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EVIDENCE FOR PHENYL BRIDGING IN BENZYLDIMETHYLGERMYL RADICALS BY ELECTRON SPIN RESONANCE

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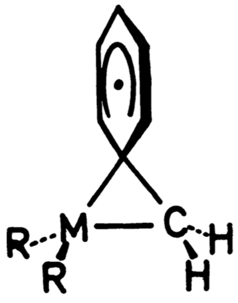
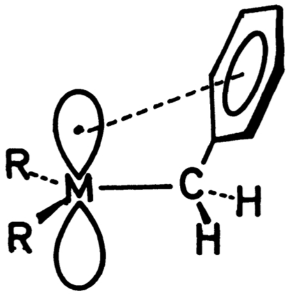
Benzyldimethylgermyl radicals were observed by ESR for the first time in solution at low temperatures. The ESR parameters indicated partial bridging of the phenyl group to the germanium radical center in a preferred conformation.

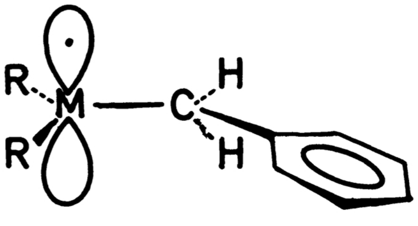
Although radical 1,2-migration of a phenyl group from group 4B metal to carbon has been postulated to pass through an intermediate such as I,1) there has been no ESR evidence for phenyl bridging in β-phenyl-substituted group 4B metal centered radicals.1c) Kochi *et al.* have recently revealed that β-phenethyl radicals exist in the conformation III (M=C) rather than I or in the assymmetrically bridged structure II.2) During the course of a study on organogermyl radicals by ESR,3,4) we have found the first definitive evidence for partial phenyl bridging in benzyldimethylgermyl radicals such as II (M=Ge), while the corresponding silyl radicals have not been observed by ESR in spite of repeated experiments.5)



I

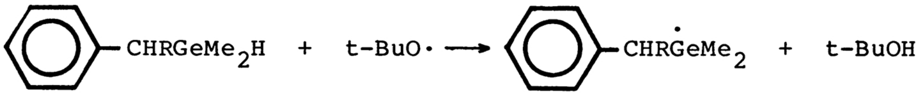


II



III

Irradiation of a mixture of benzyldimethylgermane(1a) and di-tert-butyl peroxide in cyclopropane as a solvent in an ESR cavity gave the corresponding benzyldimethylgermyl radical(2a) at low temperatures(eq. 1). The ESR spectra of 2a at various temperatures are shown in Figure 1.



(1)

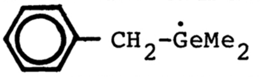
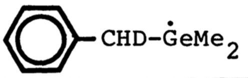
1a; R=H, 1b; R=D   2a; R=H, 2b; R=D

The structure of 2a was confirmed by the following analysis of the ESR spectrum. The ESR spectra of 2a were found to consist of a septet due to 6 methyl protons which splits further into a triplet due to the 2 benzyl protons. Although the outer-most lines of the septet are lost in the noise, the spectral pattern was reasonably reproduced by computer simulation. The large g factor is also characteristic for germanium centered radicals.3) The benzyl proton hyperfine splitting constant(hfsc) was ensured by the ESR spectrum of the benzyl-d_1-dimethylgermyl radical(2b) whose ESR parameters were found to be the same as derived from 1a within an experimental error with an exception that the splitting due to the benzyl proton was a doublet. The g factor and hfsc's of these benzyldimethylgermyl radicals at various temperatures are summarized in Table 1.

As shown in Table 1 and Figure 2, the hfsc's of the benzyl protons were unusually small and showed marked temperature dependence, while the methyl proton hfsc's were almost constant in the temperature range investigated. Thus, the hfsc's of the benzyl protons decrease with decreasing temperature without selective line broadening. The temperature-dependent behavior of the benzyl proton hfsc's is only consistent with the view that in the most stable conformation of this radical the phenyl group essentially eclipses the p orbital on the germyl radical, while the methyl groups are rotating freely in this temperature range.

