table 2. The major reaction products are azetidine **10f** (resulting from **1f**) and pyrrolidine **10g** (resulting from **1g**) (see Scheme 3).

Heterocycles **10f** and **10g** are presumed to originate from the cationic intermediate **11f** or **11g**, by cyclization (**10f**) or by 1,2-silicon rearrangement[17] and subsequent cyclization (**10g**). The nature of the N-substituent is critical for the final product, and steric factors certainly determine the reaction pathway.

Reactivity of Propargyltrimethylsilane. Table 3 depicts the products **6** and **7** resulting from the reaction of benzotriazole derivatives **1a**−**e** with propargyltrimethylsilane. The results endorse the mechanism described above for the reaction with allyltrimethylsilane involving rearrangement and subsequent hydride migration from the cationic intermediate initially formed (Scheme 4).

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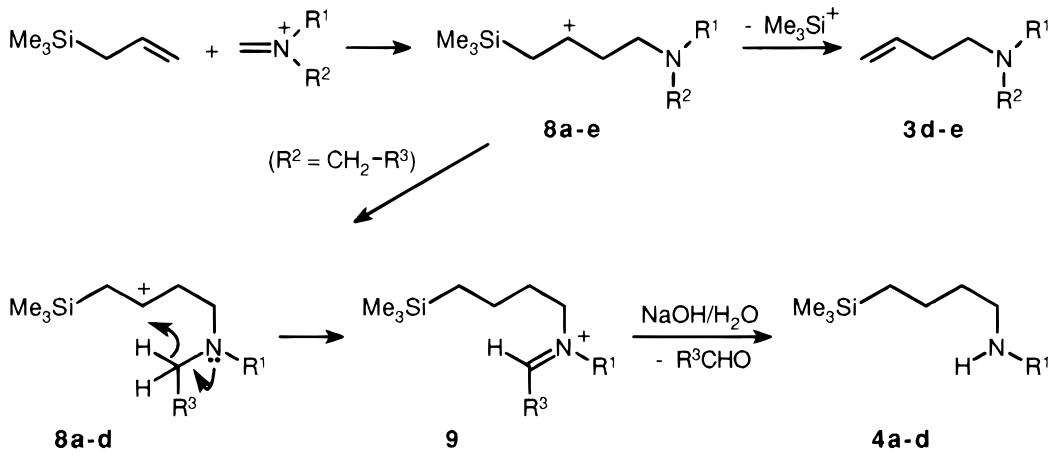
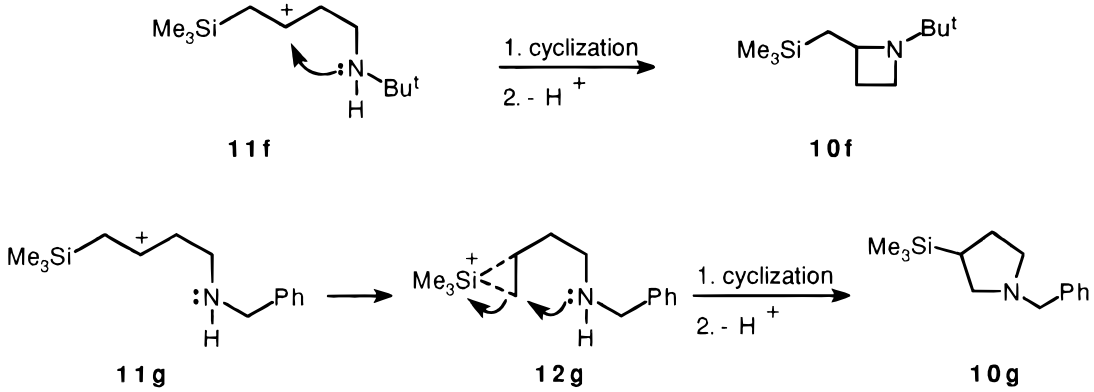
Scheme 2



