NOTES *Bull. Chem. Soc. Jpn.*, **67**, 1510—1513(1994) [Vol. 67, No. 5

Silylation of 2- or 3-Alkenenitriles with Iodosilanes/Triethylamine Affording 2- or 4-Silyl-2-alkenenitriles

Hiroshi YAMASHITA,† N. Prabhakar REDDY,† and Masato TANAKA*,†,††
†National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305
††Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

(Received January 20, 1994)

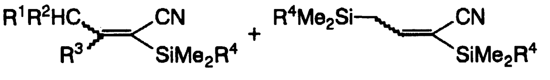
Synopsis. 2- or 3-Alkenenitriles, $(R^1R^2HC)R^3C{=}CHCN$ or $R^1R^2C{=}CR^3CH_2CN$ (R^1, R^2, R^3=H, Me, etc.), react with iodosilanes, R^4Me_2SiI (R^4=Me, Me_3Si), in the presence of Et_3N to give 2-silyl-2-alkenenitriles, $(R^1R^2HC)R^3C{=}C(SiMe_2R^4)(CN)$, in good to moderate yields with high *E* selectivity (R^3=H). A 2-methylalkenenitrile, $H_2C{=}CHCHMe(CN)$ or $MeCH{=}CMe(CN)$, is silylated with Me_3SiI to provide a 4-silyl-2-alkenenitrile, $Me_3SiCH_2CH{=}CMe(CN)$.

Alkenylsilanes such as vinyl- and allysilane derivatives are versatile and widely used reagents in organic synthesis.[1)] One of the most practical methods for their preparation is silylation of vinyl- or allylmetals with chlorosilanes, although the reaction in general required alkali or alkaline earth metals or organoalkali metal bases to generate the vinyl- or allylmetal species. We report here a simple and convenient silylation procedure of 2- or 3-alkenenitriles by the combined use of iodosilanes and an organic base, Et_3N, which is easier to be handled, providing cyano group-substituted vinyl- or allylsilane derivatives, 2- or 4-silyl-2-alkenenitriles.[2)]

Treatment of 3-butenenitrile (**1a**) with a mixture of Me_3SiI (**2a**) and Et_3N[3)] (molar ratio of **1a**/**2a**/Et_3N=4/1/8.6) at 120 °C for 30 min gave an α-silylated 2-alkenenitrile, 2-trimethylsilyl-2-butenenitrile (**3a**), in a high yield (86% based on **2a**) and high *E* stereoselectivity (*E*/*Z*=98/2), with precipitation of an amine salt, Et_3NHI, Eq. 1 (Table 1, Run 1). A small amount of an α,γ-disilylated compound, 2,4-bis(trimethylsilyl)-2-butenenitrile (**4a**), was also formed in 2% yield. Longer reaction times and/or use of smaller amounts of Et_3N resulted in lower yields of **3a**; the yields of **3a** and **4a** using a half amount of Et_3N were respectively 48 and 14% (reaction time=30 min), 47 and 14% (2 h), and 21 and 5% (10 h). Compound **4a** was obtained as the major product, when the ratio of **2a**/**1a** was increased from 1/4 to 2.5/1; yields of **4a** and **3a** based on **1a** were 26 and 11%, respectively (Run 2). The stereochemistry of **3a** was confirmed by stereospecific transformation of (*E*)- and/or (*Z*)-**3a** into (*Z*)- and/or (*E*)-2-butenenitrile with 1 M-NaOH/MeOH,[2a)] while an attempted similar conversion of **4a** failed. Silylation of **1a** with Me_3SiCl mediated by MeLi was previously reported.[4)] However, the product was disilyl compound **4a**, even when one equivalent of MeLi was used.

