Bull. Chem. Soc. Jpn., 57, 796—801 (1984) [Vol. 57, No. 3

Conformational Studies of Neopentyl- and Trimethylsilylmethyl-substituted Germyl Radicals by Electron Spin Resonance

Kunio Mochida
Department of Chemistry, Faculty of Sciences, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171
(Received August 30, 1983)

Conformational analyses of a series of neopentyl- and trimethylsilylmethyl-substituted germyl radicals by electron spin resonance (ESR) were investigated on the basis of the modified $\cos^2\theta$ rule. Dimethylneopentylgermyl radical has the conformations with the neopentyl group rotating freely. On the other hand, dimethyl(trimethylsilylmethyl)germyl radical has the preferred conformations with trimethylsilylmethyl group eclipsing with the singly occupied orbital on a germanium atom. The ESR spectra of dineopentylmethylgermyl and bis(trimethylsilylmethyl)methylgermyl radicals showed the existence of two kinds of methylene protons due to the nonplanar geometries and the slow inversion of these germyl radicals. Conformations of trineopentylgermyl and tris(trimethylsilylmethyl)germyl radicals are also discussed.

In connection with stabilization of the radicals and stereoselectivity in homolytic reactions, the structures and conformations of alkyl radicals have been widely studied by ESR.[1] Substituents located in the β position of group 4B-centered radicals also stabilize the radicals and exert stereochemical effects in group 4B-centered radical reactions.[2] However, there are few reports on the structures and conformations of β-substituted 4B-centered radicals by ESR.[3–6]

We have previously reported on the ESR spectra of benzyl-substituted germyl radicals.[5,6] Benzyl-substituted germyl radicals have nonplanar configurations and the preferred conformations of these germyl radicals are those with the phenyl ring of the benzyl group eclipsing the singly occupied orbital on a germanium atom on the basis of the values of the hyperfine splitting constants (hfsc) of the benzylic protons and the marked temperature dependence. Such preferred conformations of benzyl-substituted germyl radicals are due to the interaction between a singly occupied orbital on a germanium atom and the phenyl π orbitals.

In this paper, the ESR spectra of neopentyl- and trimethylsilylmethyl-substituted germyl radicals are reported. Neopentyl and trimethylsilylmethyl groups are more hindered sterically and interacted less electronically with a singly occupied orbital on a germanium atom than a benzyl group. Therefore, the conformations of neopentyl- and trimethylsilylmethyl-substituted germyl radicals are expected to be different from those of benzyl-substituted germyl radicals.

Results and Discussion

Neopentyl- and trimethylsilylmethyl-substituted germyl radicals were generated by abstraction of hydrogen from the corresponding hydrogermanes using photochemically generated t-butoxyl radicals.[7,8]

$$\mathrm{(CH_3)_3CO\text{-}OC(CH_3)_3} \xrightarrow{h\nu} \mathrm{2(CH_3)_3CO\cdot} \tag{1}$$

$$\mathrm{R_nMe_{3-n}GeH + (CH_3)_3CO\cdot} \longrightarrow \mathrm{R_nMe_{3-n}Ge\cdot + (CH_3)_3COH} \tag{2}$$

$$\mathrm{R = CH_2C(CH_3)_3,\ CH_2Si(CH_3)_3}$$

$$n = 1-3$$

The g factors and hfsc's of a series of neopentyl- and trimethylsilylmethyl-substituted germyl radicals at various temperatures are summarized in Table 1.

ESR Spectra of Neopentyl-substituted Germyl Radicals. Figure 1 shows the ESR spectrum of dimethylneopentylgermyl radical at −100 °C. It consists of a nonet arising from the circumstance that the magnitude of the coupling constant of the methyl protons is the same as that of the methylene protons. The line intensities of this germyl radical are satisfactorily reproduced by computer simulation. The outermost lines of the

Table 1 The g factors and hyperfine splitting constants of neopenthyl- and trimethysil ylmethyl-substituted germyl radicals

Radicals	Temp/°C	g factors	Hfsc/G		
			a(CH$_3$)	a(CH$_2$)	Others
$\mathrm{Me_2\dot{G}eCH_2Bu^t}$	−70	2.0107	5.45	5.45	
	−135		5.46	5.46	
$\mathrm{Me\dot{G}e(CH_2Bu^t)_2}$	20		5.49	6.65, 3.58	
	−60	2.0106	5.54	6.68, 3.67	
	−120		5.49	6.51, 3.83	
$\mathrm{\dot{G}e(CH_2Bu^t)_3}$	50	2.0107		4.96	
	−120			5.14	
$\mathrm{Me_2\dot{G}eCH_2SiMe_3}$	−60	2.0100	5.35	4.18	
	−140		5.38	3.27	
$\mathrm{Me\dot{G}e(CH_2SiMe_3)_2}$	10		5.34	6.11, 3.95	
	−60	2.0098	5.35	5.98, 3.63	
$\mathrm{\dot{G}e(CH_2SiMe_3)_3}$	40			5.07	$a(^{29}\mathrm{Si})=5.0$
	−90	2.0094		5.07	

nonet are lost in the noise. The spectrum of dimethylneopentylgermyl radical was measured over a temperature range between —70 and —135 °C. As shown in Table 1, the methylene and methyl protons hfsc's are equivalent and there is no temperature dependence with experimental error over the investigated temperature range.

