

Bulb-to-bulb distillation gave 388 mg (89% yield) of pure (*Z*)-2-nonenyltrimethylsilane (7) boiling at 110 °C (22 mmHg) (bath temperature).

**Preparation of Authentic Cyclopropyltrimethylsilane.** According to the published procedure,<sup>11</sup> (*E*)-5-decenytrimethylsilane (320 mg, 1.5 mmol) and diiodomethane (0.21 mL, ca. 2 mmol) were added to a mixture of CuCl (340 mg, 3.4 mmol), zinc powder (210 mg, 3.2 mmol), and dry diethyl ether (3 mL). The mixture was refluxed for 22 h. The yield of the desired cyclopropane derivative was only several percent. The product 13 was isolated by GLC and analyzed by <sup>1</sup>H NMR (Table II). The authentic sample of 15 was also prepared under similar conditions.

**Hydrogen Peroxide Oxidation of Rearrangement Products. Typical Procedure.** The AlCl<sub>3</sub>-catalyzed rearrangement of 1 (297 mg, 1.36 mmol) was carried out as described above. To the reaction mixture were added dry diethyl ether (5 mL), methanol (0.17 mL, ca. 4 mmol), and triethylamine (0.57 mL, ca. 4 mmol). After being stirred at room temperature for 1 h, the mixture was poured into water and extracted with ether three times. The combined organic layer was dried over sodium sulfate, and the solvent was evaporated. To the remaining oil, which should be mainly (*Z*)-2-nonenyltrimethylmethoxysilane, were successively added DMF (5 mL), potassium fluoride (250 mg, 4.3 mmol), and 30% H<sub>2</sub>O<sub>2</sub> (2.1 mL, 21 mmol). The mixture was heated at 60 °C for 6 h with stirring, poured into water, and extracted with ether five times. The combined ether layer was washed once with 10% NaHSO<sub>3</sub> solution and twice with saturated sodium bicarbonate solution and then dried over sodium sulfate. After evaporation of the solvent bulb-to-bulb distillation gave 94 mg (48% overall yield) of (*Z*)-2-nonen-1-ol (21): bp 110 °C (22 mmHg) (bath temperature); <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 0.76–1.01 (m, 3 H), 1.11–1.58 (m, 9 H, including a singlet at 1.44 due to OH), 1.85–2.19 (m, 2 H), 4.07 (d, *J* = 5 Hz, 2 H), 5.26–5.67 (m, 2 H).

Other results have been obtained in a similar manner. Compound 3 gave a mixture of 4,4-dimethyl-2-penten-1-ol (22) and 2-(1,1-dimethylethyl)-1-cyclopropanol (23) in the ratio of 87:13 (48% total yield): bp 80 °C (110 mmHg) (bath temperature); IR (liquid film) 962 cm<sup>-1</sup> (trans olefin). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):

compound 22, δ 1.023 (s, 9 H), 1.531 (s, 1 H), 4.104 (dd, *J* = 1.3 and 5.9 Hz, 2 H), 5.548 (dt, *J* = 5.9 and 15.6 Hz, 1 H), 5.711 (dt, *J* = 1.3 and 15.6 Hz, 1 H); compound 23, δ 0.451–0.500 (m, 1 H), 0.563–0.611 (m, 1 H), 0.830 (s, 9 H), 0.842–0.919 (m, 1 H), 1.531 (s, 1 H), 2.130–2.190 (m, 1 H). Anal. Found: C, 73.53; H, 12.59. Calcd for C<sub>7</sub>H<sub>14</sub>O: C, 73.63; H, 12.36.

Compound 4 formed (*E*)-2-butyl-2-hepten-1-ol (24), together with the *Z* isomer as a minor product in the ratio of 92:8 (43% total yield): bp 85 °C (13 mmHg) (bath temperature). These isomers were also compared with authentic samples that were prepared via lithiation<sup>10</sup> of (*E*)- and (*Z*)-5-bromo-5-decene and the subsequent treatment with formaldehyde. <sup>1</sup>H NMR (100 MHz, CCl<sub>4</sub>): *E* isomer, δ 0.54–1.06 (m, 6 H), 1.06–1.64 (m, 9 H, including OH), 1.88–2.19 (m, 4 H), 3.89 (s, 2 H), 5.27 (t, *J* = 7 Hz, 1 H); *Z* isomer (authentic sample), δ 0.54–1.10 (m, 7 H, including OH), 1.10–1.54 (m, 8 H), 1.74–2.18 (m, 4 H), 3.97 (s, 2 H), 5.06 (t, *J* = 7 Hz, 1 H).

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**Registry No.** 1, 91898-55-4; 2, 91898-56-5; 3, 91898-57-6; 4, 91898-58-7; 5, 91898-59-8; 6, 91898-60-1; 7, 63922-75-8; 8, 63922-74-7; 9, 91928-37-9; 10, 91898-61-2; 11, 71814-09-0; 12, 91898-62-3; 13, 91898-63-4; 14, 91898-64-5; 15, 91898-65-6; 16, 91898-66-7; 17, 3144-74-9; 18, 91928-38-0; 19, 1719-57-9; 20, 91898-67-8; 21, 41453-56-9; 22, 64081-43-2; 23, 91898-68-9; (*E*)-24, 91898-69-0; (*Z*)-24, 91898-70-3; 1-octyne, 629-05-0; (*E*)-1-octenyl bromide, 51751-87-2; 3,3-dimethyl-1-butene, 917-92-0; 5-decyne, 1942-46-7; 1-bromo-1-cyclooctene, 4103-11-1; 1-(trimethylsilyl)-1-octyne, 15719-55-8.

## Enamines of Acylsilanes: An Easy Access from $\alpha$ -Siloxy Nitriles<sup>1</sup>

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Reductive silylation of  $\alpha$ -siloxy nitriles (O-silylated cyanohydrins) by Me<sub>3</sub>SiCl/lithium in THF at 0 °C afforded an easy access to enamines of acylsilanes, a potentially interesting class of compounds in organic and organosilicon syntheses. Concurrently, the reaction led to the formation of  $\alpha$ -siloxy silanes by substitution of the cyano group in the starting molecules.