1a: $R^1 = R^2 = R^3 = H$
1b: $R^1 = Me$, $R^2 = R^3 = H$
1c: $R^1 = R^2 = Me$, $R^3 = H$
1d: $R^1 = NCCH_2$, $R^2 = R^3 = H$
5a: $R^1 = R^2 = R^3 = H$
5b: $R^1 = Me_2C{=}CHCH_2$, $R^2 = H$, $R^3 = Me$
2a: $R^4 = Me$
2b: $R^4 = Me_3Si$

(1)



3 4

3a: $R^1 = R^2 = R^3 = H$, $R^4 = Me$
3b: $R^1 = R^4 = Me$, $R^2 = R^3 = H$
3c: $R^1 = R^2 = R^4 = Me$, $R^3 = H$
3d: $R^1 = NCCH_2$, $R^2 = R^3 = H$, $R^4 = Me$
3e: $R^1 = Me_2C{=}CHCH_2$, $R^2 = H$, $R^3 = R^4 = Me$
3f : $R^1 = R^2 = R^3 = H$, $R^4 = Me_3Si$
4a: $R^4 = Me$
4f : $R^4 = Me_3Si$

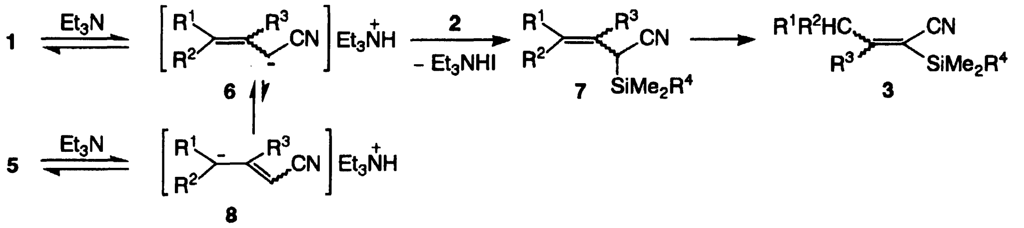
Other 3-alkenenitriles **1a**—**d**, $R^1R^2C{=}CHCH_2CN$ (**1b**: R^1=Me, R^2=H; **1c**: R^1=R^2=Me; **1d**: R^1=$NCCH_2$, R^2=H), also reacted with **2a** under reaction conditions similar to those for **1a** to give the corresponding 2-silyl-2-alkenenitriles **3d**—**d**, $(R^1R^2HC)CH{=}C(SiMe_3)(CN)$, in 59, 52, and 44% yields, respectively (Runs 3—5). The reactivity of **3d** was significantly high, and prolonging the reaction time caused decomposition of **3d** into unidentified nonvolatile products; the yields of **3d** (time) were 39% (30 min), 27% (2 h), 18% (10 h), and ca. 1% (30 h). High *E* stereoselectivity of the products was confirmed in the cases of **3b**, **d** by the stereospecific desilylation reaction (vide supra).

While the reactions of **1a**—**d** were in progress, their regioisomers, 2-alkenenitriles, were transiently formed in considerable amounts, suggesting isomerization between 3-alkenenitriles and 2-alkenenitriles taking place. This indicates a possibility of the use of 2-alkenenitriles instead of 3-alkenenitriles. Indeed, 2-butenenitrile (**5a**, *E*/*Z*=38/62) could react with **2a** to give **3a** and **4a** in 70 and 14% yields, respectively, although its reactivity was somewhat lower than that of **1a** (Run 6). Like-

Table 1. Silylation of 2- and 3-Alkenenitriles with Iodosilanes/Et$_3$N[a]

Run	Nitrile	Silane	Et$_3$N equiv[b]	Time	Product (Yield[c]/%)	E/Z[d] of **3** or **10**
1	**1a**	**2a**	8.6	30 min	**3a** (86[50]), **4a** (2)[e]	98/2
2[f]	**1a**	**2a**	3.2	2 h	**3a** (11),[g] **4a** (26[23])[e,g]	80/20
3	**1b**	**2a**	4.3	10 h	**3b** ([59])	97/3
4[h]	**1c**	**2a**	4.3	10 h	**3c** (52)	—[e]
5	**1d**	**2a**	4.3	2 min	**3d** (44[39])	ca. 100/0
6	**5a**	**2a**	8.6	1 h	**3a** (70), **4a** (14)[e]	98/2
7	**5b**	**2a**	8.6	4 h	**3e** (48)	55/45
8[i]	**1a**	**2b**	21.5	1.5 h	**3f** (65[61]),[j] **4f** (21[15])[e]	97/3
9	**9**	**2a**	4.3	10 h	**10** (46)	35/65
10	**11**	**2a**	4.3	10 h	**10** (50)	32/68

