$C_{24}H_{21}Mn_3O_6Te$: C, 41.14; H, 300. Found: C, 41.18; H, 3.22. IR spectrum in ether: 1994 s, 1939 s, 1901 s cm^{-1}.

Synthesis of $(\mu\text{-Te})[Mn(CO)_2(\eta^5\text{-}C_5Me_5)]_2$ was carried out by following the method of Herrmann[4] which is very similar to the preparation of Herberhold.[3] Purification by column chromatography and recrystallization yielded a black crystalline compound. Anal. Calcd for $C_{24}H_{30}Mn_2O_4Te$: 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 °C quantitatively produced a blue compound of composition $(\mu\text{-}\eta^2\text{-TeCH}_2)$ $[Mn(CO)_2(\eta^5\text{-}C_5Me_5)]_2$. Anal. Calcd for $C_{25}H_{32}Mn_2O_4Te$: 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}.

$(\mu\text{-Te})[Cr(CO)_3(\eta^5\text{-}C_5H_5)]_2$ was obtained by stirring an excess of elemental tellurium in a THF solution of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ at room temperature for 1 h.[1] 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 γ-ray was monitored through the 6-keV escape peak in a Xe/CO_2 proportional counter. The spectra were accumulated in a Nuclear Date 66 analyzer as 256-channel spectra and were subsequently computer fitted to Lorentzians[9] 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.[6] In computer fitting the spectra, the line widths were left unconstrained except in the case of $(\mu\text{-Te})[V(CO)_3diphos]_2$. 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 Δ in this compound of 3.8 mm s^{-1}.

Acknowledgment. C.H.W.J. wishes to acknowledge a grant in support of this research from the Natural Sciences and Engineering Research Council of Canada.

Registry No. $(\mu\text{-Te})[V(CO)_3diphos]_2$, 88000-23-1; $(\mu_3\text{-Te})(Mn(CO)_2(\eta\text{-}C_5H_5)]_3$, 84074-22-6; $(\mu_3\text{-Te})[Mn(CO)_2(\eta^5\text{-}MeC_5H_4)]_3$, 84074-24-8; $(\mu\text{-Te})[Mn(CO)_2(\eta^5\text{-}C_5Me_5)]_2$, 92840-52-3; $(\mu,\eta^2\text{-}TeCH_2)[Mn(CO)_2(\eta^5\text{-}C_5Me_5)]_2$, 88056-69-3; $(\mu\text{-Te})[Cr(CO)_3(\eta^5\text{-}C_5H_5)]_2$, 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.[1] Organogermanium compounds, the middle element compounds of periodic group IVA (14^{20}), 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 tetraorganocompounds of silicon, germanium, and tin.[2]

The Peterson reaction[3] has been applied for the synthesis of silylated olefins from α,α-disilylated carbanions with carbonyl compounds: e.g., 1-(trimethylsilyl)-1-alkenes from [bis(trimethylsilyl)methyl]lithium,[4] 2-(trimethylsilyl) 2,3-unsaturated carboxylic acid esters from *tert*-butyl lithiobis(trimethylsilyl)acetate.[5] Previously, we reported a synthesis of (*Z*)-alk-2-enenitriles from aldehydes with tris(trimethylsilyl)ketene imine (**2**).[6]

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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(2) (a) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 410. (b) Oda, H.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 3221. (c) Oda, H.; Oshima, K.; Nozaki, H. *Chem. Lett.* **1985**, 53.

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(5) (a) Hartzell, S. L.; Rathke, M. W. *Tetrahedron Lett.* **1976**, 2737. (b) Sato, Y.; Takeuchi, S. *Synthesis* **1983**, 734.

(6) (a) Sato, Y.; Niinomi, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 56. (b) Matsuda, I.; Okada, H.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 528.