Enamines have proven to be very useful intermediates in organic synthesis.<sup>2,3</sup> Moreover, organosilylated derivatives are becoming increasingly useful as reagents in this field.<sup>4,5</sup> In following up our continuing interest in acyl-

silanes,<sup>6</sup> we have focused our attention on enamines 2 derived from these peculiar carbonyl compounds, with the hope they could serve as efficient and versatile synthetic tools.

(1) This has been the subject of poster sessions at the 6th International Symposium on Organosilicon Chemistry, Budapest, Hungary, 1981, and at the "Journées de Chimie Organique, Société Chimique de France", Palaiseau, France, 1981.

(2) Cook, A. G. "Enamines: Synthesis, Structure and Reactions"; Marcel Dekker: New York, 1969.

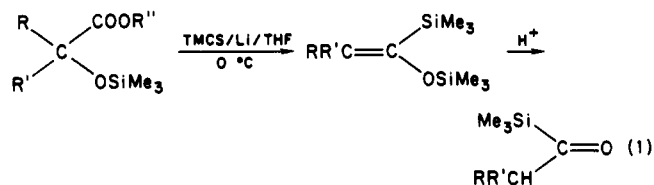
(3) Hickmott, P. W. *Tetrahedron* 1982, 38, 1975, 3363.

(4) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981.

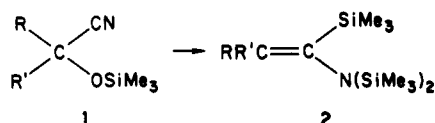
(5) Weber, W. P. "Reactivity and Structures, Concepts in Organic Synthesis"; Springer-Verlag: New York, 1983; Vol. 14.

(6) Calas, R.; Picard, J.-P.; Dunoguès, J.; Duffaut, N. *J. Organomet. Chem.* 1969, 19, 33. Picard, J.-P.; Calas, R.; Dunoguès, J.; Duffaut, N. *Ibid.* 1971, 26, 183. Dunoguès, J.; Bolourtchian, M.; Calas, R.; Duffaut, N.; Picard, J.-P. *Ibid.* 1972, 43, 157. Calas, R.; Picard, J.-P.; Bernadou, F. *Ibid.* 1973, 60, 49. Dunoguès, J.; Ekouya, A.; Calas, R.; Picard, J.-P.; Duffaut, N. *Ibid.* 1974, 66, C 39. Picard, J.-P.; Ekouya, A.; Dunoguès, J.; Duffaut, N.; Calas, R. *Ibid.* 1975, 93, 51. Couret, C.; Satgé, J.; Picard, J.-P. *Ibid.* 1977, 141, 35. Picard, J.-P.; Calas, R.; Dunoguès, J.; Duffaut, N.; Gerval, J.; Lapouyade, P. *J. Org. Chem.* 1979, 44, 420. Brook, A. G.; Nyburg, S. C.; Reynolds, W. F.; Poon, Y. C.; Chang, Y. M.; Lee, J. S.; Picard, J.-P. *J. Am. Chem. Soc.* 1979, 101, 6750.

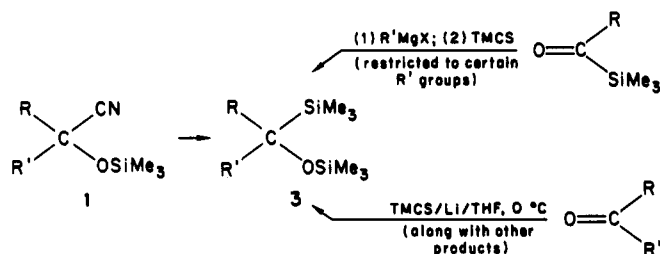
An observation made during the course of our studies on the reductive silylation of functional esters<sup>7</sup> provided us with the key to a possible synthesis of 2. When  $\alpha$ -siloxy esters were treated with the reagent trimethylchlorosilane (TMCS)/lithium/tetrahydrofuran (THF), an enoxysilane was obtained which, upon hydrolysis, led to the corresponding acylsilane (eq 1).<sup>8</sup>



We anticipated that, starting from  $\alpha$ -siloxy nitriles 1 (O-silylated cyanohydrins), the same reaction could lead to the desired enamines 2.



However, it is known that the reductive silylation of nitriles, in some instances, can afford products resulting from the substitution of the cyano group by a silyl group.<sup>9</sup> In our case, such a reaction would give  $\alpha$ -siloxy silanes 3, compounds which have been previously described<sup>10</sup> but which were not easily available (alkylation of acylsilanes<sup>11</sup> is restricted to Grignard reagents having no  $\beta$ -hydrogen atom; reductive silylation of ketones<sup>12</sup> occurs with low yields and formation of numerous side products).



In this paper we report the results of the reductive silylation of  $\alpha$ -siloxy nitriles 1.

## Results and Discussion

When  $\alpha$ -siloxy nitriles were treated at 0 °C with lithium in the presence of TMCS, using THF as the solvent, a mixture of 2 and 3 generally was obtained in variable yields. To the results summarized in Table I, we add the following remarks:

In most cases, 1 was not consumed entirely in spite of the various conditions employed (see Experimental Sec-

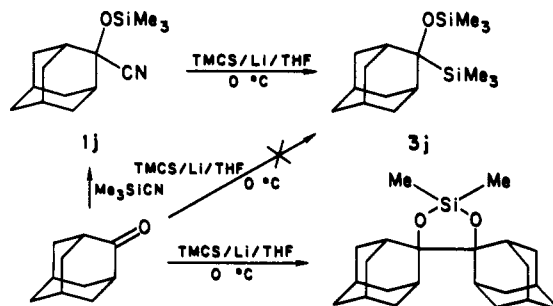
tion), and we cannot supply a satisfactory explanation for this.<sup>13</sup>

No traces of trimethylcyanosilane, which could have been formed from the silylation of the cyanide ion liberated during the formation of 3, were found nor were found any of the persilylated methylamines resulting from the reductive silylation of this eventually formed cyanosilane.<sup>14</sup>

In the aliphatic series (entries 1–4), the nature of the alkyl groups R and R' has no detectable influence on the yields of 2 and 3.