a) Alkenenitrile 4.0 mmol, iodosilane 1.0 mmol, 120 °C. b) Based on **2**. c) GC yields based on **2**. Figures in brackets are isolated yields. d) Estimated by GC. e) Nearly one stereoisomer was obtained in each case, although its stereochemistry has not been confirmed. f) **1a** 0.8 mmol, **2a** 2.0 mmol. g) Yields based on **1a**. h) **1c** 1.5 mmol, **2a** 0.5 mmol. **1c** contained 4-methyl-4-pentenenitrile (**1c′**, ca. 0.5 mmol). i) **1a** 3.64 mmol, **2b** 0.91 mmol. j) 4-Pentamethyldisilanyl-2-butene (**3f′**, nearly pure E form) ca. 4% yield.



Scheme 1.

wise, a trisubstituted 2-alkenenitrile, 3,7-dimethyl-2,6-octadienenitrile (**5b**, E/Z=60/40), underwent the silylation, albeit at a lower rate, to provide the corresponding 2-silyl-2-alkenenitrile **3e** in 48% yield (E/Z=55/45) (Run 7).

In contrast with the iodosilane **2a**, Me$_3$SiCl did not react with alkenenitriles under the present conditions. However, Me$_3$SiBr did react, although the reactivity was much lower than **2a**; the yields of **3a** and **3d** were respectively 86 and 46% for **2a**, while they were ca. 1 and 14% for Me$_3$SiBr (molar ratio of **1a**/halosilane/Et$_3$N=4/1/8.6, 120 °C, 30 min for **3a** and 10 min for **3d**). The tendency of the reactivity of halosilanes is similar to that of C–X (X=I, Br, Cl) compounds toward nucleophiles.

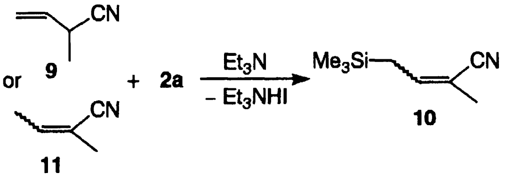
The present procedure is applicable to disilanylation of an alkenenitrile. Thus, the reaction of **1a** with Me$_3$SiMe$_2$SiI (**2b**) smoothly proceeded to provide disilanyl and bis(disilanyl) compounds, **3f** (65% yield) and **4f** (21%), accompanied by a small amount of a regioisomer of **3f**, 4-disilanyl-2-butenenitrile (**3f′**, nearly pure E form ca. 4%) (Run 8). No Si–Si bond cleavage took place during the reaction, offering a method to prepare new polysilanes functionalized with cyanoalkenyl groups.

The formation of **3** from 3-alkenenitrile **1** is presumably explained by the reaction sequence shown in Scheme 1 that involves generation of the allylic anion species (**6**) from **1** via α-proton abstraction by Et$_3$N, α-attack of an iodosilane **2** to **6** resulting in the 2-silyl-3-alkenenitrile (**7**), and regioisomerization of the C=C double bond providing **3** with a favorable α,β-conjugation system. We believe that 2-alkenenitrile **5** is silylated after isomerization of the initially formed allylic anion (**8**) into the more stable anion **6**.[5] The high E selectivity observed for most of **3** (R^3=H) is probably originated from the steric repulsion between the silyl group and the γ-carbon moiety in the isomerization process from **7** to **3**.

Disilylated compounds, **4a** and **4f**, are formed presumably via **3a** and **3f**. Unlike the other products **3b**—**e**, **3a** and **3f** are expected to undergo γ-proton abstraction rather readily and the resulting allylic anions are not so sterically demanding, because of the lack of electron-releasing (i.e., destabilizing) γ-alkyl substituents. Consequently, **3a** and **3f** are prone to react, via corresponding allylic anions, with a second molecule of the iodosilane to form **4a** and **4f**.