Scheme 3



Scheme 4

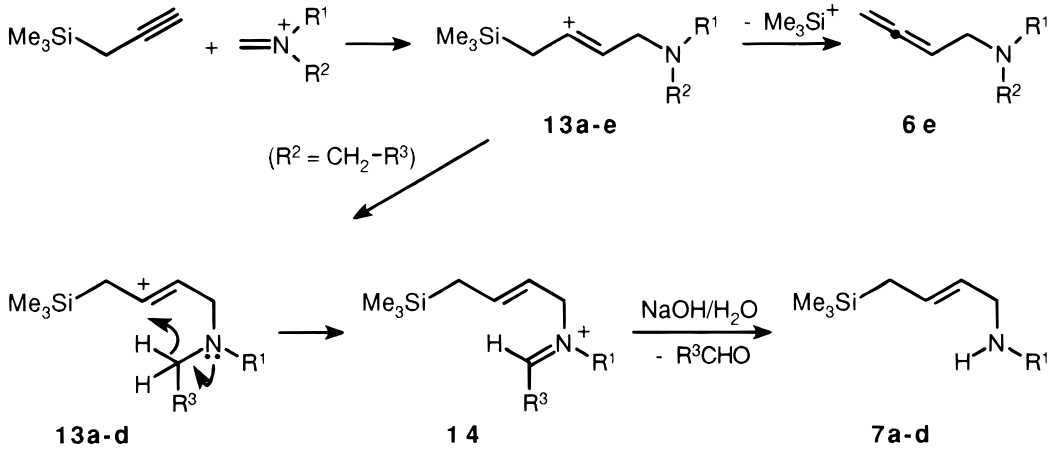


Table 3. Reaction of 1-[(Dialkylamino)methyl]benzotriazoles with Propargyltrimethylsilane

entry	$BtCH_2NR^1R^2$ [a] (**1**) R^1	R^2	$CH_2{=}C{=}CHCH_2NR^1R^2$ (**6**), %	(E)-$Me_3SiCH_2CH{=}CHCH_2NHR^1$ (**7**), %
a	Et	Et		43
b	Pr^n	Pr^n		49
c	Pr^i	Pr^i		16
d	Bn	Bn		61[b]
e	$-(CH_2)_2O(CH_2)_2-$		29	

[a] Conditions: 5 mmol of [(dialkylamino)methyl]benzotriazole, 20 mL of dichloromethane, 10 mmol of $AlCl_3$, 6 mmol of propargyltrimethylsilane, 3 h at 40 °C. [b] Benzaldehyde, 37% yield; dibenzylamine, 4% yield.

There are a few observations regarding the data reported in Table 3. (i) 4-(Trimethylsilyl)aminoalk-2-enes **7a**−**d** were obtained as major reaction products, presumably by the rearrangement shown in Scheme 4. (ii) The expected compound **6e** was obtained only in the case of benzotriazole **1e**, while the corresponding amine **7e** was not formed, most likely because of the unfavorable geometry for a hydride ion migration. (iii) The isolation of benzaldehyde along with the major product **7d** is an indication for the proposed mechanism. (iv) The low yield of **7c** could be justified by the sensitivity of the reaction to steric hindrance.

Moreover, benzylamine was also identified and isolated from the reaction mixture (4%) along with the

product **7d**; benzylamine was probably formed by decomposition of some unreacted iminium salt during the hydrolysis process.

Conclusion

Benzotriazole-containing iminium-ion equivalents, i.e., 1-[(dialkylamino)methyl]benzotriazoles, were previously used for the synthesis of tertiary amines. In the reaction with allyltrimethylsilane and propargyltrimethylsilane, these derivatives preserve their potential as iminium-ion equivalents, but the major reaction products were mostly 4-silylated secondary amines, obtained by nitrogen-assisted hydride migration in a cation intermediate formed as a first reaction stage. The 1,5-hydride shift reported herein is consistent with findings recently described for other systems.[18−20] The cationic intermediate is characteristic for the reactions involving both allyltrimethylsilane and propargyltrimethylsilane.[1,6,8] The consistency of the final products draws the attention to this reaction as an alternative to the preparation of various classes of silane derivatives.