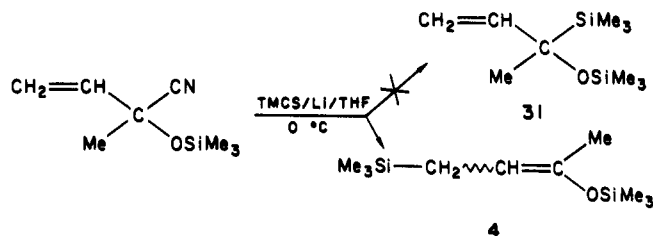
However, in the alicyclic series (entries 5–8), the ring size plays an important role: an increase in the ring size directly affected the yield of 3 and inversely the yield of 2. Compounds 1i and 1j did not lead to the formation of any enamine (entries 9 and 10).

It is worth noting (entry 10) that, under the same conditions, adamantyl derivative 3j could be formed from 1j, but adamantanone itself did not lead to 3j, as expected, but to a pinacolic product.<sup>15</sup>



*tert*-Butyl compound 2k (entry 11) was obtained with numerous other lower boiling compounds among which we identified pivalaldehyde, which probably resulted from the hydrolysis of unreacted 1k during the workup of the reaction mixture.

The vinylic derivative 1 (entry 12) did not give any of the expected enamine 2l but gave instead the enoxysilane 4, an isomer of the expected 3l. From this, it follows that the substitution of the cyano group took place with allylic transposition. Compound 4 had been reported to be obtained previously from methyl vinyl ketone in the same yield.<sup>12</sup>



Most of the alkoxy silanes 3 obtained (3a,<sup>16</sup> 3c,<sup>16</sup> 3e,<sup>17</sup> 3f,<sup>17</sup> 3g,<sup>12</sup> and 3h<sup>17</sup>) have been previously described. Compound 3a was hydrolyzed to the corresponding alcohol 5, which

(7) Picard, J.-P.; Dunoguès, J.; Duffaut, N.; Calas, R. *J. Chem. Res., Synop.* 1977, 54.

(8) Picard, J.-P., unpublished results.

(9) Ekouya, A.; Dunoguès, J.; Duffaut, N.; Calas, R. *J. Organomet. Chem.* 1978, 148, 225.

(10) See, for example: Reich, H. J.; Rusek, J. J.; Olson, R. E. *J. Am. Chem. Soc.* 1979, 101, 2225. Kuwajima, I.; Kato, M. *J. Chem. Soc., Chem. Commun.* 1970, 708. Kuwajima, I.; Kato, M.; Mori, A. *Tetrahedron Lett.* 1980, 29, 2745, 4291. Reich, H. J.; Olson, R. E.; Clark, M. C. *J. Am. Chem. Soc.* 1980, 102, 1423. Reich, H. J.; Kelly, M. J. *Ibid.* 1982, 104, 1119. Wilson, S. R.; Hague, R. S.; Misra, R. N. *J. Org. Chem.* 1982, 47, 748.

(11) Brook, A. G. *Adv. Organomet. Chem.* 1968, 7, 95.

(12) Dunoguès, J.; Ekouya, A.; Calas, R.; Duffaut, N. *J. Organomet. Chem.* 1975, 87, 151.

(13) A reviewer has suggested that we employ a catalytic amount of naphthalene to act as a soluble electron-transfer reagent. We have not observed any significant variations in the yield of products 1, 2, and 3, and this could have resulted from the consumption of naphthalene through reductive silylation (Laguerre, M.; Dunoguès, J.; Calas, R. *Tetrahedron Lett.* 1981, 22, 1227). Another suggestion was to substitute THF for HMPA: this was also ineffective as the nitrile was not entirely transformed.

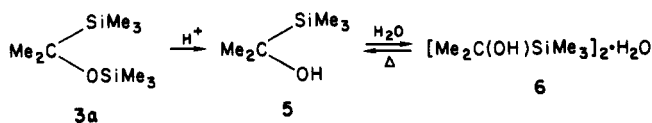
(14) Picard, J.-P.; Elyusufi, A., to be submitted for publication.

(15) Ekouya, A.; Dunoguès, J.; Calas, R. *J. Chem. Res., Synop.*, 1978, 296.

(16) Dunoguès, J.; Calas, R.; Duffaut, N. *J. Organomet. Chem.* 1973, 49, C9.

(17) Ekouya, A. Thèse d'Etat, Université de Bordeaux I, 1978.

combined with water to form the hydrate **6** as reported.<sup>16</sup>



All the enamines **2**, which were very easily obtained as a mixture of geometric *Z/E* isomers in most cases (they were not separated), are new products, to our knowledge. However, it must be noted that reductive silylation of aromatic nitriles (benzo- and  $\alpha$ -naphthonitriles) with TMCS/Mg/HMPA afforded a peculiar species of enamines that can also be regarded as derivatives of acylsilanes, for example, eq 2.<sup>18</sup>



On the basis of the radical anion mechanism very often invoked to explain C-silylation reactions given by the TMCS/Li/THF reagent when reacted with functional derivatives,<sup>19</sup> we propose the following reaction scheme, exemplified by the  $\alpha$ -siloxy nitrile **1a** (Scheme I). This compound can capture an electron from the lithium to form a radical anion that can evolve either to the formation of a  $\alpha$ -siloxy radical with elimination of the cyanide ion or to a radical anion where the electron can be localized on the nitrile function (such a radical anion has already been suggested to explain reductive silylation of aromatic nitriles by TMCS/Mg/HMPA<sup>18,20</sup>). Then a cascade of reductions of radical species, silylations of anionic species, and eliminations of silanolate anion or hexamethyldisiloxane ( $\beta$ -effect<sup>4,21</sup>) would yield the observed products.