When 2-methyl-3-butenenitrile (**9**) was allowed to react with **2a**, a 4-silyl-2-alkenenitrile **10** (E/Z=35/65)[6] was obtained as the major product in 46% yield, Eq. 2 (Run 9). α-Proton abstraction of **9** generates an allylic anion that is somewhat unstable and unreactive because of the α-methyl group. The allylic anion tends to isomerize, as a result, to give another allylic anion that corresponds to γ-proton abstraction of 2-methyl-

2-butenenitrile (**11**), and this allylic anion is considered to react with **2a** to end up with **10**. In good agreement with this explanation, treatment of **11** with **2a**/Et_3N indeed gave **10** in a little better yield (50%) (Run 10).



(2)

Experimental

^1H, ^{13}C, and ^{29}Si NMR spectra were measured in $CDCl_3$ on Bruker AC-200 and/or Bruker ARX-300 instruments. Chemical shifts are referred to Me_4Si (0 ppm) or $CHCl_3$ (7.25 ppm) for ^1H NMR, $CDCl_3$ (77.0 ppm) for ^{13}C NMR, and Me_4Si (0 ppm) for ^{29}Si NMR. Infrared spectra were recorded on JASCO A-302 and/or JASCO FT/IR-5000 spectrometers. GC-MS and GC-HRMS spectra (EI, 70 eV) were measured on Shimadzu QP-1000 and JEOL DX-303 spectrometers, respectively. Liquid alkenenitriles and Et_3N were dried by usual methods, and distilled under nitrogen or in vacuo. 3-Hexenedinitrile was recrystallized from EtOH–H_2O. 4-Methyl-3-pentenenitrile (**1c**)[8a)] was obtained by cyanation of prenyl bromide with CuCN[8b)] as a mixture with 4-methyl-4-pentenenitrile (**1c′**,[8c)] **1c**/**1c′**≈3/1), and was used without further purification. Me_3SiI (**2a**)[9a)] and Me_3SiMe_2SiI (**2b**)[9b)] were synthesized according to the literature procedures.

A typical procedure of the reaction is as follows (Table 1, Run 1). A mixture of **1a** (4.0 mmol), **2a** (1.0 mmol), and Et_3N (8.6 mmol) was heated under nitrogen in a sealed glass tube at 120 °C for 30 min. To the reaction mixture, which contained the precipitation of Et_3NHI, were added an internal standard for GC (cyclooctane, 20 μl), ether (ca. 3 ml), and water (ca. 1 ml). The ether layer was separated, and the water layer was washed with ether (ca. 1 ml×2). The combined ether layer was dried with $MgSO_4$. GC analysis of the ether solution revealed that **3a** and **4a** were formed in 86% ($E/Z=98/2$) and 2% yields, respectively. Concentration of the solution followed by preparative TLC (silica gel, hexane/ether=5/1) gave **3a** in 50% yield.

Similarly, **3a**—**f**, **3f′**, **4a**, **f**, and **10** were obtained in the reactions of **1a**—**d**, **5a**, **b**, **9**, and **11** with **2a**, **b** under the conditions specified in Table 1 (Runs 2—10). Compounds **3c**, **e**, and **10** were purified by preparative GC. The stereochemistry of **3a**, **b**, **d**—**f** was determined by their stereospecific desilylation into the corresponding 2-alkenes with 1 M-NaOH/MeOH[2a)] (**3** 0.03—0.24 mmol, NaOH 0.7—1 equiv) in ether (1.5—2 ml) at ca. 0 °C for 20 min (**3a**, ca. 40% conversion), 2 h (**3b**, ca. 100%), ca. 0.5 min (**3d**, ca. 100%), 80 min (**3e**, ca. 15%), and 20 min (**3f**, ca. 10%). Desilylation of **3e** ($E/Z\approx9/1$) was much slower, and partial isomerization between *E* and *Z* forms took place during the reaction to give **5b** ($Z/E\approx3/2$).