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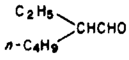
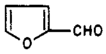
Table I. Reaction of Bis(trimethylsilyl)acetonitrile (3), (Trimethylgermyl)(trimethylsilyl)acetonitrile (4), and Bis(trimethylgermyl)acetonirile (5) Anions with Aldehydes 12

run		aldehyde	reagent	reactn conditns (T, °C/t, h)	product	product yield,[a] %	ratio[b] (E/Z)
1	**12a**	n-$C_7H_{15}CHO$	3	0/2	**15a**	96	(90/10)
2			4	0/2	**20a**	89	(75/25)
3			5	0/2	**20a**	24	(82/18)
4	**12b**		3	0/2	**15b**	87	(96/4)
5			4	0/3	**20b**	82	(71/29)
6			5	0/2	**20b**	70	(97/3)
7	**12c**	c-$C_6H_{11}CHO$	3	0/2	**15c**	72	(95/5)
8			4	0/3	**20c**	77	(78/22)
9			5	0/3	**20c**	71	(95/5)
10	**12d**	$(CH_3)_3CCHO$	3	0/24 to room temp/22	**15d**	25	(95/5)
11			4	0/4	**20d**	67	(93/7)
12			5	0/2	**20d**	85	(98/2)
13	**12e**	C_6H_5CHO	3	−78/1.5	**15e**	40[c]	(83/17)
14			4	−78/1.5	**20e**	87	(55/45)
15			5	−78/1.5 to 0/1	**20e**	89	(77/23)
16	**12f**		4	−78/1.5	**20f**	86	(55/45)

[a] Isolated yields. [b] Determined by GLC analyses. [c] Compound 17 was isolated in 32% yield (see Table II).

Table II. Reaction of Lithiobis(trimethylsilyl)acetonitrile (11) with Benzaldehyde (12e)

run	mol ratio of 12e	solv	reactn conditns	% yield and ratio of products			
				15	(E/Z)	17	(E/Z)
1	1.2	Et_2O	−78/1.5	40	(83/17)	32	(44/56)
2	2.2	Et_2O	−78/2	41	(70/30)	40	(50/50)
3	2.2	THF	−78/2	66	(76/24)	6	(17/83)

and/or trimethylgermyl groups (3–5) with a variety of aldehydes (12). Preparation of the desired trisubstituted ketene imines was difficult.

Results and Discussion

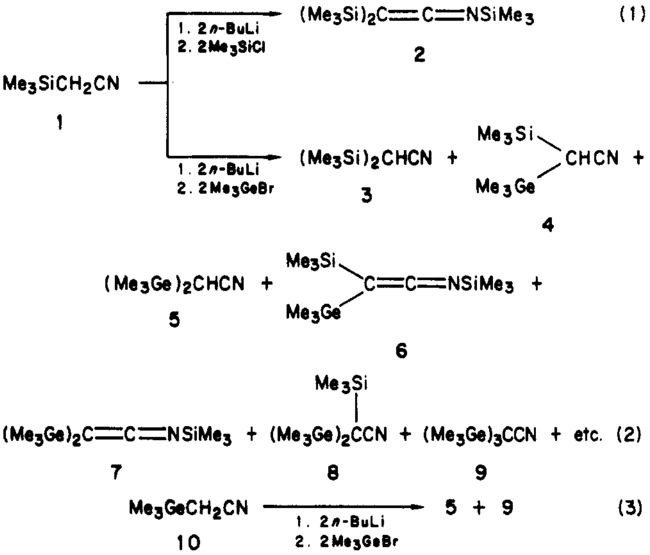
Attempts to prepare the trisubstituted ketene imines by trimethylgermylation of (trimethylsilyl)acetonitrile (1) or (trimethylgermyl)acetonitrile (10) using the preparation scheme of 2 (eq 1) were unsuccessful. The reaction of 1 gave a complicated mixture consisting of at least seven components (3–9 in eq 2), which were characterized by GC–mass spectroscopy. The main product from 10 was not the desired tris(trimethylgermyl)ketene imine but tris(trimethylgermyl)acetonitrile (9).

Bis(trimethylsilyl)acetonitrile (3) is easily obtained by the partial hydrolysis of 2.[7] (Trimethylgermyl)(trimethylsilyl)acetonitrile (4) and bis(trimethylgermyl)acetonitrile (5) were synthesized in moderate yields by the reverse addition of an equimolar amount of lithio(trimethylsilyl)acetonitrile or lithio(trimethylgermyl)acetonitrile to bromotrimethylgermane.

