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ORGANOGERMANIUM COMPOUNDS

VI.* ELECTRON SPIN RESONANCE SPECTRA OF ARYL-SUBSTITUTED GERMYL RADICALS.

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Summary

Electron spin resonance spectra of five aryl-substituted germyl radicals are recorded. For phenyl-substituted radicals, $Ph_3Ge\cdot$, $Ph_2MeGe\cdot$, and $PhMe_2Ge\cdot$, π-spin populations are calculated by the McLachlan MO method. In $Ph_3Ge\cdot$, 82% of the spin is localized at germanium which reflects the small extent of 4p–2p conjugation. An excellent linear relation between g factors and spin densities at germanium was found. These observations provide the first evidence showing the spin delocalization through 4p–2p conjugation. The tri-p-tolylgermyl and trimesitylgermyl radicals also were studied by esr.

Introduction

Radicals centered at a Group IVB element have been of considerable interest as homologs of carbon-centered radicals and

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* For part V, see ref.1.

in this connection, their chemical and spectroscopic properties have been compared with those of the more familiar carbon radicals [2]. On the other hand, the problem of multiple bonding between carbon and its congeners such as silicon and germanium, has been a subject of considerable interest, and a variety of physical techniques has been employed to shed a light on this problem [3]. Examination of the electron spin resonance (esr) spectra of aryl-substituted Group IVB radicals will give quantitative information regarding possible multiple bonding between carbon and the other Group IVB elements.

In this paper we describe the esr spectra of several aryl-substituted germyl radicals. Reports of $H_3Ge\cdot$ [4], $Cl_3Ge\cdot$ [5] and $Me_3Ge\cdot$ [6] have appeared previously.* As far as we are aware, our work also represents the first observation of delocalization of an unpaired electron into a phenyl ring from a heavy Group IVB atom-centered radical.

Results and Discussion

Esr spectra

Aryl-substituted germyl and carbon radicals were generated by abstraction of hydrogen from the corresponding substrates using photochemically generated tert-butoxy radcials [7,8].

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

$$R_3MH + (CH_3)_3CO\cdot \longrightarrow R_3M\cdot + (CH_3)_3COH$$

The g factors and hyperfine coupling constants (h.f.c.c.) of a series of aryl-substituted germyl radicals are given in Table 1 together with those of analogous carbon radicals.

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* For a preliminary report of this work, see ref. [1].

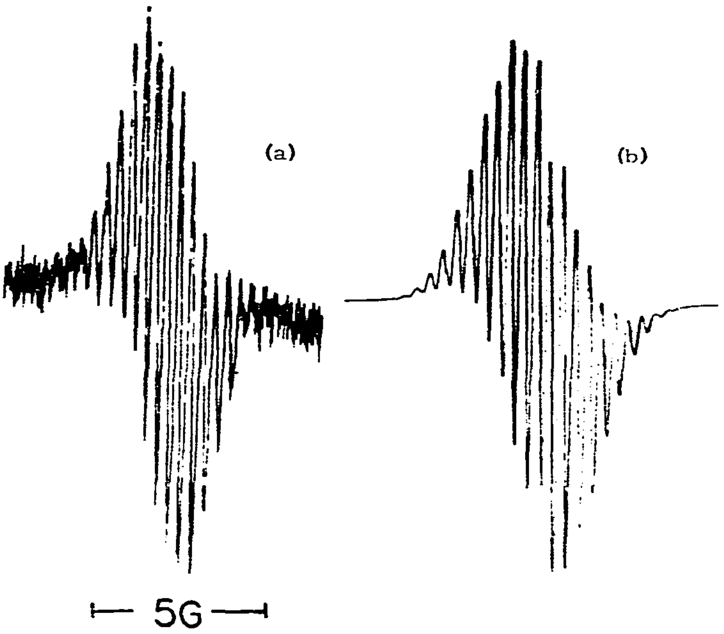


Figure 1. Esr spectra of the triphenylgermyl radical:
(a) experimental; (b) computer simulated.