Experimental Section

General Comments. Melting points were determined with a hot-stage apparatus and are uncorrected. IR spectra were obtained by using a Spectrum 1000 FTIR Perkin-Elmer spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX 90 spectrometer operating at 90 MHz for ^{1}H and 22.5 MHz for ^{13}C. All chemical shifts, reported in δ units, were referenced to the NMR solvent ($CDCl_3$). Mass spectra were obtained by using a GC 8000/Trio 1000 FISONS Instruments spectrometer either in a CI (CH_4) or in a EI (70 eV) mode. Elemental analyses were measured by service central d'Analyse du CNRS (Vernaison, France). Gas−liquid chromatography (GLC) was used extensively in this work in the analysis of reaction mixtures, determination of yields (by the internal standard method), and isolation of pure products for analyses and spectroscopy. GLC was conducted with 2 m analytical columns filled with either 20% SE 30 or CARBOWAX 20 M deposited on Chromosorb W. Dichloromethane was distilled over phosphorus pentoxide under argon. Other solvents were dried by using standard methods. All reactions with air-sensitive compounds were carried out under argon. Benzotriazoles **1** were prepared by methods previously described in the literature.[21−23] Allyltrimethylsilane and propargyltrimethylsilane were commercial products.

General Procedure for the Reaction of Benzotriazoles 1a−g with Allyltrimethylsilane. To a solution of aminomethylbenzotriazole (**1**; 5 mmol) in dichloromethane (20 mL) at 5 °C was added aluminum chloride (1.3 g, 10 mmol) with stirring. After 5 min, the temperature was raised from 5 to 10 °C, and a white precipitate was formed. Allyltrimethylsilane (0.69 g, 6 mmol) was added, and the mixture was stirred at reflux for 3 h. The reaction was quenched with aqueous sodium hydroxide (2 M, 25 mL) and extracted with dichloromethane (3 × 30 mL). The combined extracts were washed successively with aqueous sodium hydroxide (1 M, 3 × 20 mL) and water (3 × 30 mL), dried over $MgSO_4$, filtered, and concentrated. The residue was subjected to a bulb-to-bulb distillation. Amines were purified, if necessary, by GLC.

The reaction was carried out similarly in the presence of zinc chloride, using 2.2 M $ZnCl_2{\cdot}OEt_2$ in dichloromethane (4.6 mL, 10 mmol) instead of aluminum chloride.[10]

Amines 3. 4-(Dibenzylamino)but-1-ene (3d). Yield: 6 mg (5%). IR (film; ν, cm^{-1}): 3073 (w), 1640 (m), 990 (m), 910 (s) (CH_2=CH); 3063 (w), 3027 (m), 1602 (w), 1494 (s), 745 (s), 698 (s) (C_6H_5). ^{1}H NMR ($CDCl_3$; δ, ppm): 2.10−2.65 (m, 4H, CH_2-CH_2); 3.57 (s, 4H, CH_2); 4.80−5.15 (m, 2H, CH_2=); 5.50−6.00 (m, 1H, CH=); 7.15−7.45 (m, 10H, C_6H_5). ^{13}C NMR ($CDCl_3$; δ, ppm): 31.59 (CH_2); 52.86 (NCH_2); 58.14 ($CH_2C_6H_5$);115.31 (CH_2=); 126.77, 128.11, 128.73, 139.77 (C_6H_5); 136.97 (CH=). MS (EI; *m*/*z* (relative intensity)): 251 (M^+, 1); 211 (16); 210 (75); 181 (14); 92 (22); 91 (100); 65 (30).