Figure 2 shows the ESR spectrum of dineopentylmethylgermyl radical at —60 °C. It consists of a quartet due to 3 methyl protons further split into two sets of triplets (6.68 and 3.67 G, 1 G=10^{-4} T), indicative of the existence of two kinds of methylene protons. The hfsc's of the two sets of triplets showed small temperature dependence, while the methyl proton hfsc was almost constant. The experimental spectra of dineopentylmethylgermyl radical were reproduced by computer simulation with the listed hfsc's.

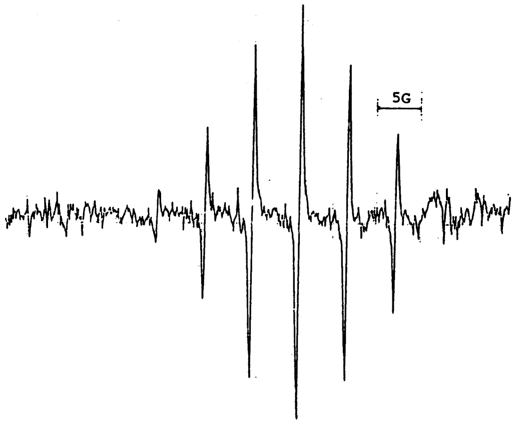


Fig. 1. ESR spectrum of dimethylneopentylgermyl radical at —100 °C.

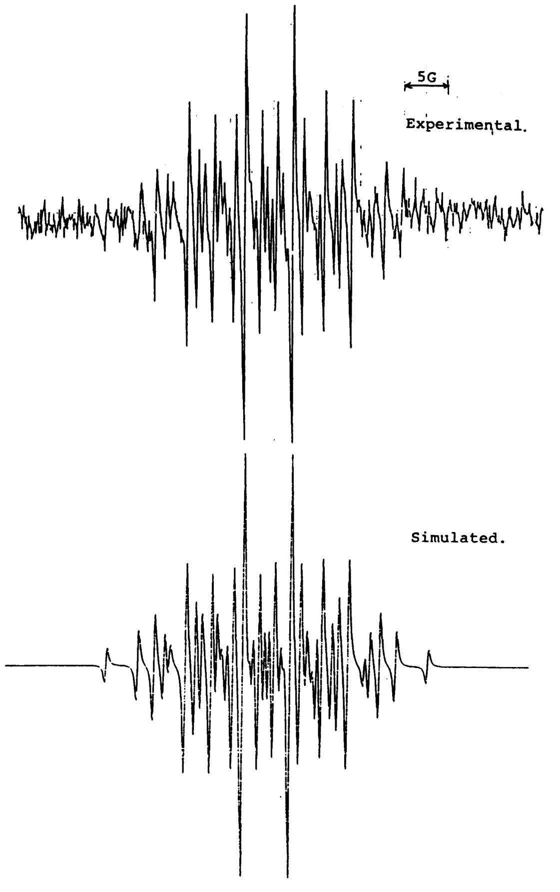


Fig. 2. ESR spectrum of dineopentylmethylgermyl radical at —60 °C.

Figure 3 shows the ESR spectrum of trineopentylgermyl radical at —60 °C which consists of a septet due to 6 equiv methylene protons. The methylene protons hfsc's showed small negative temperature dependence.

ESR Spectra of Trimethylsilylmethyl-substituted Germyl Radicals. Figure 4 shows the ESR spectrum of dimethyl(trimethylsilylmethyl)germyl radical at —120 °C which consists of a septet due to 6 methyl protons split further into a triplet due to 2 methylene protons. As shown in Table 1, the methylene proton hfsc's were temperature dependent while the methyl proton hfsc's were almost constant over the investigated temperature range. The methylene proton hfsc's decreased without selective line broadening as the temperature was lowered.

