Tetragermadimercurocane: Precursor of New Germanium Heterocycles and Low-Coordinate Germanium Species

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The new heterocycle 1,3,5,7,2,6-tetragermadimercurocane, $Me_2\underline{GeHgGe(Me_2)CH_2Ge(Me_2)HgGe(Me_2)CH_2}$ (1), was prepared in high yield from bis(dimethylgermyl)methane and di-*tert*-butylmercury. Thermal or UV photochemical decomposition of 1 leads to the 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-perhydrotetragermine, $Me_2\underline{GeGe(Me_2)CH_2Ge(Me_2)Ge(Me_2)CH_2}$ (2). 1 reacted with alkynes $RC{\equiv}CH$ (R = COOMe, CH_2NMe_2) and the allene $CH_2{=}C{=}CMe_2$ to give 1,3,4-substituted digermolenes and 4-methylene-1,3-digermolane. These compounds are formally the adducts of the supposed 1,1,2,2-tetramethyl-1,2-digermirane [$Me_2\underline{GeGe(Me_2)CH_2}$] and the alkynes or allenes, but an alternative route to these heterocycles cannot be ruled out. With dichloro-*tert*-butylphosphine, 1 forms oligomers $(t\text{-}BuP)_{3,4}$ via transient di-*tert*-butyldiphosphene (t-BuP=P-t-Bu). Sulfuration (or oxidation) of 1 leads first to the dithia- (or dioxa-) digermolane $Me_2\underline{GeCH_2Ge(Me_2)Y\text{-}Y}$ (Y = S or O) and then by loss of sulfur (or oxygen) to the thia- (or oxa-) digermetane $Me_2\underline{GeCH_2Ge(Me_2)Y}$ (Y = S or O). These four-membered heterocycles simultaneously dimerize and dissociate with formation of dimethylgermanethione (or germanone) ($Me_2Ge{=}Y$) (Y = S or O) and dimethylgermaethylene ($Me_2Ge{=}CH_2$) intermediates.

Introduction

Many compounds having M_{14}—Hg bonds have already been described in the literature,[1] some with M_{14}=Ge by our laboratory.[2–4] They are usually linear or rings of the type $[R_2GeHg]_n$ that have a great tendency to undergo homolytic cleavage to produce trivalent radicals (eq 1) or divalent germylenes (eq 2).

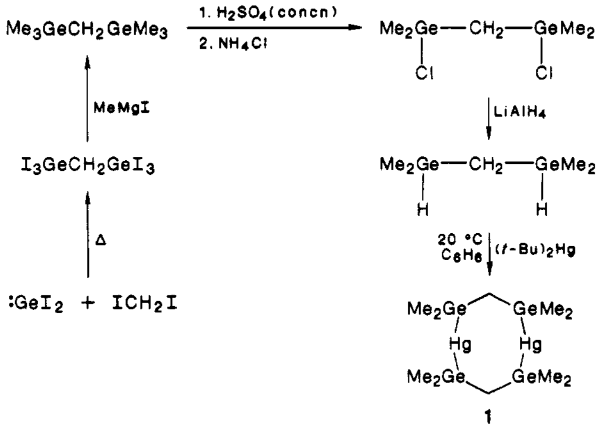
$$R_3GeHgGeR_3 \xrightarrow{-Hg} 2R_3Ge\cdot \qquad (1)$$

$$[R_2GeHg]_n \xrightarrow{-Hg} nR_2Ge: \qquad (2)$$

In this paper, we describe the preparation of the new 1,1,3,3,5,5,7,7-octamethyl-1,3,5,7,2,6-tetragermadimercurocane, $Me_2\underline{GeHgGe(Me_2)CH_2Ge(Me_2)HgGe(Me_2)CH_2}$, that behaves as an excellent precursor of novel organometallic heterocycles.

Results and Discussion

The tetragermadimercurocane 1 was obtained in high yield by the exchange reaction between bis(dimethylgermyl)methane and di-*tert*-butylmercury (eq 3) that occurs cleanly at 20 °C in benzene.