NMR, IR, and GC-(HR)MS spectra and/or analytical data of **3a**—**f**, **3f′**, **4a**, **f**, and **10** are as follows.

2-Trimethylsilyl-2-butenenitrile (3a). **(*E*)-3a:** ^1H NMR $\delta=0.20$ (9H, s, $SiCH_3$), 2.09 (3H, d, $J=6.6$ Hz, CCH_3), and 6.64 (1H, q, $J=6.6$ Hz, =CH); ^{13}C NMR $\delta=-2.2$ ($SiCH_3$), 20.2 ($=C\underline{C}$), 116.6 (=CSi), 118.2 (CN), and 157.0 (=CH); ^{29}Si NMR $\delta=-0.7$; IR (neat) 2204 (CN), 1601 (C=C), 1255 (SiMe), and 847 cm^{-1} (SiMe); MS *m/z* (rel intensity) 139 (M^+; 24), 124 (45), 97 (77), 84 (45), 73 (100), 45 (20), and 43 (40). Found: *m/z* 139.0821. Calcd for $C_7H_{13}NSi$: M, 139.0817.

(*Z*)-3a:[2c)] ^1H NMR $\delta=0.27$ (9H, s, $SiCH_3$), 1.94 (3H, d, $J=7.2$ Hz, CCH_3), and 7.16 (1H, q, $J=7.2$ Hz, =CH); ^{29}Si NMR $\delta=-5.0$; MS *m/z* (rel intensity) 139 (M^+; 2), 124 (19), 97 (27), 84 (20), 73 (100), 45 (22), and 43 (28). Found: *m/z* 139.0822. Calcd for $C_7H_{13}NSi$: M, 139.0817.

2-Trimethylsilyl-2-pentenenitrile (3b). Bp ca. 113 °C/8666 Pa ($E/Z=97/3$, Kugelrohr).

(*E*)-3b: ^1H NMR $\delta=0.19$ (9H, s, $SiCH_3$), 1.06 (3H, t, $J=7.5$ Hz, $CH_2C\underline{H}_3$), 2.38—2.56 (2H, m, CH_2), and 6.53 (1H, t, $J=7.2$ Hz, =CH); ^{13}C NMR $\delta=-2.2$ ($SiCH_3$), 12.8 ($CH_2\underline{C}H_3$), 27.8 (CH_2), 114.5 (=CSi), 118.2 (CN), and 163.5 (=CH); IR (neat) 2205 (CN), 1596 (C=C), 1254 (SiMe), and 846 cm^{-1} (SiMe); MS *m/z* (rel intensity) 153 (M^+; 3), 138 (85), 111 (43), 84 (25), 73 (100), 59 (24), 45 (26), and 43 (41). Found (a mixture with *Z* form, $E/Z=97/3$): C, 62.76; H, 9.56; N, 9.38%. Calcd for $C_8H_{15}NSi$: C, 62.68; H, 9.86; N, 9.14%.

(*Z*)-3b: MS *m/z* (rel intensity) 153 (M^+; 2), 138 (74), 111 (31), 84 (21), 73 (100), 59 (20), 45 (23), and 43 (36).

4-Methyl-2-trimethylsilyl-2-pentenenitrile (3c). ^1H NMR $\delta=0.21$ (9H, s, $SiCH_3$), 1.05 (6H, d, $J=6.6$ Hz, $C(CH_3)_2$), 2.86—3.07 (1H, m, $C\underline{H}CH_3$), and 6.34 (1H, d, $J=9.4$ Hz, =CH); IR (neat) 2210 (CN), 1598 (C=C), 1256 (SiMe), and 846 cm^{-1} (SiMe); MS *m/z* (rel intensity) 167 (M^+; 14), 166 (14), 152 (64), 125 (26), 84 (20), 73 (100), 59 (40), 45 (30), and 43 (42). Found: *m/z* 167.1129. Calcd for $C_9H_{17}NSi$: M, 167.1130.