Figure 5 shows the ESR spectrum of bis(trimethylsilylmethyl)methylgermyl radical at —40 °C which consists of a quartet due to 3 methyl protons further split into two sets of triplets (5.98 and 3.63 G), indicative of the existence of two kinds of methylene protons. The hfsc's of two sets of triplets showed small temperature dependence, while the methyl proton hfsc was almost constant. The experimental spectra of this germyl rad-

Fig. 3. ESR spectrum of trineopentylgermyl radical at —60 °C.

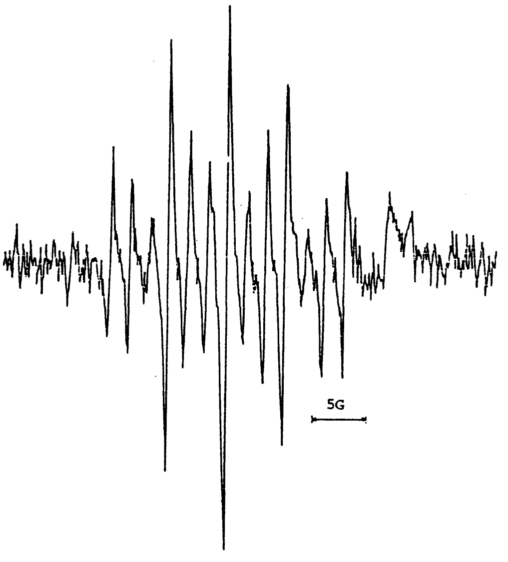


Fig. 4. ESR spectrum of dimethyl(trimethylsilylmethyl)germyl radical at —120 °C.

ical were well reproduced by computer simulation with the listed hfsc's.

Figure 6 shows the ESR spectrum of tris(trimethylsilylmethyl)germyl radical at −60 °C which consists of a septet due to 6 equiv methylene protons. The ^{29}Si species (^{29}Si natural abundance=4.7%) attributed to the principal radical was observed as shown in Fig. 6. The methylene proton hfsc's showed no temperature dependence.

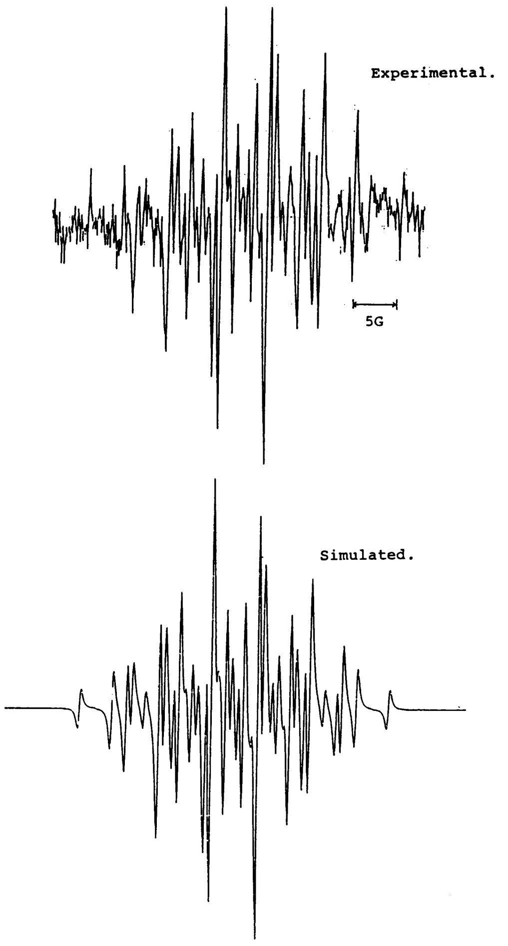


Fig. 5. ESR spectrum of bis(trimethylsilylmethyl)-methylgermyl radical at −40 °C.

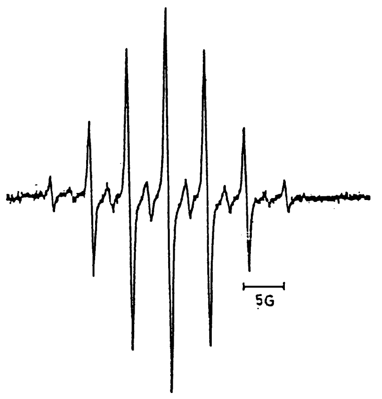
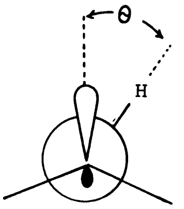


Fig. 6. ESR spectrum of tris(trimethylsilylmethyl)-germyl radical at −60 °C.