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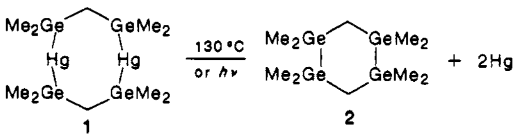

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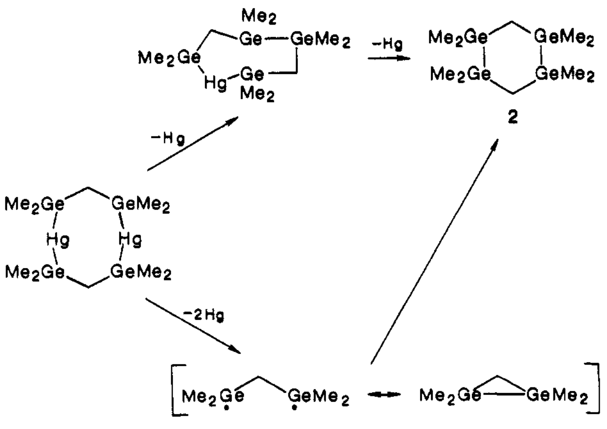
Thermal and Photochemical Stability of 1. Compound 1 is stable at room temperature, but it decomposes very rapidly above 130 °C or under UV irradiation to give 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-perhydrotetragermine, 2 (eq 4). The formation of 2 probably occurs by successive homolytic cleavage of the Ge–Hg bonds of 1 as well as by quasi-simultaneous homolytic rupture[4] via a digermyl diradical, the limiting form of 1,1,2,2-tetramethyl-1,2-digermirane (eq 5). Thermal and photolytic reactions of 1



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(1) Vyazankin, N. S.; Razuvaev, G. A.; Kruglaya, O. A. *Organomet. Chem. Rev., Sect. A* **1968**, *3*, 322 and references cited therein. Vyazankin, N. S.; Razuvaev, G. A.; Kruglaya, O. A. *Organomet. Chem. Synth.* **1971**, *1*, 205 and references cited therein. Rivière, P.; Rivière-Baudet, M.; Satgé, J. In *Comprehensive Organometallic Chemistry*; Pergamon: Elmsford, NY, 1982; Vol. 2, Part 10, and references cited therein.

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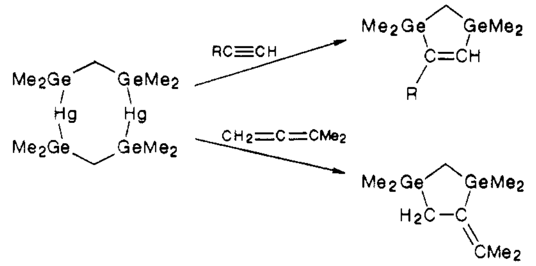
with alkynes, RC≡CH, where R = COOMe and CH_2NMe_2, and dimethylallene were carried out. ^1H NMR and GC–MS measurements showed that the expected 1,1,3,3-tetramethyl-1,3-digermolenes and 4-substituted 1,1,3,3-tetramethyl-1,3-digermolane had been formed in 25% and 15% yields, respectively (eq 6). Although the formation of these heterocycles and the absence of larger heterocycles such as $Me_2GeCH_2Ge(Me_2)Ge(Me_2)CH_2Ge(Me_2)CH{=}C$-(R) or $Me_2GeCH_2Ge(Me_2)CH{=}C(R)Ge(Me_2)CH_2Ge$-$(Me_2)CH{=}C(R)$ are suggestive of the formation of the digermirane intermediate, an alternative route to these heterocycles cannot be ruled out. But compound 2 can be ruled out as the precursor of the "digermirane adducts": in all reaction between 2 and RC≡CH or $CH_2{=}C{=}CMe_2$ there is no evidence for the formation of these heterocycles.



