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ELECTRON SPIN RESONANCE SPECTRA OF 6-SILYL-SUBSTITUTED CYCLOHEXADIENYL RADICALS PRODUCED BY THE REACTION OF SILYL RADICALS WITH BENZENE[1]

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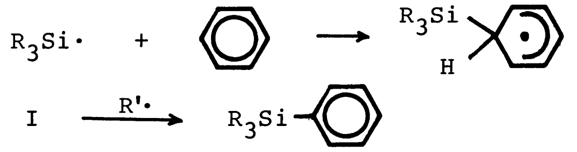
ESR spectra of three 6-silyl-substituted cyclohexadienyl radicals, generated by the reaction of the corresponding silyl radicals with benzene, are recorded and analyzed.

Organosilyl radicals produced by the reaction of the corresponding hydrosilane and di-t-butyl peroxide (DTBP) under thermal or photochemical condition in an aromatic solvent undergo homolytic aromatic silylation.[2,3] Silylcyclohexadienyl radicals (I) have been postulated as an intermediate of the reaction[3] after other homolytic aromatic substitution.[4]

$$R_3SiH + t\text{-}BuO\cdot \longrightarrow R_3Si\cdot + t\text{-}BuOH$$



(I)

On the other hand, a number of such silyl-substituted cyclohexadienyl radicals have been generated by the hydrogen abstraction from cyclohexadiene derivatives.[5] ESR spectra of these radicals revealed interesting features concerning the geometry of radicals.[5a]

It is rather rare that the intermediate cyclohexadienyl radicals can be observed directly by ESR under the reaction condition of the homolytic aromatic substitution because of the low steady state concentration of the radical.[6,7] We now report the direct ESR evidence of the formation of silyl-substituted cyclohexadienyl radicals (I, $R_3Si=Me_3Si$, Et_3Si, and Me_3SiMe_2Si).

A 1:5:1 mixture of trimethylsilane/benzene/DTBP in a sealed quartz tube was photolyzed with a high-pressure 500W mercury-arc lamp in the cavity of a Varian E-12 ESR spectrometer. At -60°, an ESR spectrum shown in Figure 1 was obtained. Although the central part of the spectrum is masked by a large signal presumably due to the trimethylsilyl radical ($g=2.0031$, $a_{\beta\text{-}H}=6.34G$),[8] the outer part gives enough informations to the analysis of the spectrum. Fig. 2 shows the ESR spectrum of a similar radical generated from 3,6-bis(trimethylsilyl)cyclohexa-1,4-diene ($a_{H_{2,4}}=2.15G$, $a_{H_{1,5}}=8.00G$, $a_{H_6}=35.9$ at $-100°C$).[5] These two spectra show almost identical triplets which should be ascribed to couplings with 1- and 2-protons. A doublet (12.45G) can be identified in the spectrum shown in Fig. 1. This should

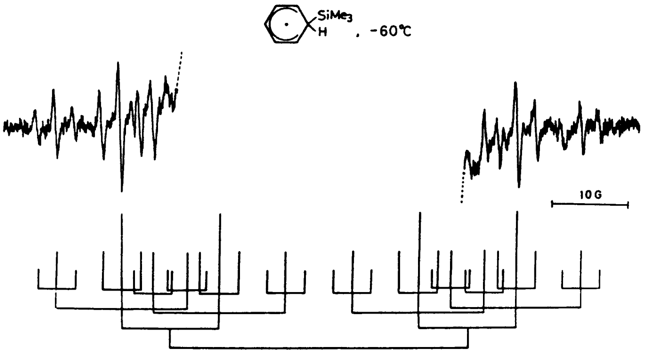


Fig. 1 ESR spectrum of 6-trimethylsilylcyclohexadienyl radical

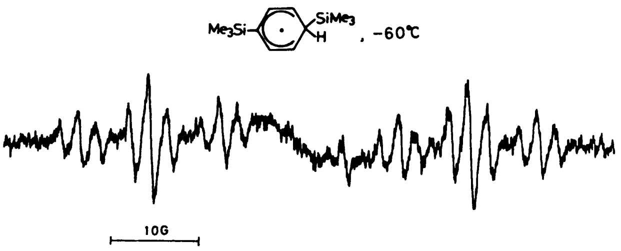
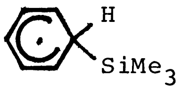
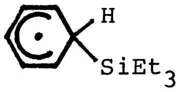
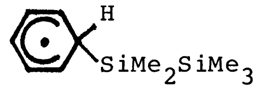


Fig. 2 ESR spectrum of 3,6-bis(trimethylsilyl)cyclohexadienyl radical

Table 1 ESR Parameters of 6-Silyl-Substituted Cyclohexadienyl Radicals

Radical	Temp/°C	Hfcc/G			
		$a_{H_{1,5}}$	$a_{H_{2,4}}$	a_{H_3}	a_{H_6}
	- 60	8.34	2.43	12.45	37.8
	- 60	8.34	2.43	12.43	40.2
	- 60	8.30	2.40	12.28	38.1

be the coupling with the 3-proton. One more doublet due to the 6-proton, which is actually hidden in the central part, can be found as indicated in Fig. 1. Thus, the spectrum in Fig. 1 is deduced to that of the 6-trimethylsilylcyclohexadienyl radical.

ESR spectra of 6-triethylsilyl- and 6-pentamethyldisilanylcyclohexadienyl radicals were similarly obtained and analyzed. ESR parameters of these radicals are tabulated in Table 1.

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