Lithiobis(trimethylsilyl)acetonitrile (11), prepared from 3 with n-butyllithium in ether,[8] was allowed to react with a variety of aldehydes (12). Table I shows that good yields of 2-(trimethylsilyl)-2-alkenenitrile (15a–c) were obtained from aliphatic aldehydes 12a–c. However, trimethylacetaldehyde (12d) gave a low yield of 15d, most likely due to a steric hindrance effect. The reaction of benzaldehyde (12e) gave a mixture of two types of products: the expected product 15e and 2-cyano-1,3-diphenyl-3-(trimethylsiloxy)-1-propene (17). A desilylated alcohol of 17 has been synthesized from 15 with 12e by the aid of fluoride anion.[9]

Compound 17 may be formed by the elimination of a trimethylsiloxy group from the intermediate 16, which was produced from the reaction of the α-carbanion intermediate 14 with 12e. The 1,3-anionic rearrangement of a silyl group from a carbon to an oxygen atom in the first adduct 13 would give 14, in which the α-carbanion is stabilized by the adjacent cyano and trimethylsilyl groups. The presence of similar α-carbanion intermediates has been supposed by Yamamoto,[10] Larcheveque,[11] Larson,[12] and their co-workers in the reactions of α-silylated carbanions with carbonyl compounds. The isolation of 17 provided conclusive proof that 14 is a key intermediate in this reaction. The major conformation of 14 would be the more stable form 14A having less steric interaction between R

Scheme I



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[8] The same results were obtained by using lithium diisopropylamide as the base.

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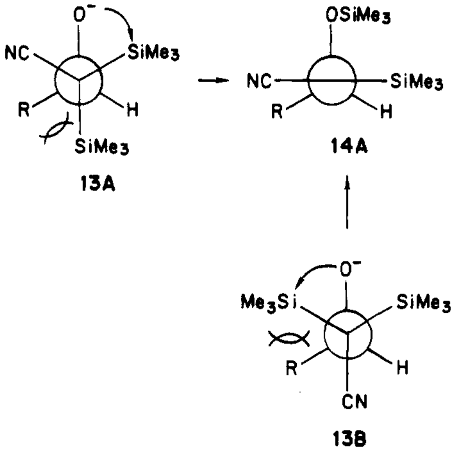
Table III. 2-(Trimethylsilyl)-2-alkenenitriles (15a–e) and 2-(Trimethylgermyl)-2-alkenenitriles (20a–f)

compd	bp, °C (mmHg) [mp, °C[a]]	IR (cm^{-1}) CN (C=C)	NMR (CDCl$_3$), δ		elemental anal. or high-resolutn MS (m/z) found (calcd)		
			Me$_3$Si or Me$_3$Ge	CH=	C	H	N
15a-E	134–135 (9)	2195 (1593)	0.22	6.54 (t, J = 7.3 Hz)	69.92 (69.88)	11.54 (11.28)	6.52 (6.27)
15a-Z	130 (18)[b]	2200 (1585)	0.31	7.29 (t, J = 7.8 Hz)	223.11761 (223.17530)		
15b-E	115–117 (10)	2190 (1595)	0.23	6.22 (d, J = 10.0 Hz)	69.80 (69.88)	11.56 (11.28)	6.18 (6.27)
15b-Z		2180 (1585)	0.31	6.85 (d, J = 11.5 Hz)	223.17542 (223.17530)		
15c-E	123–125 (10) [40–45]	2195 (1580)	0.21	6.35 (d, J = 9.0 Hz)	69.13 (69.50)	10.44 (10.21)	6.88 (6.75)
15c-Z	130 (18)[b]	2190 (1580)	0.29	7.02 (d, J = 10.8 Hz)	207.14626 (207.14443)		
15d-E	80–85 (21)[b]	2180 (1590)	0.21	6.41 (s)	181.12797 (181.12865)		
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)[b]	2190 (1595)	0.37	6.53 (t, J = 7.2 Hz)	58.14 (58.28)	9.63 (9.40)	5.21 (5.23)
20a-Z	140–145 (13)[b]	2193 (1593)	0.43	7.14 (t, J = 7.7 Hz)	58.43 (58.28)	9.54 (9.40)	5.17 (5.23)
20b-E	125 (17)[b]	2190 (1595)	0.39	6.52 (d, J = 9.6 Hz)	58.49 (58.28)	9.59 (9.40)	5.11 (5.23)
20b-Z	130–135 (15)[b]	2200 (1590)	0.45	6.92 (d, J = 10.8 Hz)	58.37 (58.28)	9.25 (9.40)	5.23 (5.23)
20c-E	125–130 (16)[b] [39.5–40.5]	2190 (1596)	0.35	6.37 (d, J = 9.4 Hz)	57.35 (57.22)	8.35 (8.40)	5.49 (5.56)
20c-Z	135–140 (16)[b]	2190 (1595)	0.44	6.96 (d, J = 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)[b]	2190 (1575)	0.51	7.27 (s)	227.07437 (227.07293)		
20e-E	130 (4)[b]	2190 (1592)	0.48	7.16 (s)	58.57 (58.63)	6.17 (6.15)	5.57[c] (5.70)
20e-Z	[81.0–82.0]	2190 (1585)	0.35	8.06 (s)			
20f-E	115–120 (10)[b]	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)