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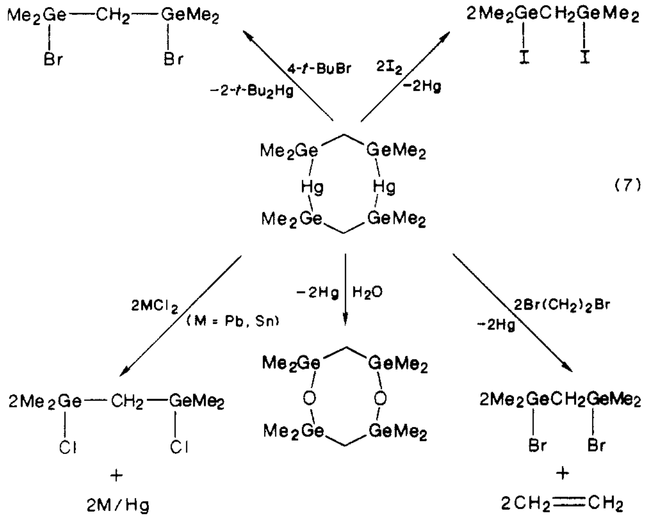
Chemical Reactivity of the Ge–Hg Bonds of 1. Compound 1 reacted instantly and almost quantitatively at 20 °C with water, halogens, and organic and organometallic halides, all of which are typical of compounds having Ge–Hg bonds[1] (eq 7).



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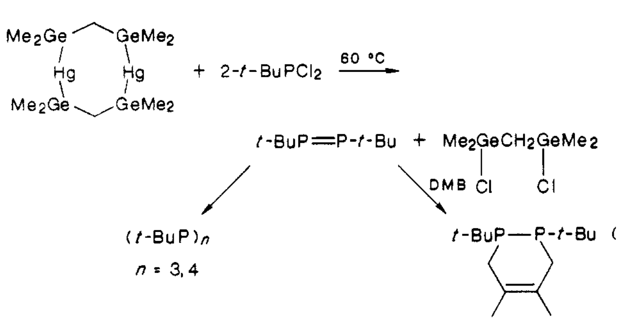
With dichloro-tert-butylphosphine, 1 produced, at 20 °C, bis(dimethylchlorogermyl)methane and cyclopolyphosphine oligomers of the type $(t\text{-BuP})_n$, where $n = 3$ or 4, probably by the intermediate di-*tert*-butyldiphosphene, (t-BuP=P-t-Bu), as this has been observed in an analogous reaction of $(Me_3Si)_2Hg$.[5,6] This divalent compound having a phosphorus–phosphorus double bond was easily characterized by its cycloaddition to 2,3-dimethylbuta-1,3-diene[7] that occurred in 30% yield (eq 8).



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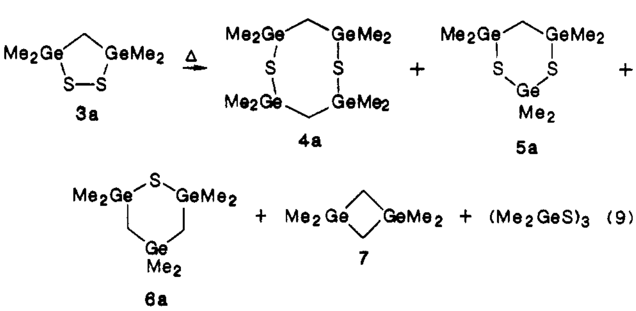
The reaction of 1 with S_8 in benzene at room temperature yielded 2,2,4,4-tetramethyl-1,5,2,4-dithiadigermolane, $Me_2GeCH_2Ge(Me_2)S\text{-}S$ (**3a**). This five-membered heterocycle is relatively stable in solution, and its composition was determined by ^1H NMR and mass spectroscopy. All attempts to distill it at low pressure resulted in the formation of 2,2,4,4,6,6,8,8-octamethyl-1,5,2,4,6,8-dithiatetragermocane (**4a**), 2,2,4,4,6,6-hexamethyl-1,3,2,4,6-perhydrodithiatrigermine (**5a**), and 2,2,4,4,6,6-hexamethyl-1,2,4,6-perhydrothiatrigermine (**6a**) in addition to small quantities of 1,1,3,3-tetramethyl-1,3-digermetane (**7**) and $(Me_2GeS)_3$ (eq 9). This product mixture is similar to that observed in the direct synthesis of 2,2,4,4-tetramethyl-1,2,4-thiadigermetane, $Me_2Ge\text{–}CH_2\text{–}Ge(Me_2)S$ (**8a**), from sodium sulfide in THF with bis(chlorodimethylgermyl)methane[8] at 20 °C. The reaction is explained as follows: (i) the formation of **8a** (revealed by ^1H NMR and mass spectrometry) by loss of sulfur from **3a** followed by (ii) simultaneous decomposition (eq 10, path a) and dimerization (eq 10, path b) of **8a**. The decomposition, analogous