4-(Morpholino)but-1-ene (3e). Yield: 23 mg (33%). IR (film; ν, cm^{-1}): 3077 (m), 1641 (m), 988 (s), 911 (s) (CH_2=CH); 1119 (s) (CO). ^{1}H NMR ($CDCl_3$; δ, ppm): 2.05−2.55 (m, 8H, CH_2); 3.55−3.75 (m, 4H, CH_2O); 4.85−5.15 (m, 2H, CH_2=); 5.55−6.05 (m, 1H, CH=). ^{13}C NMR ($CDCl_3$; δ, ppm): 30.99 (CH_2C=); 53.58 (CH_2CH_2O); 58.29 (CH_2N); 66.88 (CH_2O); 115.58 (CH_2=); 136.34 (CH=). MS (EI; *m*/*z* (relative intensity)): 141 (M^+, 2); 101 (21); 100 (100); 70 (28); 56 (66); 55 (27); 42 (61); 41 (21). Anal. Calcd for $C_8H_{15}NO$: C, 68.05; H, 10.71; N, 9.91. Found: C, 68.20; H, 10.67; N, 9.96.

4-(*tert*-Butylamino)but-1-ene (3f). Yield: 2 mg (3%). IR (film; ν, cm^{-1}): 3312 (w) (NH); 3078 (m), 1641 (m), 993 (m), 914 (s) (CH_2=CH); 1361 (s) ($C(CH_3)_3$). ^{1}H NMR ($CDCl_3$; δ, ppm): 0.86 (s, 10H, CH_3, NH); 1.85−2.15 (m, 2H, CH_2); 2.30−2.50 (m, 2H, CH_2N); 4.70−5.05 (m, 2H, CH_2=); 5.25−5.80 (m, 1H, CH=). ^{13}C NMR ($CDCl_3$; δ, ppm): 28.61 (CH_3); 34.66 (CH_2); 41.10 (CH_2N); 49.64 (C); 115.76 (CH_2=); 136.22 (CH=). MS (CI; *m*/*z* (relative intensity)): 128 (MH^+, 64); 126 (21); 112 (22); 86 (100); 72 (46); 59 (39).

4-(Benzylamino)but-1-ene (3g). Yield: 8 mg (10%). IR (film; ν, cm^{-1}): 3312 (w) (NH); 3075 (w), 1641 (s), 995 (m), 913 (s) (CH_2=CH); 3064 (w), 3028 (m), 1605 (w), 1495 (s), 734 (s), 698 (s) (C_6H_5). ^{1}H NMR ($CDCl_3$; δ, ppm): 1.88 (s, 1H, NH); 2.15−2.45 (m, 2H, CH_2C=); 2.71 (t, J = 6.6 Hz, 2H, CH_2); 3.80 (s, 2H, $CH_2C_6H_5$); 4.90−5.25 (m, 2H, CH_2=); 5.55−6.05 (m, 1H, CH=); 7.31 (s, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$; δ, ppm): 34.12 (CH_2C=); 48.21 (CH_2); 53.76 ($CH_2C_6H_5$); 116.26 (CH_2=); 136.34 (CH=); 126.85, 128.08, 128.32, 140.19 (C_6H_5). MS (CI; *m*/*z* (relative intensity)): 162 (MH^+, 82); 160 (21); 120 (100); 119 (16); 91 (86); 84 (22). Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38; N, 8.68. Found: C, 81.81; H, 9.42; N, 8.74.

Amines 4. 4-(Ethylamino)-1-(trimethylsilyl)butane (4a). Yield: 45 mg (52%). IR (film; ν, cm^{-1}): 3282 (w) (NH); 1248 (s), 835 (s), 760 (m) ($SiMe_3$). ^{1}H NMR ($CDCl_3$; δ, ppm): −0.18 (s, 9H, $SiMe_3$); 0.25−0.50 (m, 2H, CH_2Si); 0.95 (t, J = 7.1 Hz, 3H, CH_3); 0.97 (s, 1H, NH); 1.10−1.55 (m, 4H, CH_2); 2.45 (t, J = 7.0 Hz, 2H, CH_2N); 2.49 (q, J = 7.1 Hz, 2H, NCH_2CH_3). ^{13}C NMR ($CDCl_3$; δ, ppm): −1.94 ($SiMe_3$); 15.09 (CH_3); 16.46 (CH_2-Si); 21.57 ($SiCH_2CH_2$); 33.89 (CH_2); 43.97 (CH_2CH_3); 49.46 (NCH_2). MS (CI; *m*/*z* (relative intensity)): 174 (MH^+, 82); 172 (28); 158 (100); 100 (4); 73 (9); 58 (31). Anal. Calcd for $C_9H_{23}NSi$: C, 62.35; H, 13.37; N, 8.08. Found: C, 62.15; H, 13.33; N, 8.05.