[a] Recrystallized from hexane. [b] Oven temperature of Kugelrhor distillation apparatus. [c] 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 α-carbanion **19**, may also be formed at this time. Whereas the rearrangement of α-silylcabinols to siloxyalkanes in the presence of base is well-known as the Brook rearrangement,[13] the only reported case of a rearrangment of an α-germylcarbinol to an germoxyalkane is that of 9-(triphenylgermyl)-9-fluorenol to 9-[(triphenylgermyl)oxy]fluorene.[14] The Brook rearrangement of germyl group does not seem to be general. The 1,3-anionic rearrangment 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.[15]

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 α-hydrogens. The increased steric hindrance at the α-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.[4b] 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. ^{1}H NMR spectra were recorded on a JEOL JNM-PMX 60 spectrometer using Me$_4$Si as internal

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[13] (a) Brook, A. G.; Warner, C. M.; McGriskin, M. E. *J. Am. Chem. Soc.* **1959**, *81*, 981. Brook, A. G.; Schwarts, N. V. *J. Am. Chem. Soc.* **1960**, *82*, 2435. Brook, A. G.; Iachia, B. *J. Am. Chem. Soc.* **1961**, *83*, 827. (b) For a review of the Brook rearrangement, see: Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.

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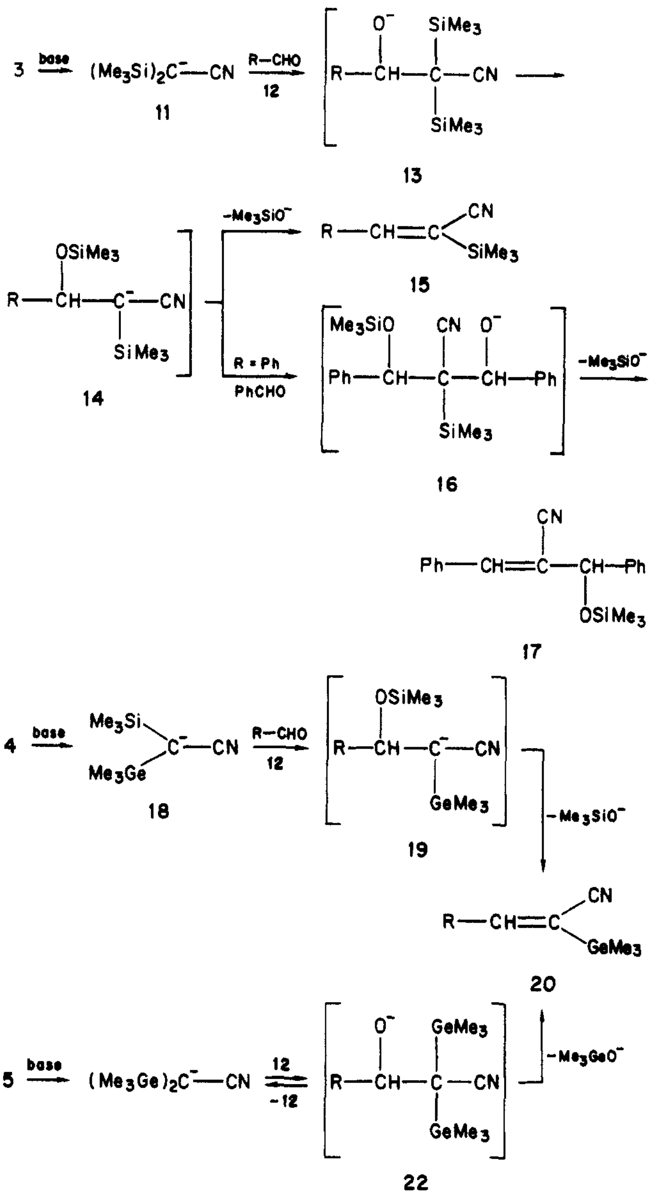
[15] Zapata, A.; Fortoul, R. C.; Acuna, A. C. *Synth. Commun.* **1985**, *15*, 179.