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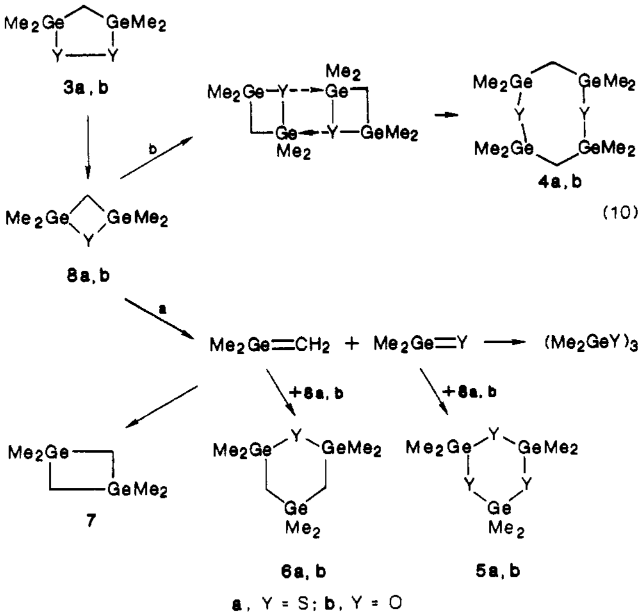

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[1]

(5) Markovski, L. N.; Romanenko, V. D.; Kirsanov, A. V. *International Converence of Phosphorus Chemistry*; Nice, Sept 1983; Abstract 8.

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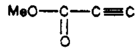
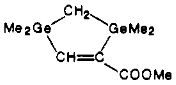
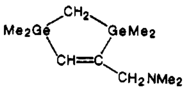
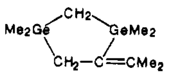
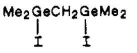
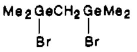
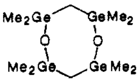
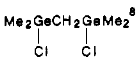
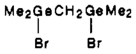
Table I

reagent	product	yield, %		^1H NMR, ppm	high-resolution mass spectrum
		$h\nu$	Δ		found (calcd)[a]
 $MeO-C(=O)-C\equiv CH$		12	25	δ_{Me} 0.30, 0.42 (12 H), δ_{CH_2} 0.20 (2 H), δ_{CH} 4.82 (1 H), δ_{OMe} 3.62 (3 H)	$C_8H_{18}O_2Ge_2$ 303.9746 (303.9740)
$Me_2NCH_2C\equiv CH$		8	21	δ_{Me} 0.25, 0.38 (12 H), δ_{CH_2} 0.18 (2 H), δ_{CH} 4.63 (1 H), δ_{CH_2N} 3.10 (2 H), δ_{Me_2N} 2.15 (6 H)	$C_{10}H_{23}NGe_2$ 303.0268 (303.0264)
$Me_2C=C=CH_2$		13	15	δ_{Me} 0.35, 0.40 (12 H), δ_{CH_2} 0.16 (2 H), δ_{CMe_2} 1.65 (6 H)	$C_{10}H_{22}Ge_2$ 288.0161 (288.0155)