Thus reductive silylation with the TMCS/Li/THF reagent proves again to be a very powerful and useful reaction. The readily available  $\alpha$ -siloxy nitriles (ketone +  $\text{Me}_3\text{SiCN}$ <sup>22,23</sup>) gave rise to  $\alpha$ -siloxy silanes (and  $\alpha$ -hydroxy silanes through hydrolysis) by substitution of the cyano group and/or enamines of acylsilanes, a new class of organosilicon derivatives. The investigation of their chemical properties and possible uses as synthons in organic chemistry are in progress.

## Experimental Section

**General Data.** Trimethylchlorosilane (TMCS), generously supplied by Société Rhône-Poulenc (France), was distilled over magnesium powder or calcium hydride prior to use.

Lithium sand was prepared by vigorous shaking of melted lithium chips in hot paraffin oil, cooling, and washing with THF after separation by filtration.

Tetrahydrofuran (THF), from Aldrich, was used as received, as were the other commercial products we used.

Analytical gas chromatography was performed on an F&M 810 or Intersmat gas chromatograph (catharometric detector) with helium as carrier gas and using SE 30 or DC 410 silicone (10% on Chromosorb P) filled columns. Preparative gas chromatography was performed on the same apparatus, products being

(18) Biran, C.; Dédier, J.; Dunoguès, J.; Calas, R.; Duffaut, N. *J. Organomet. Chem.* **1972**, *35*, 263. See also: Bolourtchian, M. Thèse d'Etat, Université de Bordeaux, I, 1972.

(19) Calas, R.; Dunoguès, J. *J. Organomet. Chem. Libr.* **1976**, *2*, 277.

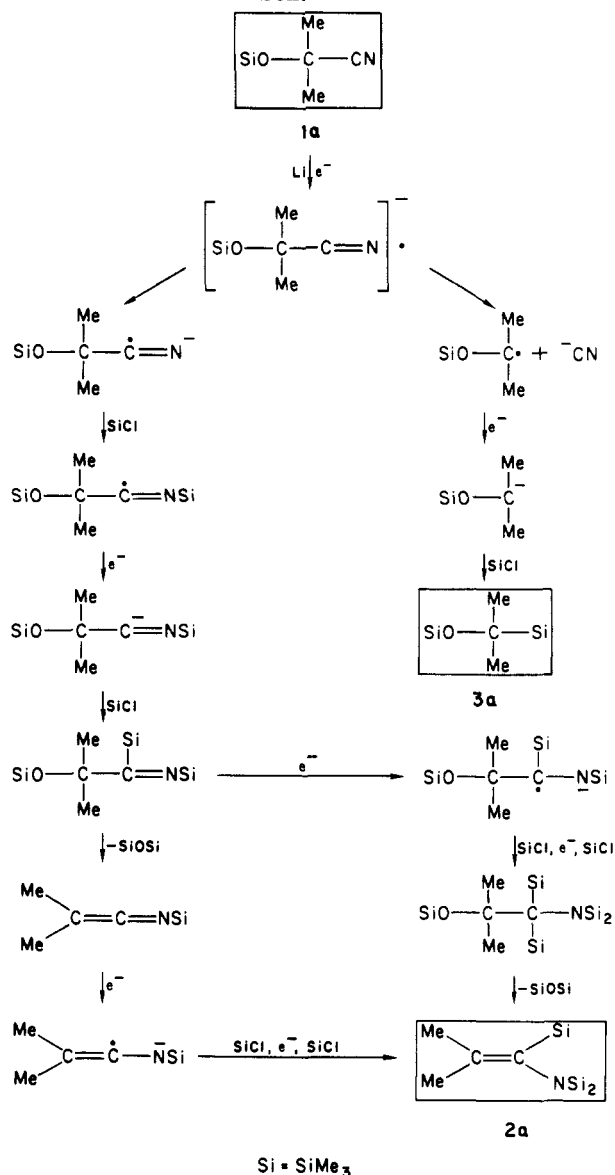
(20) Biran, C.; Calas, R.; Dunoguès, J.; Duffaut, N. *J. Organomet. Chem.* **1970**, *22*, 557.

(21) Jarvie, A. W. P. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 153.

(22) Pike, R. M.; Mangano, M. F. *J. Organomet. Chem. Libr.* **1982**, *12*, 67.

(23) Evans, D. A.; Truesdale, L. K.; Carroll, G. L. *J. Chem. Soc., Chem. Commun.* **1973**, 55. Evans, D. A.; Hoffmann, J. N.; Truesdale, L. K. *J. Am. Chem. Soc.* **1973**, *95*, 5822.

Scheme I



collected in ice-cooled traps at the end of the column.

Infrared spectra were recorded on a Perkin-Elmer 457 IR spectrophotometer using neat products.

Routine nuclear magnetic resonance spectra were recorded on a Perkin-Elmer Hitachi R-24-A, a Varian A-60-A, or a Perkin-Elmer R-12 spectrometer (60 MHz) for <sup>1</sup>H, a Bruker WH-60 spectrometer (15.07 MHz) for <sup>13</sup>C, and a Bruker WH-90 spectrometer (17.87 MHz) for <sup>29</sup>Si.

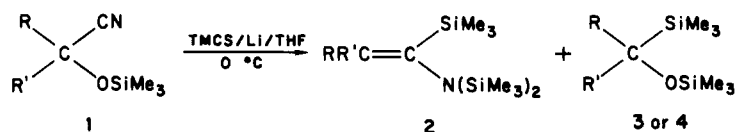
Mass spectra were obtained on a Micromass 16-F mass spectrometer (70 eV), and GC/MS runs were conducted on the same apparatus interfaced to a Pye Unicam 204 gas chromatograph.


