

$C_{24}H_{21}Mn_3O_6Te$ : C, 41.14; H, 3.00. Found: C, 41.18; H, 3.22. IR spectrum in ether: 1994 s, 1939 s, 1901 s  $cm^{-1}$ .

Synthesis of  $(\mu-Te)[Mn(CO)_2(\eta^5-C_5Me_5)]_2$  was carried out by following the method of Herrmann<sup>4</sup> which is very similar to the preparation of Herberhold.<sup>3</sup> Purification by column chromatography and recrystallization yielded a black crystalline compound. Anal. Calcd for  $C_{24}H_{21}Mn_3O_6Te$ : C, 46.5; H, 4.88. Found: C, 44.27; H, 4.81. IR spectrum in THF: 1982 s, 1926 vs  $cm^{-1}$ .

The reaction of the above compound with excess diazomethane in ether at  $-78^\circ C$  quantitatively produced a blue compound of composition  $(\mu-\eta^2-TeCH_2)[Mn(CO)_2(\eta^5-C_5Me_5)]_2$ . Anal. Calcd for  $C_{25}H_{32}Mn_3O_4Te$ : C, 47.31; H, 5.04. Found: C, 47.24; H, 4.99. IR spectrum in THF: 1978 vs, 1923 s, 1907 vs, 1862  $cm^{-1}$ .

$(\mu-Te)[Cr(CO)_3(\eta^5-C_5H_5)]_2$  was obtained by stirring an excess of elemental tellurium in a THF solution of  $[(\eta^5-C_5H_5)Cr(CO)_3]_2$  at room temperature for 1 h.<sup>1</sup> Excess tellurium was removed by filtration and the solvent then removed under vacuum to give the analytically pure compound. Anal. Calcd for  $C_{16}H_{10}Cr_2O_6Te$ : C, 36.22; H, 1.95. Found C, 35.80; H, 1.92. IR spectrum in THF: 2008 s, 1976 m, 1938 vs  $cm^{-1}$ .

**Spectroscopic Characterization.** IR spectra were recorded on a Perkin-Elmer 983 spectrometer.

Mössbauer spectra were recorded by using a Harwell Instruments constant acceleration drive, based on a Harwell 200 series wave form generator and amplifier. A 2 mCi  $^{125}Sb/Cu$  source (New England Nuclear) was used. The source and absorbers were immersed in liquid helium in a Harwell Instruments Dewar. The 35.5 keV Mössbauer  $\gamma$ -ray was monitored through the 6-keV escape peak in a  $Xe/CO_2$  proportional counter. The spectra were

accumulated in a Nuclear Data 66 analyzer as 256-channel spectra and were subsequently computer fitted to Lorentzians<sup>9</sup> using the N.D. 66 as a computer terminal for transmitting data to, and for computation on, the University IBM 4341 mainframe computer. The spectrometer was routinely calibrated by using a  $^{57}Co/Rh$  source and an iron foil absorber at room temperature. The  $^{125}Te$  isomer shifts are reported with respect to  $^{125}I/Cu$  as a reference standard, and this entailed adding 0.15 mm  $s^{-1}$  to the shifts measured against  $^{125}Sb/Cu$  as the source.<sup>6</sup> In computer fitting the spectra, the line widths were left unconstrained except in the case of  $(\mu-Te)[V(CO)_3diphos]_2$ . Here the spectrum could be fitted to a very broad single line ( $\chi^2 = 280$  for 250 degrees of freedom) or to a doublet with narrower equal line widths ( $\chi^2 = 247$  for 248 degrees of freedom); the latter yields an upper limit for  $\Delta$  in this compound of 3.8 mm  $s^{-1}$ .

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**Registry No.**  $(\mu-Te)[V(CO)_3diphos]_2$ , 88000-23-1;  $(\mu_3-Te)-(Mn(CO)_2(\eta^5-C_5H_5))_3$ , 84074-22-6;  $(\mu_3-Te)[Mn(CO)_2(\eta^5-MeC_5H_4)]_3$ , 84074-24-8;  $(\mu-Te)[Mn(CO)_2(\eta^5-C_5Me_5)]_2$ , 92840-52-3;  $(\mu,\eta^2-TeCH_2)[Mn(CO)_2(\eta^5-C_5Me_5)]_2$ , 88056-69-3;  $(\mu-Te)[Cr(CO)_3(\eta^5-C_5H_5)]_2$ , 94607-28-0.