The benzyl proton hfsc's, however, are too small in this temperature range to be accounted for by any rotational conformations about the germanium-carbon bond. If the benzyl proton hfsc's are subject to the ordinary "$\cos^2\theta$ rule" ($a^H_\beta = B\cos^2\theta$),6) the lower limit of the benzyl proton hfsc at the eclipsed conformation of the β-phenyl group ($\theta=30°$) can be evaluated as 2.6G, since B is taken as 10.4G from the $a^H_{CH_3}$ of the same radicals, where $\langle\cos^2\theta\rangle=1/2$. The observed benzyl proton hfsc's are found to be lower than 2.6G even at higher temperatures and reach to unusually

Table 1. The g factors and Hyperfine Splitting Constants of Benzyldimethylgermyl Radicals

Temp., °C	 $CH_2\text{-}\dot{G}eMe_2$			 $CHD\text{-}\dot{G}eMe_2$	
	g factor	a(CH_3), G	a(CH_2), G	a(CH_3), G	a(CHD), G
0		5.11	2.56	5.3	2.6
-20	2.0088	5.08	2.56	5.3	2.6
-40		5.15	2.00	5.2	2.1
-60	2.0088	5.13	1.76	5.2	1.6
-80		5.18	1.40	5.2	1.3
-100		5.20	—	5.1	1.0

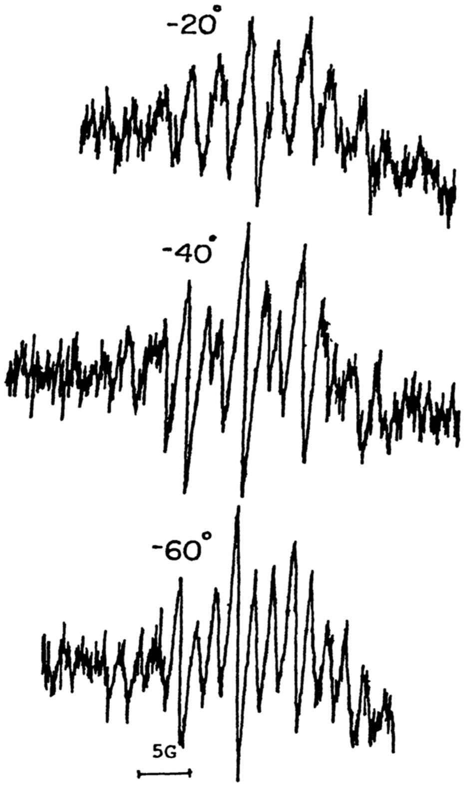


Figure 1. ESR spectra of the benzyldimethylgermyl radical at -20°, -40°, and -60°.

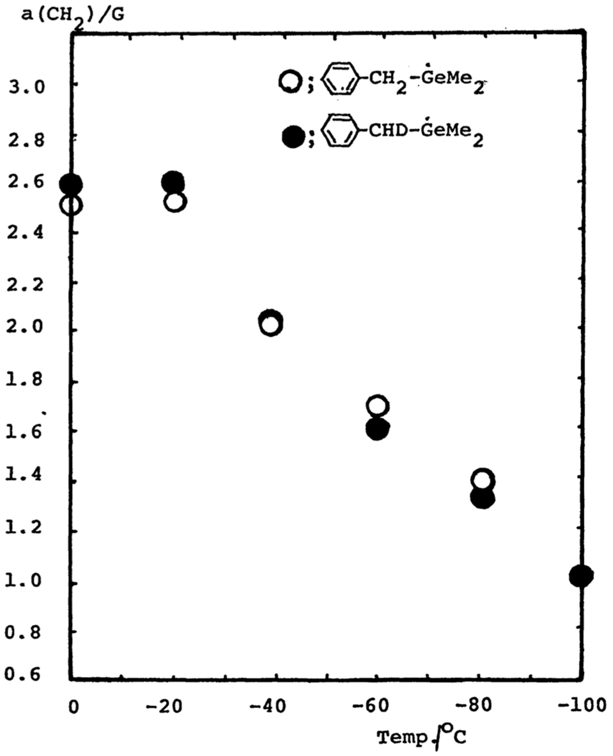


Figure 2. Temperature dependence of the methylene protons in benzyldimethylgermyl radicals.

small value of 1.0 G at -100°C. The anomaly can be resolved if the radical is distorted at the carbon so that the two equivalent protons are displaced toward the nodal plane as shown in II. Such a distortion could result from the interaction between the p orbitals of the phenyl ring and a p orbital on the germyl radical. A similar distortion effect has been observed for the β-chloroalkyl radicals.7,8)

We have already shown that the g values of germyl radicals are proportional to the spin density at the germanium. In this connection, it is interesting to note that the benzyldimethylgermyl radical has an isotropic g factor of 2.0088 which is far smaller than that of the trimethylgermyl radical (g=2.0103). The significant decrease of the g value may be another indication of phenyl bridging which causes partial delocalization of the unpaired electron to the phenyl ring.

References and Notes

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