Conformations of Neopentyl- and Trimethylsilylmethyl-substituted Germyl Radicals. Organogermyl radicals are inferred to have nonplanar configurations on the basis of the ESR parameters,[9] the IR data,[10] and the stereochemistry of a chlorine-abstraction from carbon tetrachloride with a chiral germyl radical.[11] Therefore, it is reasonable to discuss the conformations of neopentyl- and trimethylsilylmethyl-substituted germyl radicals by the modified $\cos^2\theta$ rule by Eqs. 3 and 4, where θ is the dihedral angle between the β carbon–hydrogen bond and the p orbital at the radical center.[6b,12]

$$a(\beta\text{-H}) = B\cos^2\theta\ (0°<\theta<90°) \tag{3}$$

$$a(\beta\text{-H}) = B'\cos^2\theta\ (90°<\theta<180°) \tag{4}$$



Constants B and B', depend on whether or not the β-proton is placed on the same side of the larger lobe of the singly occupied orbital. Since freely rotating methyl protons ($\langle\cos^2\theta\rangle=1/2$) showed hfsc's around 5.4 G for organogermyl radicals studied here, $(B+B')/2$ may be estimated roughly as 10.8 G. Constants B and B' may depend highly on the extent of the pyramidality of the radical center. Constants B and B' are taken roughly as 5 and 15 G, respectively, when the pyramidality of the germyl radicals may be supposed to be similar to that of 1,1-difluoroalkyl radicals where B/B' is estimated to be *ca.* 0.31 by INDO calculation.[12a)]

Conformations of Dimethylneopentylgermyl and Dimethyl(trimethylsilylmethyl)germyl Radicals. Equilibrium conformations, **1**—**12**, for the methylene protons in the germyl radicals and the corresponding phases for angular dependence are illustrated as Fig. 7. Values of the methylene protons hfsc's are calculated in Table 2.

Taking into consideration that the freely rotating methylene proton hfsc's for equilibrium conformations as shown in Fig. 7 are estimated as around 5.4 G, for radicals with conformations, **1**, **6**, **7**, or **8** (R^1=R^2=Me), the methylene proton hfsc is expected to decrease as the temperature is lowered. On the other hand, for radicals with conformations, **3**, **4**, **10**, or **11** (R^1=R^2=Me), the methylene proton hfsc is expected to increase as the temperature is lowered.

The temperature dependences of the methylene proton hfsc's of dimethylneopentylgermyl and dimethyl(trimethylsilylmethyl)germyl radicals are shown graphically in Fig. 8. It is seen that the magnitude of

Table 2. Values of the methylene protons Hfsc's for conformations, **1**—**12**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
$a(\beta\text{-H}^1)$	3.75	11.25	15	11.25	3.75	0	1.25	3.75	5	3.75	1.25	0
$a(\beta\text{-H}^2)$	3.75	0	1.25	3.75	5	3.75	1.25	0	3.75	11.25	15	11.25

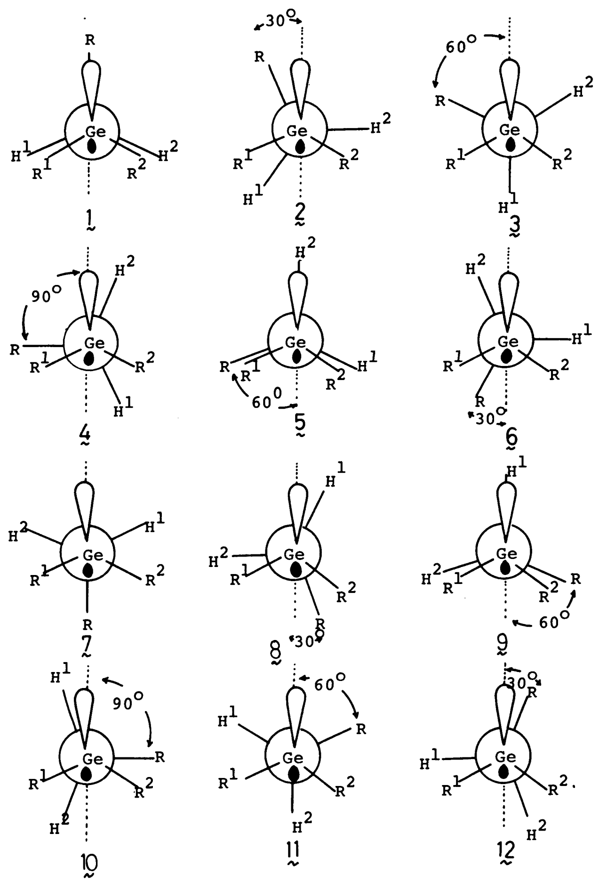


Fig. 7. Equilibrium conformations for the methylene protons in the germyl radicals and the corresponding phases for angular dependence.

the methylene proton hfsc's of dimethylneopentylgermyl radical is almost the same as that of the methyl proton hfsc's and the methylene proton hfsc's showed no temperature dependence with experimental errors. Therefore, the dimethylneopentylgermyl radical has the conformation with the neopentyl group rotating freely in the investigated temperature range.