All new products gave elemental analyses in good agreement with the proposed structures.

**Trimethylcyanosilane.**<sup>24</sup> To dry fresh potassium cyanide (32 g) placed in the flask of a distillation apparatus equipped with a short column (10 cm) was added 60.5 g of melted bis(trimethylsilyl) sulfate;<sup>25</sup> the receiver was connected to a dry KOH tube, and the reaction was conducted in a well-aerated hood. Gentle heating initiated an exothermic reaction, and prolonged heating allowed the distillation of a transparent liquid (110–120 °C) that consisted of a mixture of desired cyanosilane and hexamethyldisiloxane (10% maximum). Redistillation of this mixture afforded pure cyanosilane (33 g, 67% yield) whose physicochemical

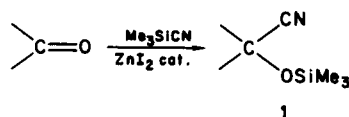
(24) Voronkov, M. G.; Roman, V. K.; Maletina, E. A. *Synthesis* **1982**, 277.













(25) Duffaut, N.; Calas, R.; Dunoguès, J. *Bull. Soc. Chim. Fr.* **1963**, 512.

Table I. Reductive Silylation of  $\alpha$ -Siloxy Nitriles 1. Results

entry	1	R	R'	recovered 1	enamines 2	siloxy silane 3 or 4
1	1a	Me	Me	25 (66) <sup>a</sup>	2a, 24 <sup>b</sup> (70)	3a, 10 <sup>b</sup> (30)
2	1b	Me	<i>n</i> -Pr	30 (46)	2b, 25 (46)	3b, 29 (54)
3	1c	Et	Et	35 (57)	2c, 28 (65)	3c, 15 (35)
4	1d	Me	<i>n</i> -Bu	10 (54)	2d, 26 (57)	3d, 20 (43)
5	1e		-(CH <sub>2</sub> ) <sub>3</sub> -	ε, (3)	2e, 70 (72)	3e, 27 (28)
6	1f		-(CH <sub>2</sub> ) <sub>4</sub> -	15 (45)	2f, 30 (55)	3f, 25 (45)
7	1g		-(CH <sub>2</sub> ) <sub>5</sub> -	60 (71)	2g, 19 (65)	3g, 10 (35)
8	1h		-(CH <sub>2</sub> ) <sub>6</sub> -	20 (45)	2h, 20 (35)	3h, 35 (65)
9	1i	Me <sub>2</sub> CCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CMe <sub>2</sub>		45 (46)		3i, 54 (100)
10	1j			53 (63)		3j, 37 (100)
11	1k	H	<i>t</i> -Bu		2k, 10	
12	1l	Me	CH=CH <sub>2</sub>			4, <sup>c</sup> 60

<sup>a</sup> Calculated percentages of unreacted nitrile 1. <sup>b</sup> Absolute yields of isolated products (relative yields are in parentheses).  
<sup>c</sup> See text.

Table II. Preparation of  $\alpha$ -Siloxy Nitriles 1. Yields and Physicochemical Data

starting ketone	yield (%) after distillatn	bp, °C (torr) or mp		<sup>1</sup> H NMR (CCl <sub>4</sub> ), $\delta$
		exptl	lit.	
	1a, 95	147 (760)	145.5–147 (760) <sup>28</sup>	0.20 (s, 9 H), 1.54 (s, 6 H)
	1b, 95	115 (60)		0.2 (s, 9 H), 1.56 (s, 3 H), 1.25–2.06 (m, 7 H)
	1c, 91	90 (30)	85 (26) <sup>29</sup>	0.2 (s, 9 H), 1.0 (t, 6 H, <i>J</i> = 7 Hz), 1.72 (q, 4 H, <i>J</i> = 7 Hz)
	1d, 90	80 (6)		0.2 (s, 9 H), 0.91 (m, 3 H), 1.47 (s, 3 H), 1.42–1.83 (m, 6 H)
	1e, 94	100 (20)		0.16 (s, 9 H), 1.56–3.2 (m, 6 H)
	1f, 80	110 (60)	159–160 (760) <sup>29</sup>	0.28 (s, 9 H), 1.5–2.4 (m, 8 H)
	1g, 75	115 (30)	72–74 (1) <sup>27</sup>	0.33 (s, 9 H), 1.2–2.26 (m, 10 H)
	1h, 75	80 (5)		0.33 (s, 9 H), 1.15–2.6 (m, 12 H)
	1i, 90	106 (2.5)		0.4 (s, 9 H), 1.15 (s, 6 H), 1.30 (s, 6 H), 1.57 (m, 6 H)
	1j, 95	35–40	92–95 <sup>30</sup>	0.45 (s, 9 H), 1.63–2.56 (m, 14 H)
	1k, 97	90 (30)		0.42 (s, 9 H), 1.20 (s, 9 H), 4.0 (s, 1 H)
	1l, 50 <sup>a</sup>	64 (25)	87 (100) <sup>31</sup>	0.21 (s, 9 H), 1.55 (s, 3 H), 5–6 (m, 3 H)

<sup>a</sup> Another preparation procedure was used; see ref 31.

characteristics (bp 117 °C (760 torr); <sup>1</sup>H NMR 0.1 ppm) were in good agreement with those from the literature.<sup>22</sup>

**$\alpha$ -(Trimethylsilyloxy)isobutyronitrile (1a).** According to Frisch and Wolf,<sup>26</sup> it was prepared by silylation of commercial acetone-cyanohydrin with trimethylchlorosilane in the presence of pyridine and separated by distillation (147 °C) in 90% yield.