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## Reaction of Bis(trimethylsilyl)acetonitrile, (Trimethylgermyl)(trimethylsilyl)acetonitrile, and Bis(trimethylgermyl)acetonitrile Anions with Aldehydes

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For a comparison of the chemical behavior of organosilicon and organogermanium compounds, bis(trimethylsilyl)acetonitrile (3), (trimethylgermyl)(trimethylsilyl)acetonitrile (4), and bis(trimethylgermyl)acetonitrile (5) were synthesized, and a Peterson type reaction was performed with them and a variety of aldehydes (12). High yields of 2-(trimethylsilyl)-2-alkenenitriles (15) from 3 and 2-(trimethylgermyl)-2-alkenenitriles (20) from 4 and 5 were obtained. High stereoselectivity giving *E* isomers was observed in the reaction of 3 and 5. The key intermediate in the reaction is also discussed.

Organosilicon and organotin chemistry have now become important in the methodology of organic synthesis.<sup>1</sup> Organogermanium compounds, the middle element compounds of periodic group IVA (14<sup>20</sup>), are assumed to have chemical properties that are also intermediate between those of the silicon and tin analogues. Only a few reports have compared the chemical behavior of the tetraorgano-compounds of silicon, germanium, and tin.<sup>2</sup>

The Peterson reaction<sup>3</sup> has been applied for the synthesis of silylated olefins from  $\alpha,\alpha$ -disilylated carbanions

with carbonyl compounds: e.g., 1-(trimethylsilyl)-1-alkenes from [bis(trimethylsilyl)methyl]lithium,<sup>4</sup> 2-(trimethylsilyl)-2,3-unsaturated carboxylic acid esters from *tert*-butyl lithiobis(trimethylsilyl)acetate.<sup>5</sup> Previously, we reported a synthesis of (*Z*)-alk-2-enenitriles from aldehydes with tris(trimethylsilyl)ketene imine (2).<sup>6</sup>

It appeared that disubstituted acetonitriles or trisubstituted ketene imines which have both the trimethylsilyl and trimethylgermyl groups, as in compounds 3-7 of eq 2, are good model compounds to directly compare the chemical reactivity between organoelement groups (Scheme I). This paper reports that the Peterson reaction of disubstituted acetonitrile anions having trimethylsilyl

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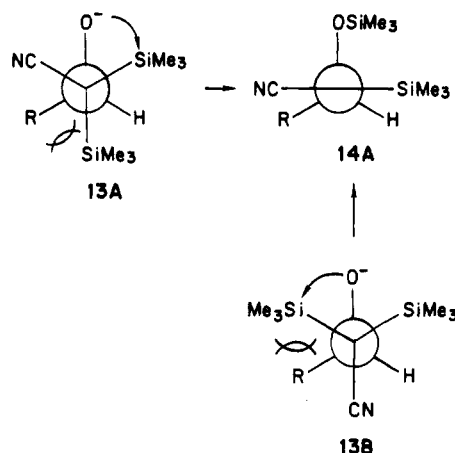


Table III. 2-(Trimethylsilyl)-2-alkenenitriles (15a-e) and 2-(Trimethylgermyl)-2-alkenenitriles (20a-f)