4-(Propylamino)-1-(trimethylsilyl)butane (4b). Yield: 62 mg (66%). IR (film; ν, cm^{-1}): 3289 (w) (NH); 1248 (s), 835 (s), 745 (m) ($SiMe_3$). ^{1}H NMR ($CDCl_3$; δ, ppm): −0.06 (s, 9H, $SiMe_3$); 0.35−0.60 (m, 2H, CH_2Si); 0.88 (t, J = 7.3 Hz, 3H, CH_3); 1.22 (s, 1H, NH); 1.25−1.65 (m, 6H, CH_2); 2.54 (t, J = 7.2 Hz, 2H, CH_2N); 2.57 (t, J = 7.0 Hz, 2H, $NCH_2C_2H_5$). ^{13}C NMR ($CDCl_3$; δ, ppm): −1.76 ($SiMe_3$); 11.69 (CH_3); 16.58 (CH_2-Si); 21.69 ($SiCH_2CH_2$); 22.76 (CH_2CH_3); 33.56 (CH_2CH_2N); 49.49 (CH_2N); 51.67 ($NCH_2C_2H_5$). MS (EI; *m*/*z* (relative intensity)): 187 (M^+, 29); 172 (56); 158 (53); 114 (32); 73 (73);

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72 (100); 59 (57); 44 (81); 30 (64). Anal. Calcd for $C_{10}H_{25}NSi$: C, 64.09; H, 13.45; N, 7.47. Found: C, 63.91; H, 13.50; N, 7.52.

4-(Isopropylamino)-1-(trimethylsilyl)butane (4c). Yield: 24 mg (26%). IR (film; ν, cm^{-1}): 3352 (w) (NH); 1248 (s), 836 (s), 758 (m) ($SiMe_3$). ^1H NMR ($CDCl_3$; δ, ppm): −0.04 (s, 9H, $SiMe_3$); 0.35−0.65 (m, 2H, CH_2Si); 1.04 (d, J = 6.2 Hz, 6H, CH_3); 1.20−1.60 (m, 5H, CH_2, NH); 2.57 (t, J = 6.8 Hz, 2H, CH_2N); 2.77 (hept, J = 6.2 Hz, 1H, CH). ^{13}C NMR ($CDCl_3$; δ, ppm): −1.68 ($SiMe_3$); 16.67 (CH_2Si); 21.84 ($SiCH_2CH_2$); 22.97 (CH_3); 34.31 (CH_2); 47.34 (CH_2N); 48.75 (CH). MS (EI; *m*/*z* (relative intensity)): 187 (M^+, 21); 172 (66); 130 (26); 114 (29); 74 (26); 73 (75); 72 (100); 58 (76); 45 (54); 44 (47); 30 (78). Anal. Calcd for $C_{10}H_{25}NSi$: C, 64.09; H, 13.45; N, 7.47. Found: C, 64.19; H, 13.40; N, 7.43.