2-Trimethylsilyl-2-hexenedinitrile (3d). Bp ca. 110 °C/107 Pa ($E/Z\approx100/0$, Kugelrohr).

(*E*)-3d: ^1H NMR $\delta=0.24$ (9H, s, $SiCH_3$), 2.53 (2H, t, $J=7.0$ Hz, CH_2CN), 2.80 (2H, td, $J=7.0$ and 7.0 Hz, $=CHC\underline{H}_2$) and 6.55 (1H, t, $J=7.0$ Hz, =CH); ^{13}C NMR $\delta=-2.3$ ($SiCH_3$), 16.3 ($\underline{C}H_2CN$), 29.3 ($=CH\underline{C}H_2$), 117.2, 118.0, and 120.2 (CN, =CSi), and 155.2 (=CH); ^{29}Si NMR $\delta=0.6$; IR (neat) 2252 (CN), 2204 (CN), 1603 (C=C), 1255 (SiMe), and 847 cm^{-1} (SiMe); MS *m/z* (rel intensity) 163 (M^+-15; 100), 84 (44), 73 (70), 45 (25), and 43 (51). Found: C, 60.56; H, 8.00; N, 15.62%. Calcd for $C_9H_{14}N_2Si$: C, 60.62; H, 7.91; N, 15.71%.

3,7-Dimethyl-2-trimethylsilyl-2,6-octadienenitrile (3e). **(*E*)-3e:** ^1H NMR $\delta=0.27$ (9H, s, $SiCH_3$), 1.61 and 1.68 (each 3H, each br s, CCH_3), 1.96 (3H, s, CCH_3), 2.15—2.25 and 2.47—2.55 (each 2H, each m, CH_2), and 5.06—5.16 (1H, m, =CH); ^{13}C NMR $\delta=-0.5$ ($SiCH_3$), 17.6 and 22.7 (CH_2), 25.6, 26.7, and 40.8 (CH_3), 108.8 (=CSi), 120.0 (CN), 122.5 (=CH), and 133.0 and 173.8 ($=\underline{C}(C)_2$); ^{29}Si NMR $\delta=-5.7$; IR (neat) 2198 (CN), 1584 (C=C), 1255 (SiMe), and 843 cm^{-1} (SiMe); MS *m/z* (rel intensity) 221 (M^+; 25), 206 (26), 153 (67), 138 (28), 74 (62), 73 (47), 69 (100), and 41 (74). Found: *m/z* 221.1601. Calcd for $C_{13}H_{23}NSi$: M,221.1600.

(*Z*)-3e: ^1H NMR $\delta=0.26$ (9H, s, $SiCH_3$), 1.61 and 1.69 (each 3H, each br s, CCH_3), 2.16 (3H, s, CCH_3), 2.09—2.20 and 2.24—2.32 (each 2H, each m, CH_2), and 4.99—5.07 (1H, m, =CH); ^{29}Si NMR $\delta=-6.1$; IR (neat) 2198 (CN), 1584 (C=C), 1255 (SiMe), and 843 cm^{-1} (SiMe); MS *m/z* (rel intensity) 221 (M^+; 16), 206 (66), 153 (22), 74 (49), 73 (100), 69 (90), and 41 (83). Found: *m/z* 221.1600. Calcd for $C_{13}H_{23}NSi$: M, 221.1600.

2-Pentamethyldisilanyl-2-butenenitrile (3f). (*E*)-3f: ^{1}H NMR δ=0.10 (9H, s, $SiCH_3$), 0.22 (6H, s, $SiCH_3$), 2.08 (3H, d, *J*=6.6 Hz, CCH_3), and 6.55 (1H, q, *J*=6.6 Hz, =CH); ^{13}C NMR δ=−4.7 and −2.4 ($SiCH_3$), 20.3 (=C$\underline{C}$), 115.5 (=CSi), 118.4 (CN), and 156.4 (=CH); ^{29}Si NMR δ= −18.8 and −17.5; IR (neat) 2202 (CN), 1597 (C=C), 1249 (SiMe), 835 (SiMe), and 799 cm^{-1} (SiMe); MS *m/z* (rel intensity) 197 (M^+; 6), 182 (17), 97 (15), 83 (14), 73 (100), 45 (27), and 43 (23). Found: *m/z* 197.1048. Calcd for $C_9H_{19}NSi_2$: 197.1056.