**$\alpha$ -Siloxy Nitriles 1. General Procedure.** These products were prepared following Evan's method<sup>27</sup> by reacting trimethylcyanosilane with the appropriate ketone in the presence of zinc iodide as a catalyst. Into a round-bottomed flask under inert atmosphere were introduced a few milligrams of zinc iodide

(26) Frisch, K. C.; Wolf, M. *J. Org. Chem.* 1953, 18, 657.

(27) Evans, D. A.; Carroll, G. L.; Truesdale, L. K. *J. Org. Chem.* 1974, 39, 914.

Table III. Boiling Points and  $^1\text{H}$  NMR Spectra of  $\alpha$ -Siloxy Silanes 3

	bp, $^\circ\text{C}$ (torr)	$^1\text{H}$ NMR ( $\text{CCl}_4$ ) $\delta$	lit. <sup>a</sup>
3a	140 (760)	0.1 (s, 9 H), 0.21 (s, 9 H), 1.37 (s, 6 H)	16
3b	71 (5)	0.1 (s, 9 H), 0.2 (s, 9 H), 0.86–1.26 (m, 3 H), 1.33 (s, 3 H), 1.43–1.8 (m, 4 H)	
3c	65 (5)	0.1 (s, 9 H), 0.2 (s, 9 H), 0.95 (t, 6 H, $J = 7$ Hz), 1.75 (q, 4 H, $J = 7$ Hz)	16
3d	85 (5)	0.1 (s, 9 H), 0.2 (s, 9 H), 1.35 (s, 3 H), 0.8–1.7 (m, 9 H)	
3e	100 (30)	0.16 (s, 9 H), 0.26 (s, 9 H), 1.2–2.6 (m, 6 H)	17
3f	80 (25)	0.16 (s, 9 H), 0.26 (s, 9 H), 1.8 (m, 8 H)	17
3g	88 (25)	0.13 (s, 9 H), 0.2 (s, 9 H), 1.4–2.5 (m, 10 H)	12
3h	130 (35)	0.13 (s, 9 H), 0.23 (s, 9 H), 1.2–2.3 (m, 12 H)	17
3i	106 (3)	0.38 (s, 9 H), 0.5 (s, 9 H), 1.25 (s, 3 H), 1.4 (s, 3 H), 1.43–1.93 (m, 6 H)	
3j	125 (0.5)	0.26 (s, 9 H), 0.33 (s, 9 H), 1.53–2.53 (m, 14 H)	

<sup>a</sup> For comparison.

Table IV. Spectroscopic Data for the Enamines 2

2	formula (Si for SiMe <sub>3</sub> )	IR (neat product), $\text{cm}^{-1}$ ; NMR $\delta$ , $^1\text{H}$ ( $\text{CCl}_4$ ), $^{29}\text{Si}$ , and $^{13}\text{C}$ ( $\text{CDCl}_3$ ); MS (70 eV), $m/e$ (rel int)
2a		IR, 1600 (C=C); $^1\text{H}$ , 0.16 (s, 18 H), 0.3 (s, 9 H), 1.83 (s, 3 H), 1.93 (s, 3 H); MS, 287 (8), 272 (4), 214 (100), 172 (12), 130 (11), 73 (100)
2b		mixture of <i>Z</i> + <i>E</i> isomers: IR, 1590 (C=C); $^1\text{H}$ , 0.13 (s, 18 H), 0.23 (s, 9 H), 0.8–2.3 (m, 10 H); $^{29}\text{Si}$ , -8.02 and +2.29; $^{13}\text{C}$ , 1.6 and 2.9 (SiMe <sub>3</sub> ) and 12 other signals due to the mixture of isomers 147.5, 146.6, 141.6, and 140.2 (quaternary carbons), 38.7, 36.8, 22.3, and 21.2 (secondary carbons), 19.6, 19.2, 14.7, and 14.3 (primary carbons)
2c		$^1\text{H}$ , 0.15 (s, 18 H), 0.23 (s, 9 H), 1.0 (m, 6 H), 2.25 (m, 4 H); $^{29}\text{Si}$ , -8.47 and +1.93; $^{13}\text{C}$ , 153.5 and 140.1 (quaternary carbons), 24.9 and 22.1 (secondary carbons), 13.1 and 11.9 (primary carbons), 3 and 1.7 (SiMe <sub>3</sub> )
2d		mixture of <i>Z</i> + <i>E</i> isomers: $^1\text{H}$ 0.16 (s, 18 H), 0.25 (s, 9 H), 0.89 and 0.97 (2 s, 3 H), 0.8–2.4 (m, 6 H), 1.55 (a) and 1.61 (b) (2 s with intensity ratio a/b = 2/3, 3 H)
2e		IR, 1590 (C=C); $^1\text{H}$ , 0.13 (s, 18 H), 0.2 (s, 9 H), 1.26–2.9 (m, 6 H); $^{29}\text{Si}$ , -7.0 and +2.29; $^{13}\text{C}$ , 150.6 and 138.9 (quaternary carbons), 33.0, 31.5 and 17.2 (secondary carbons), +0.1 and -1.7 (SiMe <sub>3</sub> )
2f		$^1\text{H}$ , 0.15 (s, 18 H), 0.20 (s, 9 H), 0.81–2.85 (m, 8 H)
2g		$^1\text{H}$ , 0.13 (s, 18 H), 0.18 (s, 9 H), 1.0–2.5 (m, 10 H); $^{29}\text{Si}$ , -8.29 and +2.24; $^{13}\text{C}$ , 150.3 and 138.2 (quaternary carbons), 33.5, 31.2, 28.4, 27.9, and 27.1 (secondary carbons), 2.9 and 1.4 (SiMe <sub>3</sub> )
2h		$^1\text{H}$ , 0.14 (s, 18 H), 0.23 (s, 9 H), 1.12–2.6 (m, 12 H)
2k		mixture of <i>Z</i> + <i>E</i> isomers ( $E/Z = 2$ ): $^1\text{H}$ , $E^a$ 0.18 (s, 18 H), 0.25 (s, 9 H), 1.2 (s, 9 H), 5.25 (s, 1 H); $Z^a$ 0.18 (s, 18 H), 0.25 (s, 9 H), 1.01 (s, 9 H), 3.75 (s, 1 H)

<sup>a</sup> This assignment was based on the reported value ( $\sim 4$  ppm) for the shift of the proton cis to nitrogen in N-metalated enamines<sup>31</sup> and also on the relationship between relative intensities of the observed signals.