compd	bp, °C (mmHg) [mp, °C <sup>a</sup> ]	IR (cm <sup>-1</sup> ) CN (C=C)	NMR (CDCl <sub>3</sub> ), δ		elemental anal. or high-resolutn MS ( <i>m/z</i> ) found (calcd)		
			Me <sub>3</sub> Si or Me <sub>3</sub> Ge	CH=	C	H	N
15a-E	134-135 (9)	2195 (1593)	0.22	6.54 (t, <i>J</i> = 7.3 Hz)	69.92 (69.88)	11.54 (11.28)	6.52 (6.27)
15a-Z	130 (18) <sup>b</sup>	2200 (1585)	0.31	7.29 (t, <i>J</i> = 7.8 Hz)	223.117 61 (223.175 30)		
15b-E	115-117 (10)	2190 (1595)	0.23	6.22 (d, <i>J</i> = 10.0 Hz)	69.80 (69.88)	11.56 (11.28)	6.18 (6.27)
15b-Z		2180 (1585)	0.31	6.85 (d, <i>J</i> = 11.5 Hz)	223.175 42 (223.175 30)		
15c-E	123-125 (10) [40-45]	2195 (1580)	0.21	6.35 (d, <i>J</i> = 9.0 Hz)	69.13 (69.50)	10.44 (10.21)	6.88 (6.75)
15c-Z	130 (18) <sup>b</sup>	2190 (1580)	0.29	7.02 (d, <i>J</i> = 10.8 Hz)	207.146 26 (207.144 43)		
15d-E	80-85 (21) <sup>b</sup>	2180 (1590)	0.21	6.41 (s)	181.127 97 (181.128 65)		
15e-E	135-136 (6)	2190 (1588)	0.33	7.22 (s)	71.32 (71.59)	7.37 (7.51)	7.23 (6.97)
15e-Z	[78.0-78.5]	2175 (1560)	0.19	8.26 (s)	71.56 (71.59)	7.51 (7.51)	6.90 (6.97)
20a-E	130-135 (14) <sup>b</sup>	2190 (1595)	0.37	6.53 (t, <i>J</i> = 7.2 Hz)	58.14 (58.28)	9.63 (9.40)	5.21 (5.23)
20a-Z	140-145 (13) <sup>b</sup>	2193 (1593)	0.43	7.14 (t, <i>J</i> = 7.7 Hz)	58.43 (58.28)	9.54 (9.40)	5.17 (5.23)
20b-E	125 (17) <sup>b</sup>	2190 (1595)	0.39	6.52 (d, <i>J</i> = 9.6 Hz)	58.49 (58.28)	9.59 (9.40)	5.11 (5.23)
20b-Z	130-135 (15) <sup>b</sup>	2200 (1590)	0.45	6.92 (d, <i>J</i> = 10.8 Hz)	58.37 (58.28)	9.25 (9.40)	5.23 (5.23)
20c-E	125-130 (16) <sup>b</sup> [39.5-40.5]	2190 (1596)	0.35	6.37 (d, <i>J</i> = 9.4 Hz)	57.35 (57.22)	8.35 (8.40)	5.49 (5.56)
20c-Z	135-140 (16) <sup>b</sup>	2190 (1595)	0.44	6.96 (d, <i>J</i> = 10.4 Hz)	57.10 (57.22)	8.60 (8.40)	5.47 (5.56)
20d-E	[47.0-48.0]	2185 (1590)	0.37	6.38 (s)	53.11 (53.18)	8.66 (8.48)	6.24 (6.20)
20d-Z	85-90 (22) <sup>b</sup>	2190 (1575)	0.51	7.27 (s)	227.074 37 (227.072 93)		
20e-E	130 (4) <sup>b</sup>	2190 (1592)	0.48	7.16 (s)	58.57 (58.63)	6.17 (6.15)	5.57 <sup>c</sup> (5.70)
20e-Z	[81.0-82.0]	2190 (1585)	0.35	8.06 (s)			
20f-E	115-120 (10) <sup>b</sup>	2180 (1602, 1580)	0.44	7.01 (s)	50.74 (50.94)	5.50 (5.56)	5.82 (5.94)
20f-Z	[63.5-64.0]	2180 (1602)	0.49	7.65 (s)	51.24 (50.94)	5.49 (5.56)	5.92 (5.94)

<sup>a</sup> Recrystallized from hexane. <sup>b</sup> Oven temperature of Kugelrohr distillation apparatus. <sup>c</sup> Analyzed as *E,Z* mixture.

and the vicinal silyl group. Thus high *E* selectivity of the product 15a-d could be regarded as a result of elimination of the trimethylsiloxy group from 14A. Use of an excess 12e in this reaction did not affect the ratio of 15 and 17, remarkably, and the formation of 17 in THF was suppressed (Table II).