4-(Benzylamino)-1-(trimethylsilyl)butane (4d). Yield: 91 mg (77%). IR (film; ν, cm^{-1}): 3340 (w) (NH); 3064 (w), 3028 (m), 1606 (w), 1495 (m), 733 (m), 697 (s) (C_6H_5); 1248 (s), 835 (s), 754 (m) ($SiMe_3$). ^1H NMR ($CDCl_3$; δ, ppm): 0.01 (s, 9H, $SiMe_3$); 0.40−0.67 (m, 2H, CH_2Si); 1.13−1.75 (m, 4H, CH_2); 1.60 (s, 1H, NH); 2.65 (t, J = 6.7 Hz, 2H, CH_2N); 3,80 (s, 2H, $CH_2C_6H_5$); 7.32 (s, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$; δ, ppm): −1.76 ($SiMe_3$); 16.53 (CH_2Si); 21.60 (CH_2CH_2Si); 33.86 (CH_2CH_2N); 49.07 (CH_2N); 54.00 ($CH_2C_6H_5$); 126.68, 127.96, 128.20, 140.46 (C_6H_5). MS (EI; *m*/*z* (relative intensity)): 235 (M^+, 12); 220 (11); 162 (27); 121 (37); 120 (100); 106 (64); 91 (98); 73 (70); 59 (22); 45 (44); 30 (20). Anal. Calcd for $C_{14}H_{25}NSi$: C, 71.42; H, 10.70; N, 5.95. Found: C, 71.32; H, 10.66; N, 5.99.

Amines 10. 1-(*tert*-Butyl)-2-(trimethylsilyl)azetidine (10f). Yield: 45 mg (45%);. IR (film; ν, cm^{-1}): 1360 (m) ($C(CH_3)_3$); 1249 (s), 862 (s), 766 (m) ($SiMe_3$). ^1H NMR ($CDCl_3$; δ, ppm): −0.14 (s, 9H, $SiMe_3$); 0.85 (s, 9H, CH_3); 0.86−1.00 (m, 2H, CH_2Si); 1.45−1.90 (m, 2H, CH_2); 2.75−3.00 (m, 2H, CH_2N); 3.15−3.50 (m, 1H, CH). ^{13}C NMR ($CDCl_3$; δ, ppm): −1.05 ($SiMe_3$); 25.18 (CH_2Si); 25.27 (CH_3); 28.22 (CH_2); 43.02 (CH_2N); 52.54 (C); 56.32 (CH). MS (EI; *m*/*z* (relative intensity)): 199 (M^+, 12); 185 (27); 184 (100); 112 (56); 102 (62); 100 (20); 86 (27); 73 (97); 56 (78). Anal. Calcd for $C_{11}H_{25}NSi$: C, 66.26; H, 12.64; N, 7.02. Found: C, 66.11; H, 12.70; N, 6.98.

1-Benzyl-3-(trimethylsilyl)pyrrolidine (10g). Yield: 22 mg (19%). IR (film; ν, cm^{-1}): 3063 (w), 3028 (m), 1605 (w), 1495 (m), 740 (m), 698 (s) (C_6H_5); 1249 (s), 836 (s), 746 (m) ($SiMe_3$). ^1H NMR ($CDCl_3$; δ, ppm): 0.01 (s, 9H, $SiMe_3$); 1.15−2.45 (m, 5H, NCH_2CH_2CH); 2.60−3.00 (m, 2H, CH_2); 3.63 (s, 2H, $CH_2C_6H_5$); 7.32 (s, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$; δ, ppm): −3.02 ($SiMe_3$); 24.19 (CH); 25.95 (CH_2); 54.95 ($CHCH_2N$); 56.27 (CH_2N); 60.65 ($CH_2C_6H_5$); 126.79, 128.20, 128.76, 139.62 (C_6H_5). MS (CI; *m*/*z* (relative intensity)): 234 (MH^+, 100); 232 (53); 218 (96); 156 (15); 148 (12); 120 (39); 91 (11); 73 (7). Anal. Calcd for $C_{14}H_{23}NSi$: C, 72.04; H, 9.93; N, 6.00. Found: C, 71.88; H, 9.91; N, 6.05.

General Procedure for the Reaction of Benzotriazoles 1a−e with Propargyltrimethylsilane. The same procedure as above was used, with propargyltrimethylsilane (0.67 g, 6 mmol) as starting material.