Table V. Elemental Analyses for New Compounds 2 and 3

compd	formula	calcd (found)			
		C	H	N	Si
2a	C <sub>13</sub> H <sub>33</sub> NSi <sub>3</sub>	54.35 (54.29)	11.49 (11.47)	4.87 (4.99)	29.66 (29.05)
2b	C <sub>15</sub> H <sub>37</sub> NSi <sub>3</sub>	57.14 (57.11)	11.74 (11.65)	4.44 (4.48)	26.66 (26.49)
2c	C <sub>15</sub> H <sub>37</sub> NSi <sub>3</sub>	57.14 (57.20)	11.74 (11.67)	4.44 (4.42)	26.66 (26.53)
2d	C <sub>16</sub> H <sub>39</sub> NSi <sub>3</sub>	58.35 (58.41)	11.89 (11.78)	4.25 (4.29)	25.53 (25.35)
2e	C <sub>14</sub> H <sub>33</sub> NSi <sub>3</sub>	56.18 (56.12)	11.03 (11.10)	4.68 (4.65)	28.09 (27.91)
2d	C <sub>15</sub> H <sub>35</sub> NSi <sub>3</sub>	57.50 (57.51)	11.18 (11.21)	4.47 (4.47)	26.83 (26.69)
2g	C <sub>16</sub> H <sub>37</sub> NSi <sub>3</sub>	58.71 (58.78)	11.31 (11.27)	4.28 (4.25)	25.68 (25.50)
2h	C <sub>17</sub> H <sub>39</sub> NSi <sub>3</sub>	59.82 (59.89)	11.43 (11.33)	4.10 (4.15)	24.63 (24.63)
2k	C <sub>15</sub> H <sub>37</sub> NSi <sub>3</sub>	not isolated in pure state <sup>a</sup>			
3b	C <sub>11</sub> H <sub>28</sub> NSi <sub>2</sub>	56.89 (56.98)	12.07 (11.99)		24.13 (24.06)
3d	C <sub>12</sub> H <sub>30</sub> OSi <sub>2</sub>	58.53 (58.58)	12.19 (12.31)		22.76 (22.75)
3i	C <sub>16</sub> H <sub>36</sub> OSi <sub>2</sub>	64 (64.19)	12 (11.98)		18.66 (18.57)
3j	C <sub>16</sub> H <sub>32</sub> OSi <sub>2</sub>	64.86 (64.83)	10.81 (10.75)		18.91 (19.01)

<sup>a</sup> Yield given in Table I is the yield estimated from GC.

and 1 equiv of ketone. Under magnetic stirring, 1 equiv of cyanosilane was added. Depending upon the ketone, the reaction was more or less exothermic and it was necessary to keep the reaction flask either in an ice bath (during the addition of the cyanosilane) or in an oil bath at 50–60  $^\circ\text{C}$  during a few hours. The reaction was monitored by GC. In most cases, quantitative yields of the  $\alpha$ -siloxy nitriles 1 were obtained that were pure enough to dispense with the distillation prior to use. Physicochemical

data and yields of distilled 1 are reported in Table II. It should be noted that no or only a very weak IR absorption (2220–2240

(28) Ykman, P.; Hall, H. K., Jr. *J. Organomet. Chem.* 1976, 116, 153.  
(29) Truesdale, L. K. Ph.D. Dissertation, University of California, Los Angeles, 1974.

(30) Mlinaric-Majercki, K.; Majercki, Z.; Pretsch, E. *J. Org. Chem.* 1975, 40, 3772.

cm<sup>-1</sup>) of the nitrile group was observed.

**Reductive Silylation of 1. General Procedure.** In a dry flask equipped with a magnetic stirring bar, flushed with an inert gas, and stoppered with a septum were introduced lithium sand (3.2 g, 450 mmol), THF (40 mL), and TMCS (42 g, 400 mmol); the mixture was cooled to -10 °C. Nitrile 1 (50 mmol) was added via syringe: an exothermic reaction took place and the reaction mixture turned progressively cloudy due to the formation of lithium chloride and cyanide. The temperature of the mixture was kept at 0 °C for 6 h and then left at ambient temperature with stirring overnight. Precipitated salts and unreacted lithium were eliminated by filtration, washed with brine until neutral, extracted with ether, and dried over sodium sulfate. Solvents and low-boiling materials were rotatory evaporated, a mixture of 3 and unreacted 1 was distilled off, and the residue was, in general, passed on a short column of silica gel (eluent hexane), yielding 2 as a colorless jellylike mass. Products 1 and 3 were separated by preparative gas chromatography.

In an effort to consume all of nitrile 1 engaged, the following variations from this general procedure were made but were unsuccessful:<sup>13</sup> lithium chips instead of lithium sand; lithium sand added in three portions during the course of the reaction; pieces of glass introduced in the reaction medium in order to scour the

lithium, as the sand, which floated on the surface of the reaction mixture and progressively sank to the bottom; diluted reaction medium (three times with more solvent); large excess of trimethylchlorosilane (two times).

No significant changes in the yield of products 2 and 3 were observed. Moreover, contact times of the reactants were prolonged to 3 days and we observed competitive formation of hexamethyldisilane that occurred via a Barbier-type reaction in a yield directly proportional to the reaction time without any substantial progress in the formation of compounds 2 and 3.

Results and description of the products obtained are reported in Tables I (yields) and III-V.