The reaction of lithio(trimethylgermyl)(trimethylsilyl)acetonitrile (18) proceeded smoothly with all aldehydes tested and gave predominantly 2-(trimethylgermyl)-2-alkenenitriles (20) in high yield. The longer bond length of Ge-C as compared to Si-C decreased the steric hindrance and permitted the nucleophilic attack of 18 with 12d. A key intermediate, the  $\alpha$ -carbanion 19, may also be formed at this time. Whereas the rearrangement of  $\alpha$ -silylcabinols to siloxyalkanes in the presence of base is well-known as the Brook rearrangement,<sup>13</sup> the only reported case of a rearrangement of an  $\alpha$ -germylcarbinol to an germoxyalkane is that of 9-(triphenylgermyl)-9-fluorenol to 9-[(triphenylgermyl)oxy]fluorene.<sup>14</sup> The Brook rear-

angement of germyl group does not seem to be general. The 1,3-anionic rearrangement of the trimethylgermyl group from carbon to oxygen is also unlikely, especially when competing with a trimethylsilyl group. The germanium analogue of 17 was not detected in the reaction with 12e. Recently, Zapata and co-workers reported that the reaction of *tert*-butyl 2-lithio-2-(tri-*n*-butylstannyl)-2-(trimethylsilyl)acetate with aldehydes gave moderate yields of 2-stannyl 2,3-unsaturated carboxylic acid esters accompanied by destannylated esters.<sup>15</sup>

High yields of 20 were also obtained from lithiobis(trimethylgermyl)acetonitrile (21) (Scheme II), except in the case of *n*-octanal (12a) (run 3). Analysis of the reaction mixture of 12a by GLC indicated that appreciable amounts of unreacted 21 (analyzed as 5) still remained even after prolonged reaction time. In contrast, 12a completely disappeared after 1 h at 0 °C. It seems likely that a trimethylgermyl group in the first adduct 22 does not rearrange to give a carbanion intermediate, which is the germanium analogue of 14 and 19, and the condensation step is reversible. Then 21 acts as a base rather than a nucleophile with 12a to induce aldol condensation. All of the other aldehydes used were secondary or had no  $\alpha$ -hydrogens. The increased steric hindrance at the  $\alpha$ -carbon atom of 12b and 12c would then promote nucleophilic attack of 21 on the carbonyl group. A similar result has been reported on the reaction of [bis(trimethylsilyl)methyl]lithium with aldehydes.<sup>4b</sup> In spite of the bis(trimethylgermyl) group having a smaller steric effect as compared to the bis(trimethylsilyl) group, high stereoselectivity giving *E* isomers was observed in the case of 20b-d. This selectivity could result from the base-induced *syn* elimination of the germoxy group in 22.

## Experimental Section

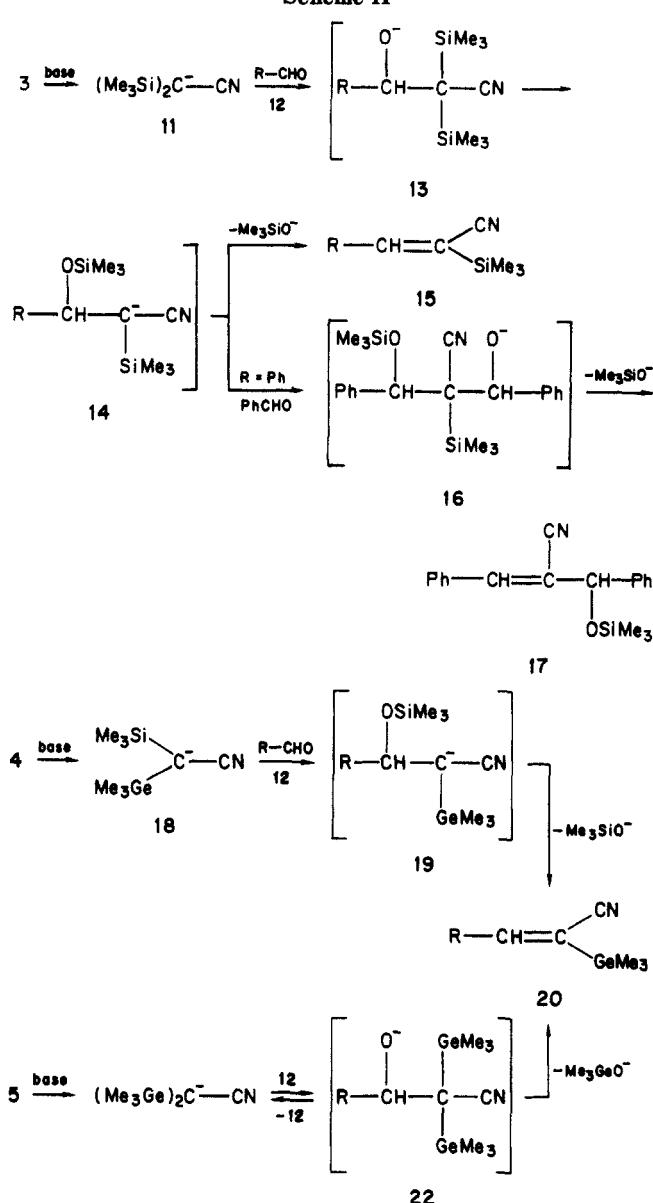
All reactions were carried out under a nitrogen atmosphere. Diethyl ether was dried by distillation from lithium aluminum hydride. Tetrahydrofuran was dried by distillation from sodium benzophenone ketyl prior to use. <sup>1</sup>H NMR spectra were recorded on a JEOL JNM-PMX 60 spectrometer using Me<sub>4</sub>Si as internal