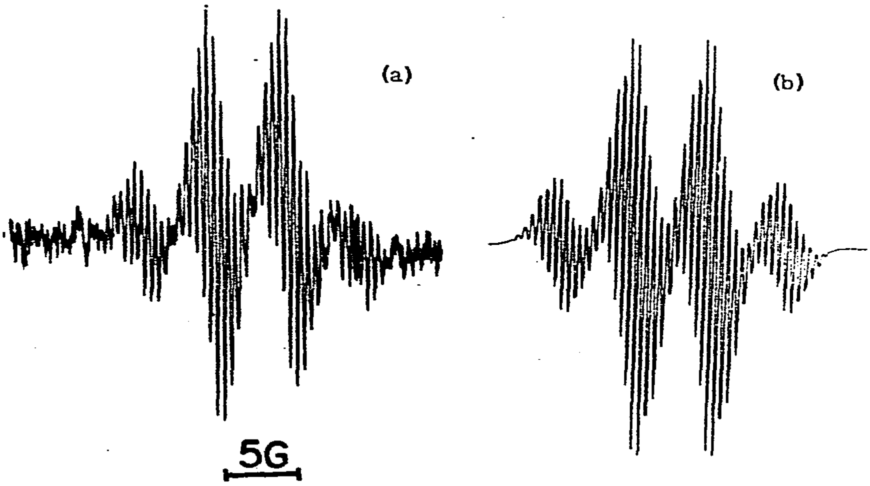


Figure 2. Esr spectra of the diphenylmethylgermyl radical:
(a) experimental; (b) computer simulated.

Figure 1 shows the esr spectrum of the triphenylgermyl radical which consists of 25 lines arising from the circumstance in which the magnitude of the coupling constant of the ortho protons is the same as that of the para protons (0.93 G) and twice as large as that of the meta protons (0.46 G). The spectrum was taken at a temperature range between -50 and -10°C and no line-broadening was observed. The triphenylgermyl radical was not persistent in contrast to the triphenylmethyl radical. When the light was turned off, the esr spectrum of the triphenylgermyl radical disappeared rather rapidly.

Figure 2 shows the esr spectrum of the diphenylmethylgermyl radical which consists of a well defined quartet (5.36 G) due to the methyl group which is split further by the ring protons. Figure 3 shows the esr spectrum of the phenyldimethylgermyl radical with a septet (5.36 G) due to the two methyl groups that is split further into nonets due to the ring protons in the intensity ratio of 1:2:4:6:6:6:4:2:1. The outermost lines of the septet are lost in the noise.

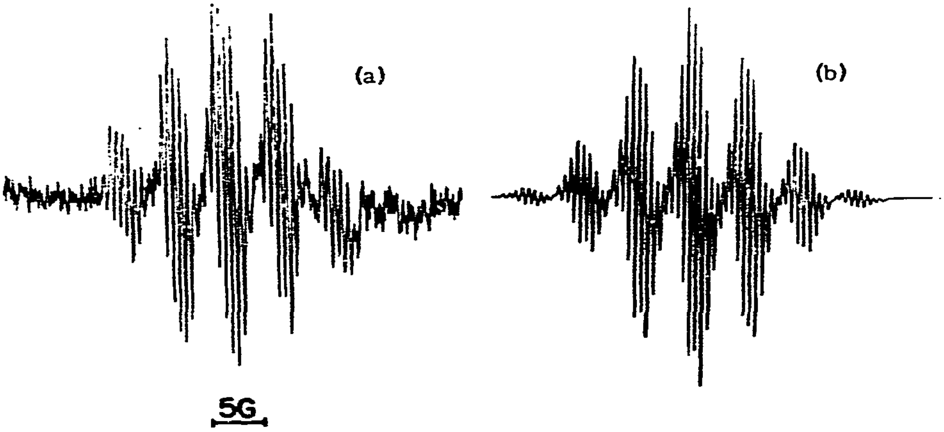


Figure 3. Esr spectra of the phenyldimethylgermyl radical:

For purposes of the comparison, esr spectra of the corresponding phenylmethyl radicals were taken. The h.f.c.c. and g values of these radicals are listed in Table 1. The esr spectrum of the triphenylmethyl radical has been observed first by Weissman [9] followed by other workers [10, 11, 12] in the reaction of triphenylmethyl chloride with metals such as silver, mercury, and zinc in toluene ($a_{\underline{o}-H}$ 2.55, $a_{\underline{m}-H}$ 1.11_5, and $a_{\underline{p}-H}$ 2.78 G). The g factors of the triphenylmethyl radical have been reported by Fraenkel [13] and Janzen [14] to be 2.002588 and 2.0024, respectively. The esr spectrum of the 1,1-diphenylethyl radical has been recorded recently by Schreiner and Berndt [15] by using the photolysis of the corresponding hydrocarbon in di-*tert*-butyl peroxide ($a_{\underline{o}-H}$ 3.19, $a_{\underline{m}-H}$ 1.30, $a_{\underline{p}-H}$ 3.47 and a_{CH_3} 15.6 G). All the spectra were reproduced satisfactorily by computer simulation using the h.f.c.c. values listed in Table 1.

Table 1

The g factors and Hyperfine Coupling Constants of Aryl-Substituted Germyl and Carbon Radicals

Radical	temp./°C	g value	h.f.c.c./G				reference
			a_{CH_3}	a_{o-H}	a_{m-H}	a_{p-H}	
$Ph_3Ge\cdot$	-30	2.0054		0.93	0.46	0.93	this work
$Ph_2MeGe\cdot$	-45	2.0070	5.36	0.97	0.49	0.97	this work
$PhMe_2Ge\cdot$	-50	2.0086	5.36	1.20	0.60	1.20	this work
$(p\text{-tolyl})_3Ge\cdot$	-30	2.0055		0.88	0.44	0.88[a]	this work
$(mesityl)_3Ge\cdot$	20	2.0066		0.70[a]		0.70[a]	this work
$Ph_3C\cdot$	20	2.0026		2.53	1.11	2.77	this work
		2.002588 2.0024		2.55	1.115	2.78	[10-14]
$Ph_2MeC\cdot$	-20	2.00265	15.14	3.24	1.24	3.35	this work
			15.6	3.19	1.30	3.47	[15]
$PhMe_2C\cdot$	-20	2.0028	15.89	4.84	1.58	5.67	this work

[a]

The characteristic features observed in the esr spectra of the aryl-substituted germyl radicals, in comparison with those of the corresponding carbon radicals, may be summarized as follows; (a) h.f.c.c. values due to the ring-protons are very small and (b) g factors of the aryl-substituted germyl radicals are very large and change significantly depending on their structures.

Judging from the magnitude of h.f.c.c. of ring-protons, π-spin populations of aryl-substituted germyl radicals are thought to be much smaller than those of the corresponding carbon radicals, in agreement with the expected small 4p-2p conjugation between germanium and carbon. In an attempt to confirm these results, Hückel molecular orbital calculations with McLachlan approximation [16] have been performed.

Molecular orbital calculations

Spin densities in the triphenylmethyl radical have been calculated and interpreted satisfactorily by McLachlan's method. Accordingly, in the present study we adopted this method.

For calculations of the π-spin population by the McLachlan MO method, parameters such as $\lambda=1.2$, $\alpha_{Ge}=\alpha_o - 0.35\beta_o$ and $\beta_{GeC}= 0.45\beta_o$ are used finally. Spin populations at the CH_3 group are then calculated by using Gerson's parameter [17]; $\alpha_{H_3}=\alpha_o - 0.5\beta_o$ $\beta_{C\equiv H_3}= 3.0\beta_o$. The resonance integral β_{Ge-C} thus obtained is consistent with values derived from studies on the germyl-substituted benzene anion radical ($\beta_{Ge-C}=0.40\beta_o$ [18] and $0.30\beta_o$ [19]) and from studies of charge transfer spectra of aryl substituted germanes ($\beta_{Ge-C}=0.50\beta_o$) [20]. This set of parameters is consistent throughout the calculation.