Scheme II

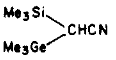
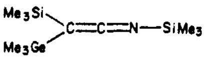
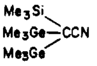


standard. IR spectra were recorded on a JASCO IRA-2 spectrometer. Mass spectral data were obtained by using a JEOL JMS-DX300 GC–MS system (70 eV). All melting points and boiling points are uncorrected.

Reaction of Lithio(trimethylsilyl)acetonitrile with Bromotrimethylgermane. To a solution of trimethylsilylacetonitrile[16] (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 was dried over anhydrous $MgSO_4$, concentrated, and distilled under reduced pressure to give 10 (11.20 g, 71%): bp 80.0–84.0 °C (25 mmHg); IR (film) 2230 cm^{-1} (CN); NMR ($CDCl_3$) δ 0.40 (9 H, s, $GeMe_3$), 1.63 (2 H, s, CH_2CN). Anal. Calcd for $C_5H_{11}NGe$: C, 38.07; H, 7.03; N, 8.88. Found: C, 38.14; H, 7.19; N, 8.55.

Table IV. GC-MS of Reaction Products[a]

retentn time, min	ratio	structure	mass spectrum, *m/z*
1.15	*b*	$Me_3GeC_4H_9$	176 (M^+), 161, 119,[c] 105
1.30	5	$(Me_3Ge)_2$	237[c] ($M^+ - 1$), 119
4.05	3	$(Me_3Si)_2CHCN$ (**3**)	185 (M^+), 170,[c] 73
5.00	28	 $(Me_3Si)(Me_3Ge)CHCN$ (4)	231 (M^+), 216, 119,[c] 73
5.55	27	$(Me_3Ge)_2CHCN$ (**5**)	275 (M^+), 260, 119[c]
6.10	26	 $(Me_3Si)(Me_3Ge)C{=}C{=}N{-}SiMe_3$ (6)	303 (M^+), 288,[c] 258, 119, 73
6.55	3	$(Me_3Ge)_2C{=}C{=}N\text{-}SiMe_3$ (**7**)	349 (M^+), 332,[c] 200, 119, 73
10.45	1	 $(Me_3Si)(Me_3Ge)_2CCN$ (8)	349 (M^+), 332,[c] 200, 119, 73
11.25	7	$(Me_3Ge)_3CCN$	365 (M^+), 376, 244, 119[c]

[a] 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. [b] Not determined due to insufficient separation with a solvent. [c] Base peak.