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Scheme II



standard. IR spectra were recorded on a JASCO IRA-2 spectrometer. Mass spectral data were obtained by using a JEOL JMS-DX300 GC-MS system (70 eV). All melting points and boiling points are uncorrected.

**Reaction of Lithio(trimethylsilyl)acetonitrile with Bromotrimethylgermane.** To a solution of trimethylsilylacetonitrile<sup>16</sup> (1, 113 mg, 1 mmol) in diethyl ether (5 mL) was added dropwise *n*-BuLi (10 w/v% in hexane, 1.4 mL, 2.2 mmol) at -78 °C. After 1 h of stirring, a solution of bromotrimethylgermane (435 mg, 2.2 mmol) in diethyl ether (3 mL) was added dropwise, and stirring was continued for 2 h at -78 °C and then overnight at room temperature. The reaction mixture was directly analyzed by a GC-MS system, and the structures of nine products were determined by analyses of their mass spectra (see Table IV).

**(Trimethylgermyl)acetonitrile (10).** A solution of chloroacetonitrile (9.06 g, 120 mmol) in benzene (10 mL) was added to a suspension of bromotrimethylgermane (19.80 g, 100 mmol) and activated granular zinc (13.08 g, 200 mmol) in a mixture of benzene (30 mL) and THF (40 mL). The reaction mixture was stirred for 20 h at 30 °C, then cooled in an ice bath, and poured into 80 mL of precooled buffer solution (AcONa/AcOH). The organic layer was separated and the water layer extracted with benzene. The combined extracts were dried over anhydrous MgSO<sub>4</sub>, concentrated, and distilled under reduced pressure to give 10 (11.20 g, 71%):

Table IV. GC-MS of Reaction Products<sup>a</sup>

retentn time, min	ratio	structure	mass spectrum, <i>m/z</i>
1.15	<i>b</i>	Me <sub>3</sub> GeC <sub>4</sub> H <sub>9</sub>	176 (M <sup>+</sup> ), 161, 119, <sup>c</sup> 105
1.30	5	(Me <sub>3</sub> Ge) <sub>2</sub>	237 <sup>c</sup> (M <sup>+</sup> - 1), 119
4.05	3	(Me <sub>3</sub> Si) <sub>2</sub> CHCN (3)	185 (M <sup>+</sup> ), 170, <sup>c</sup> 73
5.00	28	Me <sub>3</sub> Si-CHCN (4)	231 (M <sup>+</sup> ), 216, 119, <sup>c</sup> 73
5.55	27	(Me <sub>3</sub> Ge) <sub>2</sub> CHCN (5)	275 (M <sup>+</sup> ), 260, 119 <sup>c</sup>
6.10	26	Me <sub>3</sub> Si-C≡C-N-SiMe <sub>3</sub> (6)	303 (M <sup>+</sup> ), 288, <sup>c</sup> 258, 119, 73
6.55	3	(Me <sub>3</sub> Ge) <sub>2</sub> C≡C-N-SiMe <sub>3</sub> (7)	349 (M <sup>+</sup> ), 332, <sup>c</sup> 200, 119, 73
10.45	1	Me <sub>3</sub> Si-CCN (8)	349 (M <sup>+</sup> ), 332, <sup>c</sup> 200, 119, 73
11.25	7	(Me <sub>3</sub> Ge) <sub>3</sub> CCN	365 (M <sup>+</sup> ), 376, 244, 119 <sup>c</sup>

