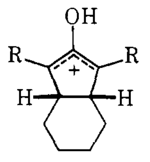
nism consisting of an initial photochemical process to cause the β,β'-bonding and subsequent rapid thermal reaction of the reactive intermediates is in accord with the experimental findings. The first photochemical disrotatory cyclization of the nine-membered cis,cis dienone **1H** leads to the bicyclic cation **13** having a cis ring fusion, whereas the 12-membered cis,trans dienone **7H** gives rise to the trans-fused bicyclic intermediate **14.** These electrocyclizations are symmetry allowed, and an analogous mechanism has been advanced for the case of the six-membered dienones (eq 1).[1] Subsequent thermal suprafacial [1,4] hydride shifts **13** → **2H** and **14** → **8H**, regardless of the forbiddenness of the processes,[6] conclude the overall photoinduced rearrangements.[7] Cationic [1,4] sigmatropic rearrangements have been known to proceed only with inversion at the migrating center.[8] Although a $[1_s,4_s]$ shift within a cationic species has been predicted to occur in certain cases,[9] no experimental evidence relevant to this prediction has been available. An explanation for the observed "symmetry-forbidden" pathway may be provided by the fact that the process involves migration of hydride. The symmetrical, low-lying (13.6 eV) 1s orbital can interact effectively with the second highest occupied molecular orbital of the 1,3-diene unit (butadiene ψ_1 11.34 eV), thereby strongly stabilizing the transition states of type **15.**[9] The smooth intramolecular change evading the possible intermolecular pathway (deprotonation from **13** or **14** followed by enol–keto tautomerization) would imply the transformation to be *energetically* concerted.[10] Furthermore, the present sigmatropic shifts would be facilitated by considerable thermodynamic driving force; an oxygen atom present in **13** or **14** does not stabilize, or even destabilizes, the cationic system because the heteroatom is located at the central carbon of the allylic moiety,[11] whereas the product **2H** or **8H** which can be represented by an oxonium ion–terminally hydroxylated allyl cation resonance hybrid is a very stable compound.



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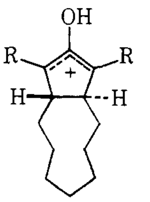

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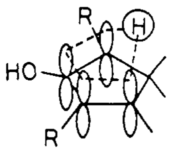

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The other type of photorearrangements **1H** → **3H** and **7H** → **9H** is considered to occur by a $[_\sigma 2_s + {}_\pi 2_s]$ mechanism; intramolecular addition of the γ-carbon–hydrogen bond (in the case of **7H,** that adjacent to the *cis*-CH═CH bond) across the diagonally situated carbon–carbon double bond leads to the bicyclic cyclopentenone products. The possible intermediacy of the hydroxyallyl cations in these reactions is highly unlikely in view of the fact that the species **13** (R = H) generated by reaction of H_2SO_4 and 2,8-*cis,trans*-cyclononadienone[12] (0°, in the dark) gave only **2H.**

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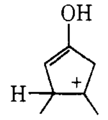

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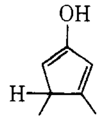

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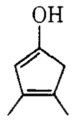

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An Electron Spin Resonance Study of Alkyl- and Aryl-Substituted Germyl Radicals[1]

Sir:

Although extensive studies of carbon-centered free radicals have been made by electron spin resonance, there have been relatively few reports on free radicals centered on group 4B elements other than carbon.[2] Particularly on germyl radicals, no report except $H_3Ge\cdot$,[3] $Cl_3Ge\cdot$,[4] and $Me_3Ge\cdot$[5] radicals has appeared. The present report describes information gained from electron spin resonance about several phenyl- and alkyl-substituted germyl radicals. So far as we are aware, this work also represents the first observation on the delocalization of an unpaired electron into a phenyl ring from the heavy group 4B atom-centered radicals. Because of the known stability of the triphenylmethyl radicals, examination of electron spin resonance spectra of such phenyl-substituted group 4B radicals is of great interest.[6]