[a] For Ge_2 combinations the most abundant mass is $^{146}Ge_2$ ($^{70}Ge^{76}Ge$, $^{72}Ge^{74}Ge$, $^{73}Ge^{73}Ge$). Calculated $^{146}Ge_2$ mass are done with the weighted arithmetic mean of the isotope combinations: $^{146}Ge_2$ = 145.843 356.[10]

Table II

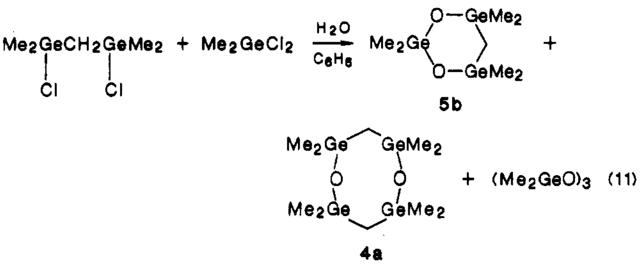
reagent	product	yield, %	^1H NMR (C_6H_6), ppm	anal.[a]		
				C	H	X
I_2	 $Me_2Ge(I)CH_2Ge(I)Me_2$	92	δ_{CH_2} 1.15 (2 H), δ_{CH_3} 0.88 (12 H)	12.75 (12.69)	2.61 (2.96)	53.85 (53.65)
$Br(CH_2)_2Br$	 $Me_2Ge(Br)CH_2Ge(Br)Me_2$	87	δ_{CH_2} 0.80 (2 H), δ_{CH_3} 0.65 (12 H)	15.74 (15.84)	3.57 (3.69)	42.28 (42.16)
H_2O		72	δ_{CH_2} 0.15 (4 H), δ_{CH_3} 0.45 (24 H)	25.49 (25.54)	5.92 (5.95)	
MCl_2 (M = Pb, Sn)	 $Me_2Ge(Cl)CH_2Ge(Cl)Me_2$[8]	80	δ_{CH_2} 0.60 (2 H), δ_{CH_3} 0.50 (12 H)			
t-BuBr	 $Me_2Ge(Br)CH_2Ge(Br)Me_2$	85				

[a] Calculated values in parentheses.

to that previously observed for 4-membered heterocycles,[9] probably proceeds by β-elimination and forms (i) dimethylgermanethione ($Me_2Ge{=}S$), which either can trimerize or can react with **8a** to give **5a**, and (ii) dimethylgermaethylene ($Me_2Ge{=}CH_2$), which can dimerize or condense with **8a** to give **6a**.

The oxidation reaction is entirely similar, resulting in oxygen homologues **3b**, **8b**, **4b**, **5b**, and **6b** (eq 10).

Compounds **3b** and **8b** are much less stable than their corresponding sulfur derivatives, with **8b** undergoing dimerization. The composition and stability of **5b** were verified independently by direct synthesis involving cohydrolysis of a mixture of dimethyldichlorogermane and bis(chlorodimethylgermyl)methane in benzene (eq 11).



Conclusion

In conclusion, the high reactivity of **1** makes it an useful reagent in the synthesis of organogermanium compounds, especially of heterocycles, and an interesting precursor in the study of germylated intermediates with low-coordinate germanium such as germanones and germanethiones (>-Ge=Y) (Y = O and S) by decomposition of various heterocycles that are difficult to obtain by other routes.

Experimental Section

All reactions were done under an atmosphere of dry argon by using standard Schlenk and high vacuum line techniques.

^1H NMR spectra were recorded on a Varian 360A spectrometer operating at 60 MHz; chemical shifts are reported in parts per million relative to internal Me_4Si as reference. ^{31}P NMR spectra were measured at 36.4 MHz by using a Bruker WP 90 spectrometer and 85% H_3PO_4 as an external reference. Gas-phase chromatography was done on an Intersmat IGC apparatus using helium as the carrier gas, a thermistor detector, and an SE 30 chromosorb column. Mass spectra were recorded on a Ribermag R 1010 or a Varian Mat 311A spectrometer operating in the electron-impact mode at 70 eV. In all cases the complex envelope of peaks obtained for polygermanes agreed with the isotopic distribution characteristic of germanium.[10]