The estimation of the Coulomb integral merits mention. The Coulomb integral generally can be estimated from the first ionization potential [21] or the electrogenativity [22]. The Coulomb integral derived from the first ionization potential of germanium metal (182 kcal/mol) is $\alpha_o -1.94\beta_o$, while $\alpha_o - 0.80\beta_o$ is derived from the electronegativity (2.01; Pauling scale), both values being quite different from the one used in the present study. However, these values seem to be "overcorrected" and the accurate Coulomb integral of germanium in the case of aryl-substituted germyl radicals should be estimated from the first ionization potential of the aryl-substituted radicals, although at this moment there are no data on the ionization potentials of aryl-substituted germyl radicals and hence the Coulomb integral cannot be calculated. The hetero atom parameters (α_{Ge} and β_{Ge-C}) for a saturated germanium atom are also available from the data of phenylgermane anion radicals [18,19]. However, the present study revealed first the parameters for an unsaturated germyl group in which the C-Ge π bond should be really originated in the 2p(C)-4p(Ge) overlap.

The calculated spin densities of aryl-substituted germyl radicals as well as of the corresponding carbon radicals are shown in Table 2.

It is well known that the proton h.f.c.c. at the carbon atom i(a_i^H) is proportional to the spin density in the corresponding orbital (ρ_i) in the case where the spin is distributed over more than one carbon center [23]. The relationship between h.f.c.c. (a_i^H) and the spin density (ρ_i) has been proposed first by McConnell as

$$a_i^H = Q_{CH}^{\pi} \; \rho_i$$

de

In the present study, the Q_{CH}^{π} value has been determined for each radical by fitting calculated values to those observed using the least-squares method. McConnell has reported that the Q_{CH}^{π} value of aryl-substituted carbon radicals is 23 [24] and the Q_{CH}^{π} values obtained in the present study are within a range of the normal value. The experimental spin densities calculated by the McConnell relationship agree excellently with the calculated spin densities for both aryl-substituted germyl and the corresponding carbon radicals as shown in Table 2.

In the triphenylgermyl radical, the spin density is localized at the germanium center to the extent of 82% of the total spin, whereas in the corresponding triphenylmethyl radical, the spin density on the central carbon is only 42% of the total spin. In other aryl-substituted germyl radicals, spin densities are also mostly localized at the germanium center.

The relationship between g factor and spin density

The g factors of organogermyl radicals were larger than those of carbinyl and silyl radicals, reflecting the large spin-orbit coupling constant of germanium (ζ_C, 29; ζ_{Si}, 149; ζ_{Ge}, 940) [25]. The g factors of isotropic germyl radicals may be given by the

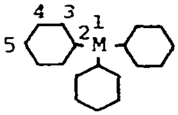
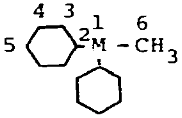
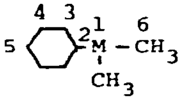
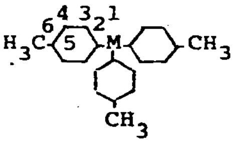
$$g = g_e + \Delta g_C + \Delta g_{Ge}$$

following equation, where g_e is the g factor of the free spin, and Δg_C and Δg_{Ge} are contributions from spins residing in alkyl (or aryl) moieties and the germanium atom, respectively. This analysis of the g factor in terms of only the unpaired spin density on germanium may be oversimplified, since it ignors the geometry of the radical center. However, in the circumstance that most of the spin is localized at the germanium radical center of similar geometry, the magnitude of the g factor depends largely on the spin density of the germanium atom. In fact, an excellent linear relation between g factors and spin densities at germanium was found for $Ph_3Ge\cdot$, $Ph_2MeGe\cdot$ and $PhMe_2Ge\cdot$, as shown in Figure 4. In this Figure, the spin density on the germanium in the germyl radical [$H_3Ge\cdot$] is taken to be 1.00.