On the other hand, the methylene protons hfsc's of dimethyl(trimethylsilylmethyl)germyl radical decreased as the temperature was lowered. Therefore, this germyl radical has the preferred conformations, **1**, **6**, **7**, or **8**; the trimethylsilylmethyl group eclipsing or nearly so with the singly occupied orbital on a germanium atom. For favoring such conformations, the odd electron is delocalized onto the carbon–silicon bond hyperconjugatively as well as onto d orbitals of the silicon atom (*p*—*d*) homoconjugatively.[13]

Conformations of Dineopentylmethylgermyl and Bis(trimethylsilylmethyl)methylgermyl Radicals. The ESR spectra of dineopentylmethylgermyl and bis(trimethylsilylmethyl)methylgermyl radicals showed the existence of two kinds of the methylene proton hfsc's without significant temperature dependence.

Recently, the activation barrier for inversion of a pyramidal germyl radical is estimated to be about 7.0 kcal mol^{-1} (1cal=4.184 J).[14] On the other hand, the barrier for rotation about the Ge–C bond is smaller than that about the C–C bond due to the longer Ge–C bond length (2.00 Å) compared to the C–C bond length (1.54 Å). Therefore, the existence of two kinds of methylene proton hfsc's of dineopentylmethylgermyl and bis(trimethylsilylmethyl)methylgermyl radicals can be explained reasonably by assuming that the configurations of these germyl radicals are fixed to nonplanar geometry and the inversion rates of these germyl radicals are much smaller than those of rotation of substituents about the Ge–C bond.

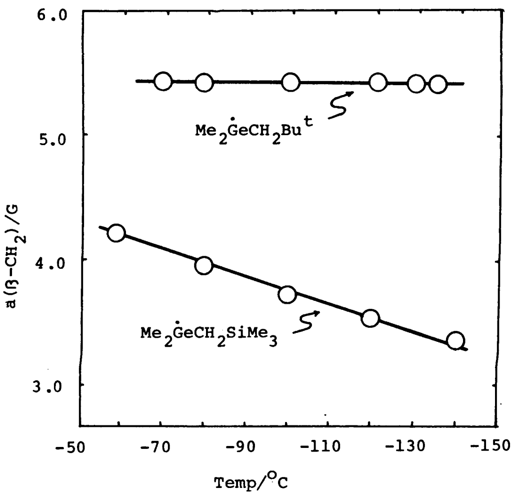
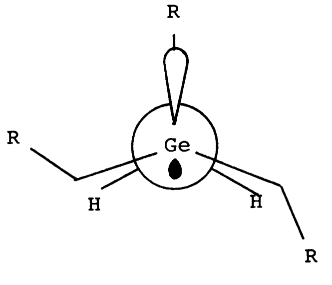


Fig. 8. Temperature dependence of $a(\beta\text{-CH}_2)$ of $\mathrm{Me_2\dot{G}eCH_2Bu}^{t}$ and $\mathrm{Me_2\dot{G}eCH_2SiMe_3}$.

Typical equilibrium conformations of dineopentylmethylgermyl and bis(trimethylsilylmethyl)methylgermyl radicals are shown in Fig. 7 ($\mathrm{R^1{=}Me}$, $\mathrm{R^2{=}CH_2R}$, R=Bu^t or SiMe$_3$). Conformations, **8**, **9**, **10**, and **11** may be eliminated due to steric repulsion between R-substituted methyl groups (R=Bu^t or SiMe$_3$) on a Ge atom and R groups on aβ-C atom. The potential energies in the various conformations as shown in Fig. 7 are not taken into consideration. However, $a(\beta\text{-H}^1)$ and $a(\beta\text{-H}^2)$ in conformations, **1**—**12** except for **8**, **9**, **10**, and **11**, average roughly 5.8 and 3.3 G, respectively, with listed hfsc's in Table 2. These values reproduce experimental data of two kinds of methylene proton hfsc's of dineopentylmethylgermyl and bis(trimethylsilylmethyl)methylgermyl radicals.

Conformations of Trineopentylgermyl and Tris(trimethylsilylmethyl)germyl Radicals. Taking into consideration the steric hindrance of *t*-butyl or trimethylsilyl groups, the conformation **1**, **2**, or **12** as shown in Fig. 7 ($\mathrm{R^1}$, $\mathrm{R^2{=}CH_2R}$, R=Bu^t or SiMe$_3$) may be selected as a candidate for the preferred conformation of trineopentylgermyl or tris(trimethylsilylmethyl)germyl radical. For example, the conformation **1** for these germyl radicals are shown in the following to minimize the steric repulsion of the substituents.