Bis(dimethylgermyl)methane. To bis(chlorodimethylgermyl)methane[8] (9.9 g, 0.034 mol) in 50 mL of diethyl ether anhydrous was added drop by drop a suspension of $LiAlH_4$ (1.40 g, 0.036 mol) in 30 mL of ether. After hydrolysis, extraction, and concentration, 6.0 g (79%) of bis(dimethylgermyl)methane was recovered by distillation: bp 135 °C (760 mmHg); ^1H NMR (C_6D_6) δ −0.1 (t, 2 H, CH_2), 4.15 (m, $^3J(GeH)$ = 2 Hz, 2 H, GeH), 0.2 (d, 12 H, CH_3). Anal. Calcd for $C_5H_{16}Ge_2$: C, 27.12; H, 7.23. Found: C, 27.43; H, 7.19.

Synthesis of 1. Bis(dimethylgermyl)methane (5.7 g, 0.026 mol) in 30 mL of benzene was added drop by drop to di-*tert*-butylmercury (8.1 g, 0.026 mol) in 50 mL of benzene. After the mixture was kept at 20 °C in the dark under argon for 30 h, yellow crystalline **1** (16.2 g, 74%) separated: mp 130 °C; ^1H NMR (CD_2Cl_2) δ 0.30 (s, 4 H, CH_2), 0.35 (s, 24 H, CH_3); mass spectrum,

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(9) Satgé, J. *Adv. Organomet. Chem.* **1982**, *21*, 214. Satgé, J. *Pure Appl. Chem.* **1984**, *56*, 137. Reference 8 and references cited therein.

(10) Carrick, A.; Glockling, F. *J. Chem. Soc. A* **1966**, 623.

m/z 840 ($M^{\cdot+}$); UV (C_6H_{12}) λ_{max} 222 nm (log ϵ 4.42). Anal. Calcd for $C_{10}H_{28}Hg_2Ge_4$: C, 14.29; H, 3.33. Found: C, 14.17; H, 3.42.

Thermolysis of 1. A sample of 1 (0.5 g, 0.59 mmol) was placed in a sealed tube for 4 h at 160 °C. Analysis by GC spectroscopy showed that 2 had formed exclusively: ^1H NMR (C_6D_6) δ 0.35 (s, 24 H, CH_3), 0.15 (s, 4 H, CH_2); mass spectrum, *m/z* 440 ($M^{\cdot+}$). Anal. Calcd for $C_{10}H_{28}Ge_4$: C, 27.27; H, 6.32. Found: C, 27.07; H, 6.15.

Photolysis of 1. Irradiation of a cyclohexane solution of 1 by a mercury lamp (254 nm) for 8 h resulted in Hg and 2 (>98% yield).

Reactivity of "1,1,2,2-Tetramethyl-1,2-digermirane": Synthesis of 4-Substituted 1,3-Digermoles and 4-methylene-1,3-digermolane. Cyclohexane solutions of 1 and various reactants (300% excess) were subjected to UV irradiation (254 nm) for 12 h, or solutions were kept at 160 °C for 7 days in sealed tubes. The results are summarized in Table I.

Reactions of 1 with Water, Iodine, and Organic and Inorganic Halides. Equimolar amounts of 1 and reagents listed in Table II reacted in the presence of benzene at 20 °C to give the results recorded in the same table.

Reaction of 1 with Dichloro-*tert*-butylphosphine. Compound 1 (1.00 g, 1.18 mmol) dissolved in 10 mL of benzene was treated with *t*-BuPCl_2 (0.20 g, 1.18 mmol). Analysis of the product mixture by GC and ^1H and ^{31}P NMR spectroscopy showed that bis(dimethylchlorogermyl)methane and $(t\text{-BuP})_{3,4}$[11] had been formed.