**Registry No.** 1a, 18296-11-2; 1b, 91390-80-6; 1c, 40326-26-9; 1d, 91409-34-6; 1e, 91390-81-7; 1f, 25438-35-1; 1g, 24731-36-0; 1h, 91390-82-8; 1i, 91390-83-9; 1j, 76454-61-0; 1k, 88522-73-0; 1l, 60550-36-9; 2a, 91390-84-0; (E)-2b, 91390-85-1; (Z)-2b, 91390-92-0; 2c, 91390-86-2; (E)-2d, 91390-87-3; (Z)-2d, 91390-93-1; 2e, 91390-88-4; 2f, 91390-89-5; 2g, 91390-90-8; 2h, 91409-35-7; (E)-2k, 91390-91-9; (Z)-2k, 91390-94-2; 3a, 40965-53-5; 3b, 91390-95-3; 3c, 55942-13-7; 3d, 91390-96-4; 3e, 91390-97-5; 3f, 60745-14-4; 3g, 55942-15-9; 3h, 91409-36-8; 3i, 91390-98-6; 3j, 91390-99-7; 4, 91391-00-3; TMCS, 75-77-4; Li, 7439-93-2; Me<sub>3</sub>SiCN, 7077-24-9; (Me<sub>3</sub>Si)<sub>2</sub>SO<sub>4</sub>, 18306-29-1; KCN, 151-50-8; ZnI<sub>2</sub>, 10139-47-6; Me<sub>2</sub>CO, 67-64-1; n-PrCOMe, 107-87-9; Et<sub>2</sub>CO, 96-22-0; n-BuCOMe, 591-78-6; t-BuCHO, 630-19-3; MeCOCH=CH<sub>2</sub>, 78-94-4; cyclobutanone, 1191-95-3; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; 2,2,6,6-tetramethylcyclohexanone, 1195-93-3; adamantanone, 700-58-3.

(31) Duboudin, F.; Cazeau, Ph.; Moulines, F.; Laporte, O. *Synthesis* 1982, 212.

(32) Brocas, J. M.; De Jeso, B.; Pommier, J. C. *J. Organomet. Chem.* 1976, 120, 217.

## Chemistry of C-Trimethylsilyl-Substituted Stannacarboranes. 1. Synthesis, Characterization, and Tin-119 Mössbauer Effect Study of 1-Sn-2-[Si(CH<sub>3</sub>)<sub>3</sub>]-3-[R]-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> Derivatives [R = Si(CH<sub>3</sub>)<sub>3</sub>, CH<sub>3</sub>, or H]

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The reaction of Na<sup>+</sup>[C-Si(CH<sub>3</sub>)<sub>3</sub>-C'-R-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>]<sup>-</sup> (R = Si(CH<sub>3</sub>)<sub>3</sub>, CH<sub>3</sub>, or H) with SnCl<sub>2</sub> in THF produces Sn[(CH<sub>3</sub>)<sub>3</sub>Si][R]C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> as a sublimable white solid in gram quantities. For each stannacarborane, the <sup>119m</sup>Sn Mössbauer effect spectrum exhibits a quadrupole split doublet, having an isomer shift (at 78 K) which is characteristic of tin in the tin(II) oxidation state. The isomer shift observed in the spectrum is significantly less positive than that associated with a "bare" Sn<sup>2+</sup> ion, and these data differ from those reported for (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Sn and SnB<sub>9</sub>C<sub>2</sub>H<sub>11</sub>. The infrared spectra, mass spectra, <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>29</sup>Si, and <sup>119</sup>Sn NMR, and <sup>119m</sup>Sn Mössbauer spectra of these compounds are all consistent with a pentagonal-bipyramidal structure with the tin atom occupying an apical position and directing its unshared electron-pair outward from the polyhedron. All the stannacarboranes quantitatively react with anhydrous HCl in THF to yield the corresponding neutral carboranes. The stannacarboranes do not react with BH<sub>3</sub>·THF or BF<sub>3</sub> to form electron donor-acceptor complexes.

### Introduction

Polyhedral carboranes in which a Group 4A heteroatom is present either as an integral part of the cage framework, except silicon,<sup>1-3</sup> or in a B-M<sup>IV</sup>-B three-center, two-electron bond on the open face of a carborane skeleton,<sup>4,5</sup> with the exception of carbon, have been synthesized. More recently, Wong and Grimes described<sup>6</sup> the synthesis of

tron bond on the open face of a carborane skeleton,<sup>4,5</sup> with the exception of carbon, have been synthesized. More recently, Wong and Grimes described<sup>6</sup> the synthesis of

(1) (a) Rudolph, R. W.; Voorhees, R. L.; Cochoy, R. E. *J. Am. Chem. Soc.* 1970, 92, 3351. (b) Voorhees, R. L.; Rudolph, R. W. *Ibid.* 1969, 91, 2173. (c) Chowdhry, V.; Pretzer, W. R.; Rai, D. N.; Rudolph, R. W. *Ibid.* 1973, 95, 4560.

(2) (a) Todd, L. J.; Burke, A. R.; Silverstein, H. T.; Little, J. L.; Wikholm, G. S. *J. Am. Chem. Soc.* 1969, 91, 3376. (b) Wikholm, G. S.; Todd, L. J. *J. Organomet. Chem.* 1974, 71, 219.

(3) Loffredo, R. E.; Norman, A. D. *J. Am. Chem. Soc.* 1971, 93, 5587.

(4) (a) Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* 1971, 622. (b) Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* 1972, 918.

(5) (a) Thompson, M. L.; Grimes, R. N. *Inorg. Chem.* 1972, 11, 1925. (b) Tabereaux, A.; Grimes, R. N. *Ibid.* 1973, 12, 792. (c) A review of group 4 carborane chemistry is given by: Grimes, R. N. *Rev. Silicon Germanium Tin Lead Compd.* 1977, 223-49. (d) Grimes, R. N.; Rademaker, W. J.; Denniston, M. L.; Bryan, R. F.; Greene, P. T. *J. Am. Chem. Soc.* 1972, 94, 1865.