However, there are some discrepancies in this interpretation. The h.f.c.c. of methyl protons in Ph_MeGe· and PhMe_Ge·

Table 2

Spin Populations of Phenyl-Substituted Germyl and Carbon Radicals

Radical	M	Position	ρ		Q^a (r)
			Calcd	$\lvert$Obsd$\rvert$	
	Ge	1	0.819		23.9 (0.999)
		2	-0.023		
		3	0.040	0.039	
		4	-0.018	0.019	
		5	0.040	0.039	
	C	1	0.419		25.2 (0.998)
		2	-0.048		
		3	0.109	0.100	
		4	-0.039	0.044	
		5	0.109	0.110	
	Ge	1	0.860		22.9 (0.999)
		2	-0.023		
		3	0.043	0.042	
		4	-0.020	0.021	
		5	0.044	0.042	
		6	-0.006		
		H_3	0.015		
	C	1	0.483		25.7 (0.999)
		2	-0.051		
		3	0.130	0.126	
		4	-0.048	0.048	
		5	0.127	0.130	
		6	-0.011		
		H_3	0.047		
	Ge	1	0.909		24.9 (0.999)
		2	-0.023		
		3	0.047	0.048	
		4	-0.023	0.024	
		5	0.050	0.048	
		6	-0.007		
		H_3	0.015		
	C	1	0.521		27.8 (0.999)
		2	-0.017		
		3	0.174	0.174	
		4	-0.062	-0.057	
		5	0.198	0.204	
		6	-0.014		
		H_3	0.051		
	Ge	1	0.821		Q^{CH}=22.1(0.999) Q^{CH_3}=23.40
		2	-0.023		
		3	0.040	0.040	
		4	-0.018	0.020	
		5	0.038	0.038	
		6	-0.001		
		H_3	0.004		

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[a] The Q values are determined to fit the McConnell relation by the least-squares method. Value r means correlation coefficient.

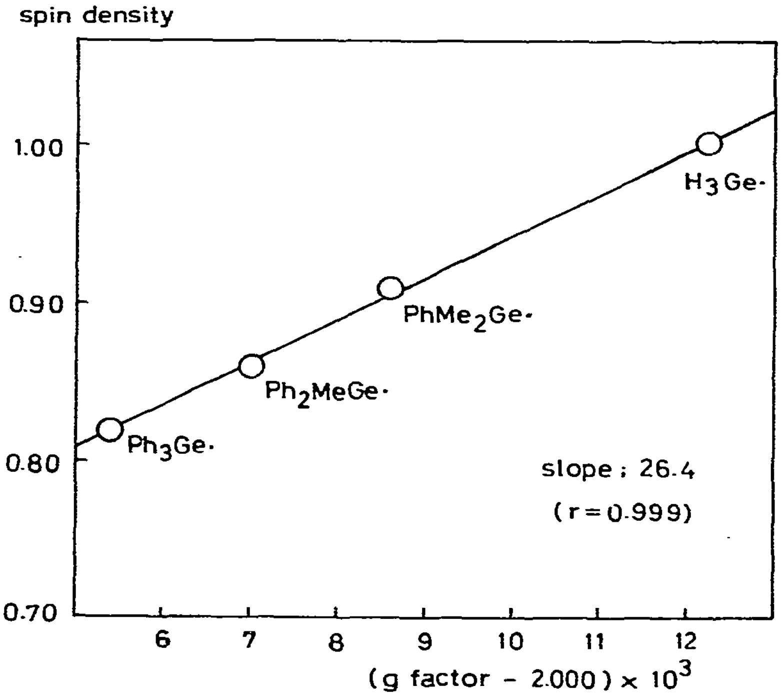


Figure 4. Plot of spin densities and g factors in alkylgermyl radicals.

(5.36 G for both radicals) fails to reflect the change in unpaired π spin density on germanium. Moreover, the g factor increased substantially on going from $PhMe_2Ge\cdot$ to $Me_3Ge\cdot$ (a_{CH_3} = 5.31 G), yet the β-CH_3 h.f.c.c. decreased. Apparently the unpaired spin density on germanium alone is insufficient to account for the change of g factors.