A mixture of *t*-BuPCl_2 (0.50 g, 0.59 mmol), and 1 (0.10 g, 0.59 mmol) was refluxed with 5 mL of 2,3-dimethylbuta-1,3-diene for 2 h. The expected diphosphorinene[7] (30% yield) was obtained and characterized by GC and ^1H and ^{31}P NMR spectra.

Reaction of 1 with Sulfur. Compound 1 (1.00 g, 1.18 mmol) in 10 mL of benzene was treated with sulfur (S_8) (0.30 g, 1.18 mmol) for 6 h. Analyses by ^1H NMR, GC, and GC–MS spectroscopy were done just after reaction, after 48 h, and after 1 week. Just after reaction these analyses showed that **3a** had been formed almost exclusively. After 48 h, products **4a**, **5a**, **6a**, 7, and $(Me_2GeS)_3$ (compounds described in ref 8) in addition to **3a** were present in relative yields of 34%, 14%, 18%, 5%, 8%, and 21%, respectively. At the end of 1 week, only compounds **4a**, **5a**, **6a**, 7, and $(Me_2GeS)_3$ were present in relative amounts of 42%, 18%, 24%, 6%, and 10%, respectively. **3a**: ^1H NMR (C_6D_6) δ 0.65 (s, 12 H, CH_3), 0.75 (s, 2 H, CH_2); mass spectrum, *m/z* 284 ($M^{\cdot+}$).

Reaction of 1 with Oxygen. Dry oxygen was bubbled through a solution of 1 (1.00 g, 1.18 mmol) in 50 mL of benzene for 0.5 h. Analyses by ^1H NMR, GC, and GC–MS spectroscopy showed the formation of **3b**, **8b**, and **4b** in relative amounts of 7%, 8%, and 80% respectively, in addition to traces of **5b**, **6b**, **7**, and $(Me_2GeO)_3$. Compounds **3b** and **8b** were too unstable while **5b**, **6b**, **7**, and $(Me_2GeO)_3$ are producted in too small quantities to be isolated, and it was only possible to characterize them by GC and GC–MS spectroscopy: **3b**, *m/z* 237 ($(M - CH_3)^+$); **8b**, *m/z* 221 ($(M - CH_3)^+$); **6b**, *m/z* 337 ($(M - CH_3)^+$). **4b** is isolated by distillation: bp 140 °C (10 mmHg); ^1H NMR (C_6D_6) δ 0.46 (s, 24 H, CH_3), 0.13 (s, 4 H, CH_2); mass spectrum, *m/z* 457 ($(M - CH_3)^+$). Anal. Calcd for $C_{10}H_{28}O_2Ge_4$: C, 25.51; H, 5.99. Found: C, 25.65; H, 6.02. **5b** was identified by GC comparison with an authentic sample synthesized in the next reaction.

Cohydrolysis of Bis(chlorodimethylgermyl)methane and Dimethyldichlorogermane. A mixture of bis(chlorodimethylgermyl)methane (1.00 g, 3.44 mmol) and dimethyldichlorogermane (0.60 g, 3.44 mmol) in 75 mL of benzene was treated with 5 mL of aqueous ammonia (20%). After extraction with petroleum ether, the solution was dried over $CaCl_2$, and a mixture of $(Me_2GeO)_3$ and **5b** was recovered by distillation (bp 110–115 °C (4 mmHg)) in addition to a mixture of **5b** and **4b** (bp > 115 °C (4 mmHg)). The yield of **5b** was estimated (by GC and NMR) to be 70%. **5b** was purified by preparative GC (SE 30 column, 8 in., 50–250 °C). **5b**: ^1H NMR (CCl_4) δ 0.1 (s, 6 H, OGe*Me*$_2$O) 0.43 (s, 12 H, *Me*$_2$GeCH$_2$Ge*Me*$_2$) 0.33 (s, 2 H, CH_2); mass spectrum, *m/z* 339 ($(M - CH_3)^+$). Anal. Calcd for $C_7H_{20}O_2Ge_3$: C, 23.75; H, 5.69. Found: C, 23.68; H, 5.53.

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