The organogermyl radicals were generated by abstraction of hydrogen from the corresponding organogermanes with photochemically generated *tert*-butoxy radicals.[8,9] The

$$R_3GeH + (CH_3)_3CO\cdot \longrightarrow R_3Ge\cdot + (CH_3)_3COH$$

g factors and hyperfine coupling constants (hfcc) for a series of organogermyl radicals are given in Table I. As a typical example, Figure 1 shows the spectrum of the triphenyl-

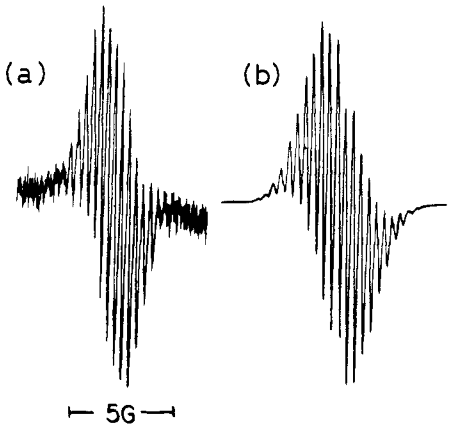
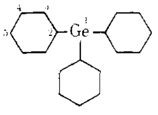
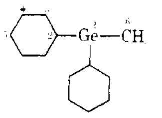
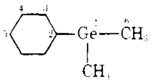


Figure 1. ESR spectra of the triphenylgermyl radical: (a) experimental; (b) computer simulated using Lorentzian line shapes and a line width of 0.28 G.

Table I. The g Factors and Hyperfine Coupling Constants of Organogermyl Radicals

Radical	Temp, °C	g Value	Hyperfine coupling constants (G) β-H	γ-H	o-H	m-H	p-H
$Ph_3Ge\cdot$	−30	2.0054			0.93	0.46	0.93
$Ph_2MeGe\cdot$	−45	2.0070	5.36		0.97	0.49	0.97
$PhMe_2Ge\cdot$	−50	2.0086	5.36		1.20	0.60	1.20
$(CH_3)_3Ge\cdot$	−60	2.0103	5.31				
$(C_2H_5)_3Ge\cdot$	−60	2,0089	4.75	0,56			
$(n\text{-}C_3H_7)_3Ge\cdot$	−60	2.0096	4.92				
$(i\text{-}C_3H_7)_3Ge\cdot$	−50	2.0074	4.34	0,69			
$(n\text{-}C_4H_9)_3Ge\cdot$	−40	2.0095	4.91				

Table II. Spin Populations of Phenyl-Substituted Germyl Radicals

Radical	Position	ρ Calcd	ρ |Obsd|	Q^a (r)
	1	0.81917		23.89
	2	−0.02274		(0.999)
	3	0.03981	0.03898	
	4	−0.01815	0.01928	
	5	0.03969	0.03898	
	1	0.86046		22.85
	2	−0.02317		(0,999)
	3	0.04267	0.04245	
	4	−0.02027	0.02144	
	5	0.04383	0.04245	
	6	−0.00600		
	H_3	0.01462		
	1	0.90887		24.89
	2	−0.02261		(0,999)
	3	0.04690	0.04821	
	4	−0.02325	0.02411	
	5	0.05048	0.04821	
	6	−0.00695		
	H_3	0.01495		

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

germyl radical that consists of 25 lines arising from the circumstance in which the magnitude of the coupling constant of ortho protons is the same with that of para protons (0.93 G) and twice as large as that of meta protons (0.46 G). All of the experimental spectra were satisfactorily reproduced by computer simulation using the hfcc listed in Table I.