A second factor affecting the magnitude of the g values for this series of radicals is the geometry of the radical center. Gordy et al. established that the $H_3Ge\cdot$ radical is pyramidal with an isotropic g factor of 2.0123 [4b]. We have also shown that a chiral germyl radical produced from an optically active hydrogermane undergoes the chlorine-abstraction reaction with retention of the configuration [26]. Therefore it is reasonable to expect germyl radicals to be pyramidal to some degree. The structure of phenyl-substituted germyl radicals may tend more toward planarity than that of alkyl germyl radicals, especially of $Me_3Ge\cdot$. This would explain the small g values and the large α-CH_3 h.f.c.c. observed for $Ph_2MeGe\cdot$ and $PhMe_2Ge\cdot$.

Tri-p-tolylgermyl and trimesitylgermyl radicals

From the linear relationship between g factors and spin densities, the spin density on the germanium atom can be estimated experimentally from the g factor of the radical. We show two additional examples.

Figures 5 and 6 show the esr spectra of the tri-p-tolylgermyl and trimesitylgermyl radicals. Coupling constants were determined as listed in Table 1 and the experimental spectra were satisfactorily reproduced by computer simulation. In the

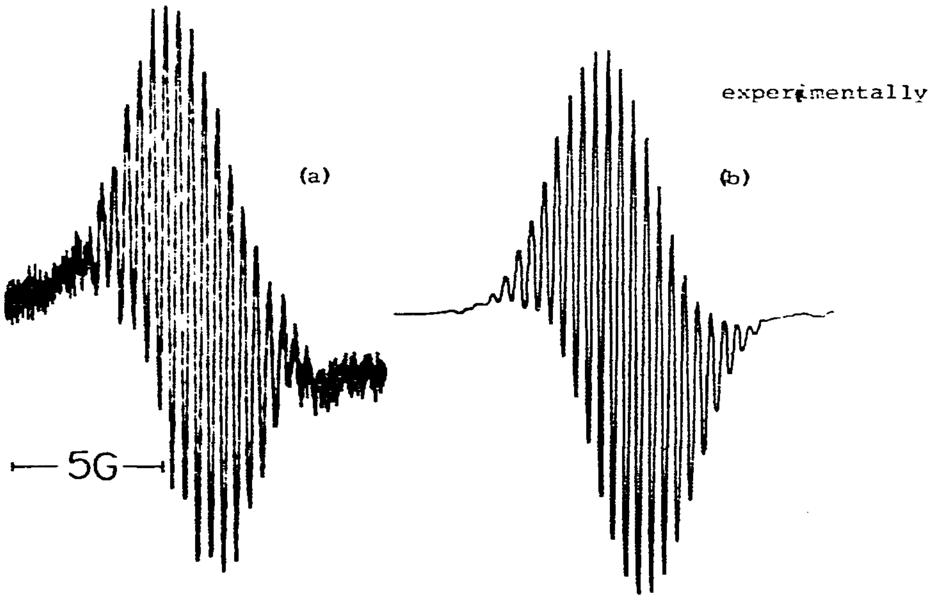


Figure 5. Esr spectra of tris(p-tolyl)germyl radical: (a) experimental: (b) computer simulated.