(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_4Cl was added and the mixture was extracted with diethyl ether. The organic layer was washed with water and saturated aqueous NaCl dried over anhydrous $MgSO_4$, 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^{-1} (CN); NMR ($CDCl_3$) δ 0.22 (9 H, s, $SiMe_3$), 0.42 (9 H, s, $GeMe_3$), 1.18 (1 H, s, CHCN); mass spectrum, *m/z* 231.05153 (M^+) (calcd for $C_8H_{19}NGeSi$ 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^{-1} (CN); NMR ($CDCl_3$) δ 0.36 (18 H, s, $GeMe_3$), 1.15 (1 H, s, CHCN). Anal. Calcd for $C_8H_{19}NGe_2$: 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^{-1} (CN); NMR ($CDCl_3$) δ 0.41 (s, $GeMe_3$). Anal. Calcd for $C_{11}H_{27}NGe_3$: 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_4Cl 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 $MgSO_4$, 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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[16] Matsuda, I.; Murata, S.; Ishii, Y. *J. Chem. Soc., Perkin Trans. 1*, **1979**, 26.

or trimethylgermyl groups in their ^{1}H NMR spectra and retention times of GLC[17] and also by the coupling constant ($^3J_{C,H}$) between the olefinic proton and the nitrile carbon in ^{13}C NMR.[18] The relations are as follows. ^{1}H NMR ($CDCl_3$): δ olefinic proton, $E < Z$; Me_3Si or Me_3Ge, $E < Z$ (except for **15e** and **20e**). GLC (silicone SE-30, DC-550, or XE-60): retention time, $E < Z$ (except for **15e** and **20e**). ^{13}C NMR ($CDCl_3$): $^3J_{C,H}$, E (17–19 Hz) > Z (9–11 Hz). The results are summarized in Table III.

Isomers of 2-(trimethylsilyl)- [or 2-(trimethylgermyl)-] cinnamonitrile (**15e**-*E*,*Z* or **20e**-*E*,*Z*) showed a reverse relation for the aliphatic analogues (**15a–d**, **20a–d**) in the chemical shift of Me_3Si or Me_3Ge ($E > Z$) (presumably anisotropic effect of a benzene ring) and the retention time ($E \geq Z$) of GLC. Their stereochemistry were confirmed by hydrolysis to cinnamonitrile. Thus, a solution of **20**-*E* (or *Z*) (246 mg, 1 mmol), n-Bu_4NF (834 mg, 3 mmol), and $KF \cdot 2H_2O$ (385 mg, 3 mmol) in acetonitrile (5 mL)[19] was stirred for 1 h at 60 °C. After the addition of H_2O, the mixture was extracted with hexane. The organic leyer was washed with water, dried ($MgSO_4$), evaporated, and then chromatographed on a silica gel column (hexane/AcOEt, 10:1) to give (*Z*)-cinnamonitrile (117 mg, 91%) from **20e**-*E* and (*E*)-cinnamonitrile (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 cm^{-1} (SiOC); NMR ($CDCl_3$) δ 0.15 (9 H, s, $SiMe_3$), 5.44 (1 H, s, CHOSi), 7.19–8.01 (11 H, m, Ph and =CH). Anal. Calcd for $C_{19}H_{21}NOSi$: 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 cm^{-1} (SiOC); NMR ($CDCl_3$) δ 0.03 (9 H, s, $SiMe_3$), 5.77 (1 H, s, CHOSi), 7.22–7.30 (11 H, m, Ph and =CH). Anal. Calcd for $C_{19}H_{21}NOSi$: 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% 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; $CHCl_3/Et_2O$, 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.[9]

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; Me_3GeBr, 1066-37-1; $Me_3GeC_4H_9$, 1000-46-0; $(Me_3Ge)_2$, 993-52-2; chloroacetonitrile, 107-14-2.

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(20) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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[1] and Frankland[2] 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 $[R_2Sn]_n$ and acyclic $R_{2n+2}Sn_n$ polystannanes (R = alkyl, aryl, halogen) was shown to vary markedly.[3] Several well-defined cyclic compounds such as $(Me_2Sn)_6$ or $(Ph_2Sn)_6$ can be prepared by treating diorganotin dihalides with sodium metal or sodium naphthalenide. During the last 2 years Masamune[4] and Neumann[5] reported the first cyclotristannanes, formed upon reduction of diorganotin

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