Judging from these data, π-spin populations of phenyl-substituted germyl radicals are smaller than those of the corresponding carbinyl radicals, in agreement with the expected small 4p–2p conjugation between germanium and carbon. In an attempt to confirm this result, Hückel molecular orbital calculations with the McLachlan approximation[10] have been performed for phenyl-substituted germyl as well as for carbinyl radicals, and the calculated spin densities with a consistent set of parameters[11] agree excellently with the experimental data as shown partly in Table II.[13] In the triphenylgermyl radical, 82% of the spin is localized at germanium, whereas in the corresponding triphenylmethyl radical the spin density of the central carbon is only 42%.[10b] The resonance integral, $\beta_{Ge\text{-}C}$, was estimated to be $0.45\beta_0$.

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).[14] The g factors of isotropic germyl radicals may be given as the following equation, where g_e is the g factor of

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

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 ignored 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 $PhMe_2Ge\cdot$. The g factors of trialkylgermyl radicals also increased linearly with increasing β-hydrogen hfcc. By the hyperconjugation model the β-hydrogen hfcc can be shown to be proportional to the spin density on the carbon radical center.[15] A similar model for germyl radicals predicts that g factors of alkylgermyl radicals being proportional to the spin density at germanium, as discussed above, can be related to the β-hydrogen hfcc values.[16]

However, there are some discrepancies in this interpretation. The hfcc of methyl protons in $Ph_2MeGe\cdot$ and $PhMe_2Ge\cdot$ (5.36 G for both radicals) fails to reflect the change in unpaired π spin density on germanium. Moreover, the g factor increased substantially in going from $PhMe_2Ge\cdot$ to $Me_3Ge\cdot$ yet the β-CH_3 hfcc decreased. Apparently the unpaired spin density on germanium alone is insufficient to account 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.[18] Gordy et al. established that the $H_3Ge\cdot$ radical is pyramidal with an isotropic g factor of 2.0123.[3b] 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.[19] Therefore it is reasonable to expect germyl radicals to be pyramidal to some degree. The structure of phenyl substituted germyl radicals may be more planar than that of alkyl germyl radicals, especially of $Me_3Ge\cdot$. This would explain the small g values and the large α-CH_3 hfcc observed for $Ph_2MeGe\cdot$ and $PhMe_2Ge\cdot$.

Acknowledgment. We thank Mitsubishi Metal Corporation for a gift of germanium oxide.

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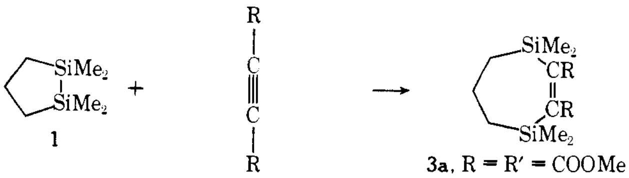
Novel [$\sigma + \pi$] Reactions of Hexaorganodisilanes with Acetylenes Catalyzed by Palladium Complexes[1]

Sir:

Recently Traven and West[2] and we[3] reported the donor properties of the silicon–silicon σ bond as evidenced by charge-transfer complexation between organopolysilanes and tetracyanoethylene. More recently, we have described that the level of the highest occupied molecular orbital of 1,2-disilacycloalkanes is raised with decreasing ring size, and, as a result, the donor property of the silicon–silicon bond is enhanced, for example, in1,1,2,2-tetramethyl-1,2-disilacyclopentane (**1**).[4] In this context, **1** is a convenient compound for an investigation of reactions in which the silicon–silicon bond may act as a donor. We report here a novel cycloaddition reaction of organodisilanes with some unsaturated compounds such as acetylenes[5] catalyzed by palladium complexes. The reaction afforded mainly *cis*-1,2-disilylethylenes and hence the mode of the reaction is formally analyzed as a thermally forbidden [$_\sigma 2_s + _\pi 2_s$] process.[6] This type of reaction for the carbon–carbon bond can be seen only for a highly strained molecule such as bicyclo[2.1.0]pentane,[7] but we are not aware of any precedented example for the silicon–silicon bond.