<sup>a</sup> 3% Silicon SE-30, 2 m; He, 17 mL/min; temperature, 80–250 °C, rate, 8 °C/min; EI, 70 eV; ionization current, 300 mA; ratio was determined by using a total ion monitor. <sup>b</sup> Not determined due to insufficient separation with a solvent. <sup>c</sup> Base peak.

bp 80.0–84.0 °C (25 mmHg); IR (film) 2230 cm<sup>-1</sup> (CN); NMR (CDCl<sub>3</sub>) δ 0.40 (9 H, s, GeMe<sub>3</sub>), 1.63 (2 H, s, CH<sub>2</sub>CN). Anal. Calcd for C<sub>5</sub>H<sub>11</sub>NGe: C, 38.07; H, 7.03; N, 8.88. Found: C, 38.14; H, 7.19; N, 8.55.

**(Trimethylgermyl)(trimethylsilyl)acetonitrile (4).** *n*-BuLi (10 w/v% in hexane, 32 mL, 50 mmol) was added to a solution of (trimethylsilyl)acetonitrile (1, 5.66 g, 50 mmol) in diethyl ether (50 mL) at -78 °C, and the mixture was stirred for 1 h. This cold mixture was added dropwise to a solution of bromotrimethylgermane (11.86 g, 60 mmol) in diethyl ether (100 mL) at -78 °C. After 2 h of stirring at the same temperature, aqueous NH<sub>4</sub>Cl was added and the mixture was extracted with diethyl ether. The organic layer was washed with water and saturated aqueous NaCl dried over anhydrous MgSO<sub>4</sub>, and then concentrated under reduced pressure. Distillation of the residue gave 9.87 g (86%) of 4: bp 118.0–125.0 °C (26 mmHg); IR (film) 2210 cm<sup>-1</sup> (CN); NMR (CDCl<sub>3</sub>) δ 0.22 (9 H, s, SiMe<sub>3</sub>), 0.42 (9 H, s, GeMe<sub>3</sub>), 1.18 (1 H, s, CHCN); mass spectrum, *m/z* 231.05153 (M<sup>+</sup>) (calcd for C<sub>8</sub>H<sub>19</sub>NGeSi 231.04973).

**Bis(trimethylgermyl)acetonitrile (5).** In a manner similar to that described for 4 was treated 10 (5.23 g, 33 mmol), *n*-BuLi (10 w/v% in hexane, 21 mL, 33 mmol), and bromotrimethylgermane (7.8 g, 40 mmol). The ethereal extract was distilled to give 3.96 g (44%) of 5: bp 127.0–132.0 °C (20 mmHg); IR (film) 2220 cm<sup>-1</sup> (CN); NMR (CDCl<sub>3</sub>) δ 0.36 (18 H, s, GeMe<sub>3</sub>), 1.15 (1 H, s, CHCN). Anal. Calcd for C<sub>8</sub>H<sub>19</sub>NGe<sub>2</sub>: C, 35.01; H, 6.98; N, 5.10. Found: C, 35.16; H, 6.99; N, 5.01.

A brown residue of the distillation was recrystallized from hexane to give 3.41 g (26%) of tris(trimethylgermyl)acetonitrile (9): mp 190.5–193.0 °C; IR (Nujol) 2160 cm<sup>-1</sup> (CN); NMR (CDCl<sub>3</sub>) δ 0.41 (s, GeMe<sub>3</sub>). Anal. Calcd for C<sub>11</sub>H<sub>27</sub>NGe<sub>3</sub>: C, 33.78; H, 6.96; N, 3.58. Found: C, 33.56; H, 7.08; N, 3.55.

**2-(Trimethylsilyl)-2-alkenenitrile (15) and 2-(Trimethylgermyl)-2-alkenenitrile (20) (General Procedure).** To a solution of 1 mmol of 3, 4, or 5 in diethyl ether (5 mL) was added dropwise *n*-BuLi (10 w/v% in hexane, 0.64 mL, 1 mmol) at 0 °C. After being stirred for 1 h, a solution of an aldehyde (12, 1.2 mmol) in diethyl ether (3 mL) was added dropwise, and then stirring was continued for 2 h at the same temperature. Saturated aqueous NH<sub>4</sub>Cl was added to the reaction mixture, and it was extracted with benzene. The organic layer was washed with water and saturated aqueous NaCl, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The residue was chromatographed on a silica gel column (a mixture of hexane and diethyl ether) to give 15-*E* and 15-*Z* or 20-*E* and 20-*Z*, respectively.