Amines 6. 4-(Morpholino)buta-1,2-diene (6e). Yield: 20 mg (29%); IR (film; ν, cm^{-1}): 3040 (w), 1954 (m), 856 (s) (CH_2=C=CH); 1116 (s) (CO).; ^1H NMR ($CDCl_3$; δ, ppm): 2.30−2.55 (m, 4H, CH_2N); 3.00 (dt, J = 7.2 Hz, J = 2.5 Hz, 2H, CH_2); 3.55−3.80 (m, 4H, CH_2O); 4.60−4.75 (m, 2H, CH_2=); 4.90−5.25 (m, 1H, CH=). ^{13}C NMR ($CDCl_3$; δ, ppm): 53.10 (CH_2N); 57.61 (CH_2); 66.80 (CH_2O); 74.76 (CH_2=); 86.19 (CH=); 209.56 (=C=). MS (EI; *m*/*z* (relative intensity)): 139 (M^+, 22); 138 (24); 124 (2); 108 (36); 100 (100); 81 (42); 80 (30); 56 (24); 54 (22); 53 (21); 42 (24). Anal. Calcd for $C_8H_{13}NO$: C, 69.03; H, 9.42; N, 10.06. Found: C, 68.87; H, 9.48; N, 10.11.

Amines 7. (2*E*)-4-(Ethylamino)-1-(trimethylsilyl)but-2-ene (7a). Yield: 37 mg (43%). IR (film; ν, cm^{-1}): 3284 (w) (NH); 1660 (m), 968 (s) (CH=CH (*E*)); 1248 (s), 851 (s), 748 (m) ($SiMe_3$). ^1H NMR ($CDCl_3$; δ, ppm): −0.09 (s, 9H, $SiMe_3$); 0.95 (s, 1H, NH); 1.01 (t, J = 7.1 Hz, 3H, CH_3); 1.35 (d, J = 6.5 Hz, 2H, CH_2Si); 2.55 (q, J = 7.1 Hz, 2H, CH_2); 3.08 (d, J = 5.3 Hz, 2H, CH_2C=); 5.32 (dt, J_{AB} = 15.2 Hz, J = 5.3 Hz, 1H, CH=); 5.52 (dt, J_{AB} = 15.2 Hz, J = 6.5 Hz, 1H, =C*H*CH_2Si). ^{13}C NMR ($CDCl_3$; δ, ppm): −2.18 ($SiMe_3$); 15.09 (CH_3); 22.46 (CH_2Si); 43.14 (CH_2); 51.76 (CH_2C=); 127.00 (=*C*HCH_2Si); 128.49 (=CH). MS (CI; *m*/*z* (relative intensity)): 172 (MH^+, 29); 170 (39); 156 (43); 127 (62); 102 (100); 73 (78); 58 (52). Anal. Calcd for $C_9H_{21}NSi$: C, 63.09; H, 12.35; N, 8.17. Found: C, 62.98; H, 12.39; N, 8.13.

(2*E*)-4-(Propylamino)-1-(trimethylsilyl)but-2-ene (7b). Yield: 45 mg (49%). IR (film; ν, cm^{-1}): 3294 (w) (NH); 1660 (m), 967 (s) (CH=CH (*E*)); 1248 (s), 850 (s), 748 (m) ($SiMe_3$). ^1H NMR ($CDCl_3$; δ, ppm): 0.10 (s, 9H, $SiMe_3$); 0.81 (t, J = 7.2 Hz, 3H, CH_3); 1.20−1.60 (m, 2H, CH_2); 1.35 (d, J = 6.6 Hz, 2H, CH_2Si); 1.49 (s, 1H, NH); 2.46 (t, J = 7.1 Hz, 2H, CH_2N); 3.07 (d, J = 5.3 Hz, 2H, CH_2C=); 5.27 (dt, J_{AB} = 15.2 Hz, J = 5.3 Hz, 1H, CH=); 5.45 (dt, J_{AB} = 15.2 Hz, J = 6.6 Hz, 1H, =C*H*CH_2Si). ^{13}C NMR ($CDCl_3$; δ, ppm): −2.15 ($SiMe_3$); 11.63 (CH_3); 22.49 (CH_2Si); 23.00 (CH_2); 50.89 (CH_2N); 51.82 (CH_2C=); 126.85 (=*C*HCH_2Si); 128.67 (=CH). MS (EI; *m*/*z* (relative intensity)): 185 (M^+, 35); 156 (10); 142 (12); 127 (61); 116 (72); 112 (62); 102 (65); 98 (88); 73 (100); 59 (38); 45 (64). Anal. Calcd for $C_{10}H_{23}NSi$: C, 64.79; H, 12.51; N, 7.55. Found: C, 64.69; H, 12.55; N, 7.60.