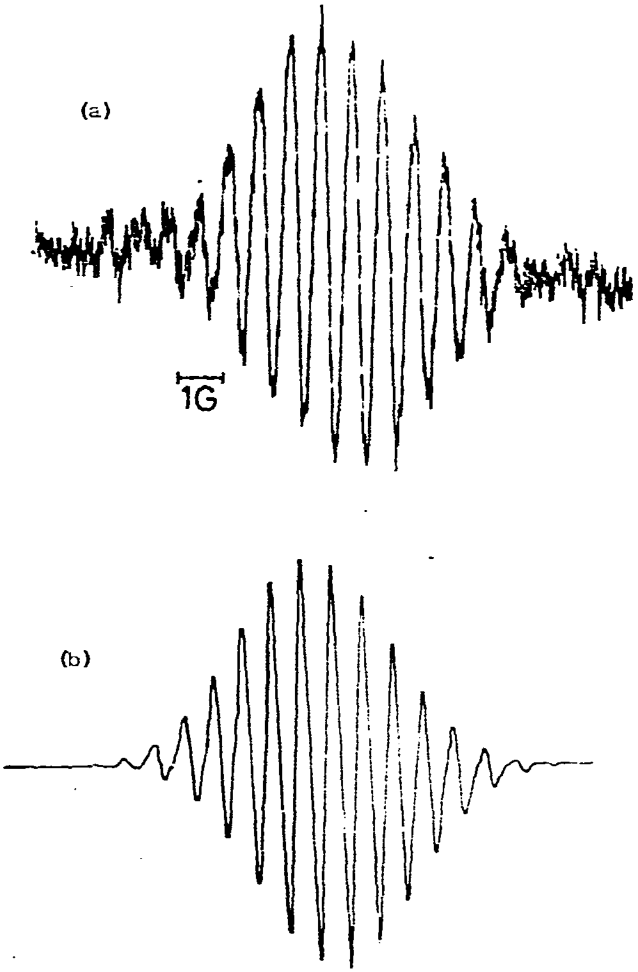


Figure 6. Esr spectra of tris(mesityl)germyl radical:
(a) experimental; (b) computer simulated.

esr spectrum of the trimesitylgermyl radical, h.f.c.c. of the meta hydrogen was not observed and the linewidth (0.38 G) was slightly larger than that of the triphenylgermyl radical (0.25 G). Therefore, h.f.c.c. of the meta hydrogen should be less than 0.06 G.

The g factor of the tri-p-tolylgermyl radical is 2.0055. Then the spin density on the germanium of the tri-p-tolylgermyl radical is estimated to be 0.821 from the relationship shown in the Figure 4. On the other hand, the spin populations of the tri-p-tolylgermyl radical were calculated as listed in Table 2 by using the same parameters as those for other phenyl-substituted radicals. The spin density on the germanium atom of the tri-p-tolylgermyl radical obtained by the McLachlan approximation is 0.821 and agrees excellently with that estimated from the linear relationship.

Similarly, bu using the relationship between the spin density and g value, the spin density on the germanium atom of the trimesitylgermyl radical is estimated to be 0.851. However, the spin density on the germanium atom of the trimesitylgermyl radical is calculated to be 0.818 by the McLachlan approximation using the same parameters. The discrepancy in the spin density on the germanium atom estimated by these two methods is ascribable to the fact that the phenyl rings of the radical are twisted with respect to each other. That is, the spin delocalization through conjugation of the p-orbitals between the germanium and phenyl ring is disrupted by these deviations from coplanarity. The degree of this deviation may be estimated by calculating the spin densities as a function of the angle θ by using McLachlan's method, where θ is the angle with respect to the reference plane defined by the three carbon atoms bonded to the central germanium atom.

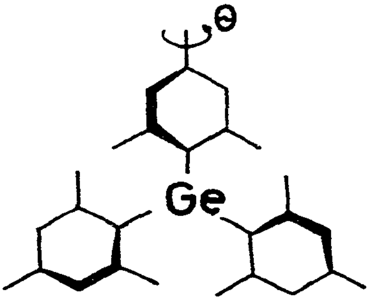
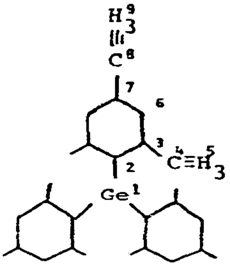


TABLE 3 SPIN POPULATION OF TRIMESITYLGERMYL RADICAL

Radical	Position	calcd. (McLachlan)			|obs.|
		$\theta = 0°$ $(0.45\beta_o)^b$	$30°$ $(0.39\beta_o)^b$	$60°$ $(0.23\beta_o)^b$	
	1	0.81816	0.86588	0.95596	
	2	-0.02525	-0.02108	-0.00878	
	3	0.03786	0.02965	0.01124	0.02991
	4	-0.00115	-0.00098	-0.00046	
	5	0.00357	0.00275	0.00100	
	6	-0.01724	-0.01438	-0.00641	0
	7	0.03735	0.02956	0.01584	0.02991
$Q^{CH_3} = 23.40^a$	8	-0.00115	-0.00098	-0.00047	
	9	0.00358	0.00280	0.00109	

[a] Q^{CH_3} value employed here is that of the freely rotating methyl protons of the tri-p-tolylgermyl radical.