When a solution of **1** (1 mmol), dimethyl acetylenedicarboxylate (**2a**) (1 mmol), and bis(triphenylphosphine)palladium dichloride (0.01 mmol) in benzene (10 ml) was heated at reflux for 3 hr under a nitrogen atmosphere, crystalline dimethyl 1,1,4,4-tetramethyl-1,4-disilacyclohept-2-ene-2,3-dicarboxylate (**3a**) was obtained in 83.4% yield.[8,9]

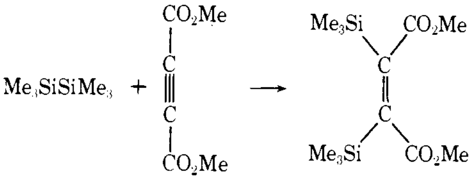


2a, R = R′ = COOMe
b, R = Ph; R′ = H
c, R = R′ = H

3a, R = R′ = COOMe
b, R = Ph; R′ = H
c, R = R′ = H

The reaction of **1** with phenylacetylene (**2b**) under similar conditions (reflux for 9.5 hr) gave the corresponding addition compound, **3b**, in 84.8% yield.[10] Unsubstituted acetylene (**2c**) also reacted with **1**, when **2c** was bubbled into a refluxing benzene solution of **1** in the presence of the catalyst, to give **3c** in 53.3% yield.[11] However, diphenylacetylene and bis(trimethylsilyl)acetylene failed to react with **1** under similar conditions, only the starting materials being recovered.

Hexamethyldisilane (**4**), an example of the unstrained hexaorganodisilane, similarly undergoes the reaction but slowly. Thus, with **2a**, **4** gave dimethyl 1,2-bis(trimethylsilyl)maleate (**5**) in 3.4% yield after refluxing for 23 hr in benzene.[12] The cis stereochemistry of **5** was tentatively assigned by comparison of the uv spectrum with **3a**.



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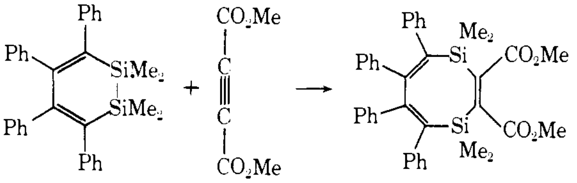
1,1,2,2-Tetramethyl-3,4,5,6-tetraphenyl-1,2-disilane (**6**)[13] gave an interesting new ring system, **7**, by the reaction with **2a** under similar conditions in 72.7% yield.[14]



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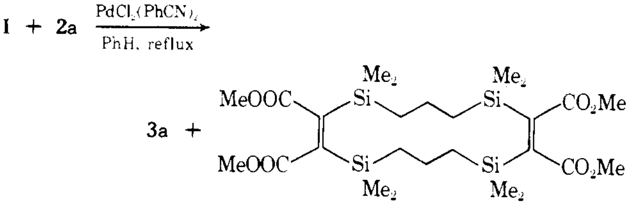
We have examined various metal complexes as a possible catalyst of the reaction and have found that the palladium complexes such as $PdCl_2(PhCN)_2$, $[(\pi\text{-allyl})PdCl]_2$, $PdCl_2(PEt_3)_2$, and $Pd(PPh_3)_4$ are also effective. With these palladium complexes, the reaction proceeds similarly, but the details of the reaction such as the rate of the reaction, yields of the products, and the nature of the by-products are different slightly with respect of each catalyst. Thus, for ex-



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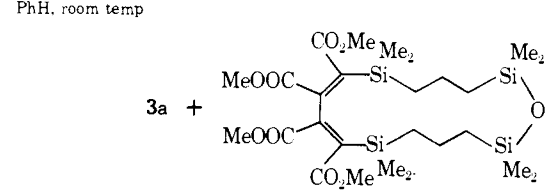

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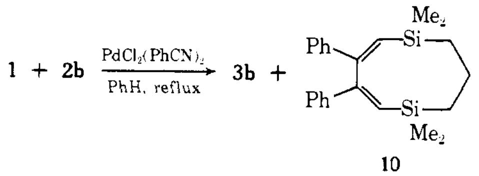

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