Fast rotational interconversion among three individual conformations, **1**, **2**, and **12** as shown in Fig. 7 (R^1, R^2=CH_2R, R=Bu^t or $SiMe_3$), of equal probability 1/3 will make the 6 methylene protons epuivalent. Such a correlated interconversion for tris(trimethylsilylmethyl)aminium ion radical has been reported.[15]

Experimental

ESR Measurements. The Varian X band spectrometer, light sources, and sample tubes are as described previously.[16]

The field sweep of the spectrometer was calibrated with an aquous solution of Fremy's salt (a_N=13.07 G). The g factors were determined by reference to that of the anthracene cation radical (g=2.002565) with a dual cavity.

All samples were throughly degassed using a freeze-pump-thaw cycle.

Materials. Di-*t*-butyl peroxide (DTBP) was distilled prior to use. Dimethyldichlorogermane, bp 121—122 °C,[17] dimethylphenylchlorogermane, bp 113 °C/17 mmHg (1 mmHg≈133.322 Pa),[18] methylphenyldibromogermane, bp 139—140 °C/15 mmHg,[19] and (chloromethyl)trimethylsilane, bp 98 °C[20] were prepared as described literatures.

Preparation of Dimethylneopentylchlorogermane. Neopentylmagnesium chloride was prepared (5.3 g, 0.22 mol) in THF (100 ml). The Grignard reagent was added to dimethyldichlorogermane (30.0 g, 0.17 mol) in ether (400 ml). After the mixture was stirred under gentle reflux for 2 h, the resulting salt was filtered off and the solvent was removed. Fractional distillation gave dimethylneopentylchlorogermane (6.5 g, 0.03 mol, 17.6%), bp 70.0—72.5 °C/16 mmHg.

Preparation of Dimethylneopentylgermane. A mixture of dimethylneopentylchlorogermane (6.5 g, 0.03 mol) and lithium aluminum hydride (1.4 g, 36.4 mmol) in ether (200 ml) was stirred with reflux for 2 h. After hydrolysis with water, the organic layer was dried over calcium chloride. The solvent was removed and then fractional distillation gave dimethylneopentylgermane (4.5 g, 25.8 mmol, 82.8%), bp 122.0—122.5 °C. n^{20} 1.4302; IR (cm^{-1}, neat) 2020 (Ge–H), 1240 (Ge–Me); NMR ($CDCl_3$) δ=0.21 (d, J=4.0 Hz, 6H), 0.92 (d, J=4.0 Hz, 2H) 0.97 (s, 9H), 3.89 (*m*, 1H). Found: C, 47.91; H, 10.46%, Calcd for $C_7H_{18}Ge$: C, 48.10; H, 10.38%.

Preparation of Dineopentylmethylphenylgermane. Neopentylmagnesium chloride was prepared from neopentyl chloride (46.0 g, 0.43 mol) and magnesium (10.5 g, 0.43 mol) in THF (300 ml). To this Grignard reagent, methylphenyldibromogermane (19.0 g, 0.06 mol) was added. The mixture was stirred with reflux for 10 h. After hydrolysis with water, the organic layer was extracted and dried over sodium sulfate. The solvent was removed and then fractional distillation gave dineopentylmethylphenylgermane (14.0 g, 0.05 mol, 84.6%), bp 92.5—93.0 °C/0.15 mmHg. NMR ($CDCl_3$) δ=0.63 (s, 3H), 0.91 (s, 18H), 1.14 (s, 4H), 7.37 (m, 5H); IR (cm^{-1}, neat) 1240 (Ge–Me).

Preparation of Dineopentylmethylchlorogermane. Iodine monochloide (7.4 g, 45.6 mmol) in dichloromethane (10 ml) was added to dineopentylmethylphenylgermane (13.5 g, 44.0 mmol) in dichloromethane (50 ml). The mixture was stirred at room temperatre for 5 h. After the solvent was removed, fractional distillation gave dineopentylmethylchlorogermane (8.1 g, 30.5 mmol, 69.3%), bp 102—103 °C/9 mmHg. NMR ($CDCl_3$) δ=0.87 (s, 3H), 1.04 (s, 18H), 1.34 (s, 4H).