(*Z*)-3f: ^{1}H NMR δ=0.13 (9H, s, $SiCH_3$), 0.33 (6H, s, $SiCH_3$), 1.92 (3H, d, *J*=7.1 Hz, CCH_3), and 7.19 (1H, q, *J*=7.1 Hz, =CH); ^{29}Si NMR δ=−22.8 and −17.8; MS *m/z* (rel intensity) 197 (M^+; 7), 182 (23), 97 (16), 83 (15), 73 (100), 45 (25), and 43 (20). Found: *m/z* 197.1065. Calcd for $C_9H_{19}NSi_2$: M, 197.1056.

4-Pentamethyldisilanyl-2-butenenitrile (3f′) (*E*)-3f′: ^{1}H NMR δ=0.078 and 0.079 (15H, each s, $SiCH_3$), 1.81 (2H, dd, *J*=8.9 and 1.2 Hz, CH_2), 5.09 (1H, dt, *J*=16.1 and 1.2 Hz, =CH(CN)), and 6.73 (1H, dt, *J*=16.1 and 8.9 Hz, =C$\underline{H}$CH$_2$); ^{13}C NMR δ=−4.6 and −2.3 ($SiCH_3$), 24.5 (CH_2), 96.1 (=$\underline{C}$H(CN)), 118.3 (CN), and 154.7 (=$\underline{C}$HCH$_2$); ^{29}Si NMR δ=−19.0 and −16.2; MS *m/z* (rel intensity) 197 (M^+; 8), 131 (67), 73 (100), 45 (30), and 43 (25). Found: *m/z* 197.1060. Calcd for $C_9H_{19}NSi_2$: M, 197.1056.

2,4-Bis(trimethylsilyl)-2-butenenitrile (4a).[4] ^{1}H NMR δ=0.07 and 0.19 (each 9H, each s, $SiCH_3$), 2.12 (2H, d, *J*=8.7 Hz, CH_2), and 6.63 (1H, t, *J*=8.7 Hz, =CH); ^{13}C NMR δ=−1.9 and −1.7 ($SiCH_3$), 28.8 (CH_2), 110.6 (=CSi), 119.1 (CN), and 160.5 (=CH); ^{29}Si NMR δ=−1.3 and 3.7; IR (neat) 2198 (CN), 1580 (C=C), 1253 (SiMe), and 841 cm^{-1} (SiMe); MS *m/z* (rel intensity) 211 (M^+; 9), 196 (23), 73 (100), 45 (25), and 43 (12). Found: *m/z* 211.1207. Calcd for $C_{10}H_{21}NSi_2$: M, 211.1213.

2,4-Bis(pentamethyldisilanyl)-2-butenenitrile (4f). ^{1}H NMR δ=0.09 (9H, s, $SiCH_3$), 0.10 (6H, s, $SiCH_3$), 0.12 (9H, s, $SiCH_3$), 0.22 (6H, s, $SiCH_3$), 2.18 (2H, d, *J*=8.7 Hz, CH_2), and 6.56 (1H, t, *J*=8.7 Hz, =CH); ^{13}C NMR δ=−4.39, −4.35, −2.3, and −2.2 ($SiCH_3$), 26.8 (CH_2), 109.2 (=CSi), 119.3 (CN), and 156.0 (=CH); ^{29}Si NMR δ=−18.94, −18.87, −18.0, and −15.2; IR (neat) 2198 (CN), 1576 (C=C), 1249 (SiMe), 835 (SiMe), and 795 cm^{-1} (SiMe); MS *m/z* (rel intensity) 312 (M^+-15; 6), 254 (46), 131 (27), 130 (29), 73 (100), and 45 (23). Found: *m/z* 327.1669. Calcd for $C_{14}H_{33}NSi_4$: M, 327.1690.