[b] $\beta_{Ge-C} = 0.45\beta_o \cos\theta$.

With θ=30° ($\beta_{Ge-C}=0.39\beta_o$), the h.f.c.c. of p-methyl protons (or spin density at position 6), which should not be affected by steric effects, is in good agreement with the experimental value (Table 3). Therefore, the result shows that the phenyl ring of the trimesitylgermyl radical is twisted about 30°. With this distorted conformation, the spin density of the germanium atom of the trimesitylgermyl radical was recalculated, using McLachlan's method, to be 0.866. This value is in good agreement with that (0.851) estimated from the g value by using the linear relationship.

Experimental

Esr measurements

A solution of di-*tert*-butyl peroxide (DTBP) in the appropriate organogermane was irradiated in sealed quartz tube in the cavity of a Varian E-12 spectrometer with a 500W super-high-pressure mercury lamp. The light was focused with a quartz lens. The solution was cooled with a stream of cold nitrogen gas which was passed through liquid nitrogen by use of a Varian variable-temperature accessory. The field sweep of the spectrometer was calibrated with an aqueous solution of Fremy's salt (a_N=13.07 G). The g facors were determined by reference to that of the anthracene cation radical (g=2.002565) using a dual cavity. Errors in the determination of coupling constants and g factors are estimated to be 0.005 G and 0.0001, respectively.

Materials

Di-*tert*-butyl peroxide (DTBP), cumene, and 1,1-diphenylethane was obtained commercially and were distilled at reduced pressure prior to use. Tetraphenylgermane, m.p. 135°C (lit.[28], 138.5°C), and triphenylmethylgermane, m.p. 71.0-71.5°C (lit.[29], 66-67°C), were prepared according to the literature.

Preparation of hydrogermanes

Triphenylgermane, m.p. 39.5°C (lit.[30], 41.0-41.5°C), diphenylmethylgermane, b.p. 105°C/6mmHg (lit.[31], 90°C/mmHg), phenyldimethylgermane, b.p. 90°C/10mmHg (lit.[32], 110-112°C/24 mmHg), and tri-p-tolylgermane, m.p. 124-125°C (lit.[33], 128-9°C), were prepared by known procedures. Satisfactory elemental analyses and spectral data were obtained for all the compounds.

Preparation of trimesitylchlorogermane

bromide and 5.0g (0.72mol) of dispersed lithium in 200ml of ether. The ether solution of mesityllithium was added to 21.4g (0.1mol) of tetrachlorogermane in 200ml of ether. The reaction mixture was refluxed for 14h. Ether was distilled away as completely as possible and 100ml of xylene was added. The mixture was stirred further at reflux for 12h. The resulting lithium salts were filtered from the mixture. After the solvent was removed, recrystallization from dry ethanol gave 14.9g (0.032mol, 32.0% yield) of trimesitylchlorogermane, m.p. 170-171°C; nmr (δ in CS_2) 2.16(6H, s, o-CH_3), 2.22(3H, s, p-CH_3), 6.67(2H, s, aromatic). Anal. Calcd. for $C_{27}H_{33}GeCl$: C, 69.65, H, 7.27%. Found: C, 70.00%; H, 7.14%.

<u>Preparation of trimesitylgermane</u>

A mixture of 14.9g (0.032mol) of trimesitylchlorogermane and 4.0g (0.1mol) of lithium aluminum hydride in 100ml of ether was stirred for 3h. After hydrolysis with water, the organic layer was dried over calcium chloride and stripped to leave 12.5g of (0.023mol, 73.5% yield) of trimesitylgermane, m.p. 186-187°C; ir(cm^{-1}, in KBr) 2000 (ν GeH), nmr (δ in CS_2) 2.04 (18H, s, o-CH_3), 2.17(9H, s, p-CH_3), 5.81(1H, s, GeH), 6.74(6H, s, aromatic). Anal. Calcd. for $C_{27}H_{34}Ge$: C, 75.21; H, 7.95%. Found: C, 74.94; H, 8.05%.

Acknowledgment

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