Preparation of Dineopentylmethylgermane. A mixture of dineopentylmethylchlorogermane (7.3 g, 27.5 mmol) and lithium aluminum hydride (1.2 g, 30.4 mmol) in ether (200 ml) was stirred with reflux for 2 h. After hydrolysis with water, the organic layer was dried over calcium chloride. The solvent was removed and then fractional distillation gave dineopentylmethylgermane (6.0 g, 26.0 mmol, 94.5%), bp 83.0—84.0 °C/19 mmHg. n^{20}1.4420; IR (cm^{-1}, neat) 2040 (Ge–H), 1240 (Ge–Me); NMR ($CDCl_3$) δ=0.25 (d, J=4.0 Hz, 3H), 0.94 (d, J=4.0 Hz, 4H), 0.97 (s, 18H), 4.02 (m, 1H). Found: C, 56.92; H, 11.52%. Calcd for $C_{11}H_{26}Ge$: C, 57.22; H, 11.35%.

Preparation of Trineopentylgermane. Neopentylmagnesium bromide was prepared from neopentyl bromide (24.2 g, 0.16 mol) and magnesium (4.0 g, 0.16 mol) in THF (200 ml). To this Grignard reagent, tetrachlorogermane (10.0 g, 0.05 mol) in ether (50 ml) was added. The mixture was stirred with reflux for 10 h. The resulting salt was filtered off and the solvent was removed. The crude trineopentylchlorogermane was added to lithium aluminum hydride (4.0 g, 0.10 mol) in ether (200 ml) and then stirred with reflux for 5 h. After hydrolysis with water, the organic layer was dried over sodium sulfate. The solvent was removed and then fractional distillation gave trineopentylgermane, bp 140 °C/16 mmHg. IR (cm^{-1}, neat) 2040 (Ge–H); NMR ($CDCl_3$) δ=0.94 (d, J=4.0 Hz, 6H), 0.97 (s, 27H), 4.03 (m, 1H). For ESR measurements, the sample was purified by preparative GLC (SE30 20% 2 m).

Preparation of Dimethylphenyl(trimethylsilylmethyl)germane. (Lithiomethyl)trimethylsilane was prepared from (chloromethyl)trimethylsilane (12.3 g, 0.10 mol) and dispersed lithium (2.8 g, 0.4 mol) in ether (200 ml) at −10 °C. To this ether solution, dimethylphenylchlorogermane (8.0 g, 0.04 mol) in ether (50 ml) was added over a period of 30 min while the temperature was maintained below 10 °C. After addition was completed, the mixture was stirred with reflux for 5 h. Methanol was added to this solution and then the mixture was hydrolyzed with water. The solution was extracted with ether and the ether solution was dried over calcium chloride. Fractional distillation gave dimethylphenyl(trimethylsilylmethyl)germane (6.8 g, 25 mmol, 63.7%), bp 115 °C/15 mmHg.

Preparation of Dimethyl(trimethylsilylmethyl)germane. Iodine monochloride (3.2 g, 0.02 mol) in dichloromethane (10 ml) was added to dimethylphenyl(trimethylsilylmethyl)germane (5.0 g, 0.02 mol) in dichloromethane (50 ml). The mixture was stirred at room temperature for 5 h. After the solvent was removed, the crude dimethyl(trimethylsilylmethyl)chlorogermane was added to lithium aluminum hydride (1.0 g, 25 mmol) in ether (100 ml). The mixture was stirred with reflux for 5 h. After hydrolysis with water, the organic layer was extracted with ether and the ether solution was dried over calcium chloride. The solvent was removed and then fractional distillation gave dimethyl(trimethylsilylmethyl)germane, bp 121 °C. n^{20} 1.4440; IR (cm^{-1}, neat) 2020 (Ge–H), 1225 (Ge–Me); NMR ($CDCl_3$) δ=−0.18 (d, J=4.0 Hz, 2H), 0 (s, 9H), 0.19 (d, J=4.0 Hz, 6H), 3.82 (m, 1H). Found: C, 37.16; H, 9.39%. Calcd for $C_6H_{18}SiGe$: C, 37.75; H, 9.51%.

Preparation of Bis(trimethylsilylmethyl)methylphenylgermane. (Lithiomethyl)trimethylsilane was prepared from (chloromethyl)trimethylsilane (12.3 g, 0.10 mol) and dispersed lithium (2.8 g, 0.40 mol) in ether (200 ml) at −10 °C. To this ether solution, methylphenyldibromogermane (6.0 g, 0.02 mol) in ether (50 ml) was added over a period of 30 min while the temperature was maintained below 10 °C. After addition was completed, the mixture was stirred with reflux for 5 h. Methanol was added to this solution and then the mixture was hydrolyzed with water. The solution was extracted with ether and the ether solution was dried over calcium chloride. Fractional distillation gave bis(trimethylsilylmethyl)methylphenylgermane, bp 105 °C/4.0 mmHg.