2-Methyl-4-trimethylsilyl-2-butenenitrile (10). (*E*)-10: ^{1}H NMR δ=0.08 (9H, s, $SiCH_3$), 1.86 (2H, dq, *J*=8.9 and 1.0 Hz, $SiCH_2$), 1.89—1.95 (3H, m, CCH_3), and 6.19 (1H, tq, *J*=8.9 and 1.4 Hz, =CH); ^{13}C NMR δ=−1.7 ($SiCH_3$), 19.8 (CH_2), 24.3 (C$\underline{C}$H$_3$), 105.5 (=$\underline{C}$CN), 118.9 (CN), and 146.3 (=CH); IR (neat) 2225 (CN), 1632 (C=C), 1254 (SiMe), and 856 cm^{-1} (SiMe); MS *m/z* (rel intensity) 153 (M^+; 33), 138 (23), 111 (29), 84 (17), 73 (100), 45 (49), and 43 (42). Found: *m/z* 153.0981. Calcd for $C_8H_{15}NSi$: M, 153.0974.

(*Z*)-10: ^{1}H NMR δ=0.05 (9H, s, $SiCH_3$), 1.69 (2H, dq, *J*=9.3 and ca. 0.6 Hz, $SiCH_2$), 1.78—1.82 (3H, m, CCH_3), and 6.45 (1H, tq, *J*=9.3 and 1.5 Hz, =CH); ^{13}C NMR δ=−1.6 ($SiCH_3$), 14.4 (CH_2), 22.1 (C$\underline{C}$H$_3$), 105.1 (=$\underline{C}$CN), 121.5 (CN), and 146.6 (=CH); IR (neat) 2225 (CN), 1628 (C=C), 1254 (SiMe), and 856 cm^{-1} (SiMe); MS *m/z* (rel intensity) 153 (M^+; 29), 138 (12), 111 (20), 84 (13), 73 (100), 45 (54), and 43 (40). Found: *m/z* 153.0964. Calcd for $C_8H_{15}NSi$: M, 153.0974.

References

1) For instance: E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981); W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer, New York (1983).

2) (*E*)-2-Silyl-2-alkenenitriles are useful percursors for (*Z*)-2-alkenenitriles. See: a) Y. Sato and Y. Niinomi, *J. Chem. Soc., Chem. Commun.*, **1982**, 56; b) I. Matsuda, H. Okada, and Y. Izumi, *Bull. Chem. Soc. Jpn.*, **56**, 528 (1983). See also: c) N. J. Fitzmaurice, W. R. Jackson, and P. Perlmutter, *J. Organomet. Chem.*, **285**, 375 (1985).

3) Iodosilane **1a** readily makes a complex with Et_3N. For complex formation of halosilanes with organic bases: J. Minamikawa and A. Brossi, *Can. J. Chem.*, **57**, 1720 (1979), and references cited therein.

4) S. Brenner and M. Bovete, *Tetrahedron Lett.*, **1974**, 1377.

5) In the deprotonation of **1a** with MeLi, only the type **6** anion was observed by NMR.[4]

6) The *E* and *Z* isomers of **10** were tentatively assigned by the comparison of NMR spectra with those of the corresponding desilylated compounds, (*E*)- and (*Z*)-2-methyl-2-butenenitrile.[7]

7) T. Funabiki, H. Hosomi, S. Yoshida, and K. Tarama, *J. Am. Chem. Soc.*, **104**, 1560 (1982).

8) a) G. Descotes and P. Laconche, *Bull. Soc. Chim. Fr.*, **1968**, 2149; b) J. V. Supniewski and P. L. Salzberg, *Org. Synth.*, Coll. Vol. I, 46 (1956); c) C. A. Grob and A. Waldner, *Helv. Chim. Acta*, **62**, 1854 (1979).

9) a) H. Sakurai, A. Shirahata, K. Sasaki, and A. Hosomi, *Synthesis*, **1979**, 740; b) M. Ishikawa, M. Kumada, and H. Sakurai, *J. Organomet. Chem.*, **23**, 63 (1970).