The *E,Z* assignment of two geometrical isomers of the products was performed, according to the reported method, by the comparison of the chemical shifts of olefinic protons and trimethylsilyl

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or trimethylgermyl groups in their  $^1\text{H}$  NMR spectra and retention times of GLC<sup>17</sup> and also by the coupling constant ( $^3J_{\text{C,H}}$ ) between the olefinic proton and the nitrile carbon in  $^{13}\text{C}$  NMR.<sup>18</sup> The relations are as follows.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  olefinic proton,  $E < Z$ ;  $\text{Me}_3\text{Si}$  or  $\text{Me}_3\text{Ge}$ ,  $E < Z$  (except for 15e and 20e). GLC (silicone SE-30, DC-550, or XE-60): retention time,  $E < Z$  (except for 15e and 20e).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $^3J_{\text{C,H}}$ ,  $E$  (17–19 Hz)  $> Z$  (9–11 Hz). The results are summarized in Table III.

Isomers of 2-(trimethylsilyl)-[or 2-(trimethylgermyl)-] cinnamionitrile (15e-*E,Z* or 20e-*E,Z*) showed a reverse relation for the aliphatic analogues (15a-d, 20a-d) in the chemical shift of  $\text{Me}_3\text{Si}$  or  $\text{Me}_3\text{Ge}$  ( $E > Z$ ) (presumably anisotropic effect of a benzene ring) and the retention time ( $E \geq Z$ ) of GLC. Their stereochemistry were confirmed by hydrolysis to cinnamionitrile. Thus, a solution of 20-*E* (or *Z*) (246 mg, 1 mmol), *n*-Bu<sub>4</sub>NF (834 mg, 3 mmol), and  $\text{KF} \cdot 2\text{H}_2\text{O}$  (385 mg, 3 mmol) in acetonitrile (5 mL)<sup>19</sup> was stirred for 1 h at 60 °C. After the addition of  $\text{H}_2\text{O}$ , the mixture was extracted with hexane. The organic layer was washed with water, dried ( $\text{MgSO}_4$ ), evaporated, and then chromatographed on a silica gel column (hexane/AcOEt, 10:1) to give (*Z*)-cinnamionitrile (117 mg, 91%) from 20e-*E* and (*E*)-cinnamionitrile (124 mg, 96%) from 20e-*Z*.

**Reaction of Lithiobis(trimethylsilyl)acetonitrile (11) with Benzaldehyde (12e).** According to the general procedure described for 15 or 20, 3 (185 mg, 1 mmol), *n*-BuLi (0.64 mL, 1 mmol), and 12e (127 mg, 1.2 mmol) was reacted. Four reaction

products were detected on a silica gel TLC, and they were chromatographed on a silica gel column (hexane/diethyl ether, 20:1) and eluted in the following order: 15e-*E*, 66 mg (33%); (*E*)-2-cyano-1,3-diphenyl-3-[(trimethylsilyl)oxy]-1-propane (17-*E*), 43 mg (14%); 15e-*Z*, 14 mg (7%), and (*Z*)-2-cyano-1,3-diphenyl-3-[(trimethylsilyl)oxy]-1-propane (17-*Z*), 55 mg (18%).

The characteristic data of 15e-*E,Z* are summarized in Table III.

17-*E*: mp 74.0–75.0 °C (from hexane); IR (Nujol) 2220 (CN), 1063  $\text{cm}^{-1}$  (SiOC); NMR ( $\text{CDCl}_3$ )  $\delta$  0.15 (9 H, s,  $\text{SiMe}_3$ ), 5.44 (1 H, s, CHOSi), 7.19–8.01 (11 H, m, Ph and =CH). Anal. Calcd for  $\text{C}_{19}\text{H}_{21}\text{NOSi}$ : C, 74.22; H, 6.88; N, 4.56. Found: C, 74.02; H, 6.71; N, 4.54.