(*E*)-4-(Isopropylamino)-1-(trimethylsilyl)but-2-ene (7c). Yield: 15 mg (16%). IR (film; ν, cm^{-1}): 3316 (w) (NH); 1660 (m), 967 (s) (CH=CH (*E*)); 1248 (s), 852 (s), 748 (m) ($SiMe_3$). ^1H NMR ($CDCl_3$; δ, ppm): −0.04 (s, 9H, $SiMe_3$); 1.01 (d, J = 6.3 Hz, 6H, CH_3); 1.40 (s, 1H, NH); 1.41 (d, J = 6.5 Hz, 2H, CH_2Si); 2.80 (hept, J = 6.3 Hz, 1H, CH); 3.13 (d, J = 5.3 Hz, 2H, CH_2); 5.34 (dt, J_{AB} = 15.1 Hz, J = 5.3 Hz, 1H, CH=); 5.53 (dt, J_{AB} = 15.1 Hz, J = 6.5 Hz, 1H, =C*H*CH_2Si). ^{13}C NMR ($CDCl_3$; δ, ppm): −2.06 ($SiMe_3$); 22.58 (CH_2Si); 22.79 (CH_3); 47.61 (CH); 49.52 (CH_2); 127.09 (=*C*HCH_2Si); 128.67 (=CH). MS (EI; *m*/*z* (relative intensity)): 185 (M^+, 6); 170 (2); 142 (4); 116 (23); 112 (11); 98 (16); 85 (11); 73 (100); 59 (10); 45 (14); 30 (13). Anal. Calcd for $C_{10}H_{23}NSi$: C, 64.79; H, 12.51; N, 7.55. Found: C, 64.60; H, 12.46; N, 7.51.

(*E*)-4-(Benzylamino)-1-(trimethylsilyl)but-2-ene (7d). Yield: 71 mg (61%). IR (film; ν, cm^{-1}): 3314 (w) (NH); 3063 (w), 3027 (m), 1604 (w), 1495 (m), 734 (s), 698 (s) (C_6H_5); 1660 (m), 967 (s) (CH=CH (*E*)); 1248 (s), 851 (s), 751 (m) ($SiMe_3$). ^1H NMR ($CDCl_3$; δ, ppm): 0.05 (s, 9H, $SiMe_3$); 1.51 (d, J = 6.8 Hz, 2H, CH_2Si); 1.91 (s, 1H, NH); 3.24 (d, J = 5.4 Hz, 2H, CH_2C=); 3.80 (s, 2H, CH_2); 5.44 (dt, J_{AB} = 15.2 Hz, J = 5.4 Hz, 1H, CH=); 5.62 (dt, J_{AB} = 15.2 Hz, J = 6.8 Hz, 1H, =C*H*CH_2Si); 7.33 (s, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$; δ, ppm): −2.03 ($SiMe_3$); 22.61 (CH_2Si); 51.19 (CH_2C=); 52.83 (CH_2N); 126.56 (=*C*HCH_2Si); 129.27 (=CH); 126.74, 128.11, 128.23, 140.22 (C_6H_5). MS (EI; *m*/*z* (relative intensity)): 233 (M^+, 31); 164 (45); 160 (32); 146 (56); 133 (39); 120 (69); 106 (49); 91 (100); 73 (90); 45 (47). Anal. Calcd for $C_{14}H_{23}NSi$: C, 72.04; H, 9.93; N, 6.00. Found: C, 72.16; H, 9.88; N, 6.03.

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