Preparation of Bis(trimethylsilylmethyl)methylchlorogermane. Iodine monochloride (1.6 g, 0.01 mol) in dichloromethane (20 ml) was added to bis(trimethylsilylmethyl)methylphenylgermane (30 g, 8.8 mmol) in dichloromethane (10 ml). The mixture was stirred at room temperature for 5 h. After the solvent was removed, fractional distillation gave bis(trimethylsilylmethyl)methylchlorogermane, bp 98—103 °C/12 mmHg.

Preparation of Bis(trimethylsilylmethyl)methylgermane. A mixture of bis(trimethylsilylmethyl)methylchlorogermane (2.0 g, 6.7 mmol) and lithium aluminum hydride (1.0 g, 25.0 mmol) in ether (200 ml) was stirred with reflux for 2 h. After hydrolysis with water, the organic layer was extracted with ether. The ether solution was dried over calcium chloride. The solvent was removed and then fractional distillation gave bis(trimethylsilylmethyl)methylgermane (1.2 g, 4.6 mmol, 68.7%), bp 89 °C/30 mmHg. n^{25} 1.4627; IR (cm^{-1}, neat) 2020 (Ge-H), 1250 (Ge-Me,Si-Me); NMR ($CDCl_3$) $\delta=-0.16$ (d, J=4.0 Hz, 4H), 0 (s, 18H), 0.22 (d, J=4.0 Hz, 3H), 3.91 (m, 1H). Found: C, 41.19; H, 9.70%. Calcd for $C_9H_{26}Si_2Ge$: C, 41.09; H 9.96%.

Preparation of Tetrakis(trimethylsilylmethyl)germane. (Lithiomethyl)trimethylsilane was prepared from (chloromethyl)trimethylsilane (61.3 g, 0.5 mol) and dispersed lithium (13.9 g, 2.0 mol) in ether (300 ml) at −10 °C. To this ether solution, tetrachlorogermane (21.4 g, 0.10 mol) in ether (50 ml) was added over a period of 30 min while the temperature was maintained below 10 °C. After the addition was completed, the mixture was stirred with reflux for 10 h. Methanol was added to this solution and the mixture was hydrolyzed with water. The solution was extracted with ether and the ether solution was dried over calcium chloride. Fractional distillation gave tetrakis(trimethylsilylmethyl)germane (14.0 g, 33 mmol, 33.0%), bp 127—130 °C/5 mmHg. n^{16} 1.4725; IR (cm^{-1}, neat) 1240 (Si-Me); NMR ($CDCl_3$) $\delta=-0.13_5$ (s, 2H), −0.04 (s, 9H). Found: C, 45.17; H, 10.03%. Calcd for $C_{16}H_{44}Si_4Ge$: C, 45.60; H, 10.52%.

Preparation of Tris(trimethylsilylmethyl)bromogermane. Tris(trimethylsilylmethyl)bromogermane was prepared by bromination of tetrakis(trimethylsilylmethyl)germane (10.0 g, 23 mmol) with an equivalent amount of bromine (4.0 g, 24 mmol) in 50 ml of refluxing 1,2-dibromoethane for 30 min. The solvent was removed under reduced pressure, leaving about 10 ml of residue. Fractional distillation gave crude tris(triethylsilylmethyl)bromogermane (7.5 g, 18 mmol, 78.7%), bp 125—126 °C/5 mmHg. NMR (CCl_4) $\delta=-0.02_3$ (s, 2H), 0.05 (s, 9H).

Preparation of Tris(trimethylsilylmethyl)germane. A mixture of tris(trimethylsilylmethyl)bromogermane (7.5 g, 18 mmol) and lithium aluminum hydride (3.0 g, 79.2 mmol) in ether (200 ml) was stirred with reflux for 3 h. After hydrolysis with water, the organic layer was dried over calcium chloride. The solvent was removed and then fractional distillation gave tris(triethylsilylmethyl)germane (4.3 g, 13 mmol, 71.3%), bp 117—118 °C/18 mmHg. n^{16}1.4620; IR (cm^{-1}, neat) 1985 (Ge-H), 1235 (Si-Me); NMR (CCl_4) $\delta=-0.19$ (d, J=3.8 Hz, 6H), −0.05 (s, 27H), 4.00 (sept., J=3.8 Hz, 1H). Found: C, 43.03; H, 10.09%. Calcd for $C_{12}H_{34}Si_3Ge$: C, 42.99; H, 10.22%.

The author is grateful to Professor Hideki Sakurai and Dr. Mitsuo Kira of Tohoku University for their interests, encouragements, and computer simulation of ESR spectra. I also thank Professor Tadashi Suehiro of Gakushuin University for accomodation of a Varian E-9 ESR spectrometer and Mr. Isoo Miyagawa for preparation of dimethylneopentylgermane and dineopentylmethylgermane.

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