17-*Z*: bp 140 °C (3 mmHg, oven temperature of Kugelrohr distillation apparatus); IR (film) 2220 (CN), 1065  $\text{cm}^{-1}$  (SiOC); NMR ( $\text{CDCl}_3$ )  $\delta$  0.03 (9 H, s,  $\text{SiMe}_3$ ), 5.77 (1 H, s, CHOSi), 7.22–7.30 (11 H, m, Ph and =CH). Anal. Calcd for  $\text{C}_{19}\text{H}_{21}\text{NOSi}$ : C, 74.22; H, 6.88; N, 4.56. Found: C, 73.87; H, 6.85; N, 4.56.

A mixture of 17-*E* (62 mg) and 1%  $\text{HCl-MeOH}$  (5 mL) was stirred for 1 h at room temperature. After the addition of 50 mL of ether, the mixture was washed with saturated NaCl, the solvent was removed, and then the residue was purified on a preparative TLC (silica gel;  $\text{CHCl}_3/\text{Et}_2\text{O}$ , 10:1) to give 49 mg (96%) of (*E*)-2-cyano-1,3-diphenyl-3-hydroxy-1-propene, which was identical with an authentic sample.<sup>9</sup>

**Registry No.** 1, 18293-53-3; 3, 18881-60-2; 4, 101652-74-8; 5, 101652-75-9; 6, 101652-76-0; 7, 101652-77-1; 8, 101652-78-2; 9, 101652-79-3; 10, 101652-80-6; 12a, 124-13-0; 12b, 123-05-7; 12c, 2043-61-0; 12d, 630-19-3; 12e, 100-52-7; 12f, 98-01-1; (*E*)-15a, 86536-63-2; (*Z*)-15a, 101652-87-3; (*E*)-15b, 82125-00-6; (*Z*)-15b, 101652-89-5; (*E*)-15c, 82124-99-0; (*Z*)-15c, 85520-60-1; (*E*)-15d, 95085-49-7; (*Z*)-15d, 101652-92-0; (*E*)-15e, 82125-02-8; (*Z*)-15e, 96475-95-5; (*E*)-20a, 101652-81-7; (*Z*)-20a, 101652-88-4; (*E*)-20b, 101652-82-8; (*Z*)-20b, 101652-90-8; (*E*)-20c, 101652-83-9; (*Z*)-20c, 101652-91-9; (*E*)-20d, 101652-84-0; (*Z*)-20d, 101652-93-1; (*E*)-20e, 101652-85-1; (*Z*)-20e, 101652-94-2; (*E*)-20f, 101652-86-2; (*Z*)-20f, 101652-95-3;  $\text{Me}_3\text{GeBr}$ , 1066-37-1;  $\text{Me}_3\text{GeC}_4\text{H}_9$ , 1000-46-0; ( $\text{Me}_3\text{Ge}$ )<sub>2</sub>, 993-52-2; chloroacetonitrile, 107-14-2.

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## Preparation of Tin and Germanium Metallocenes from Tetravalent Precursors

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A selective reduction of appropriate tetravalent compounds provides an alternative synthetic approach to tin and germanium metallocenes. The preparation of decamethylstannocene (1) was carried out by treating bis(pentamethylcyclopentadienyl)tin dihalides with lithium metal, lithium naphthalenide, and dilithium cyclooctatetraenide. For the reduction of bis(pentamethylcyclopentadienyl)dichlorogermane to decamethylgermanocene (4), dipotassium cyclooctatetraenide was found to be the appropriate reagent.

### Introduction

Since the work of Löwig<sup>1</sup> and Frankland<sup>2</sup> in the middle of the last century, it is known that the reduction of diorganotin dihalides with electropositive metals such as sodium and zinc leads to diorganotin(II) compounds. Modern analytical methods revealed these to be oligomeric or even polymeric. The degree of polymerization among cyclic  $[\text{R}_2\text{Sn}]_n$  and acyclic  $\text{R}_{2n+2}\text{Sn}_n$  polystannanes ( $\text{R} =$

alkyl, aryl, halogen) was shown to vary markedly.<sup>3</sup> Several well-defined cyclic compounds such as  $(\text{Me}_2\text{Sn})_6$  or  $(\text{Ph}_2\text{Sn})_6$  can be prepared by treating diorganotin dihalides with sodium metal or sodium naphthalenide. During the last 2 years Masamune<sup>4</sup> and Neumann<sup>5</sup> reported the first cyclotristannanes, formed upon reduction of diorganotin

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