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AN ELECTRON SPIN RESONANCE STUDY OF A BRIDGEHEAD SILYL RADICAL

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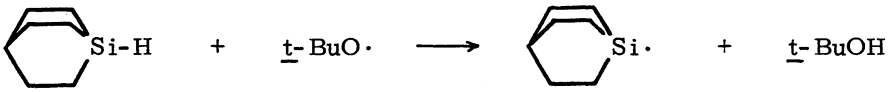
Electron spin resonance spectrum of the bicyclo[2. 2. 2]- 1-silaoctyl radical revealed β-, γ-, and δ-hydrogen coupling constants to be 1. 53, 0. 37, and 0. 37 G, respectively. The small β-hydrogen coupling constant is ascribed to the pyramidal structure of the bridgehead silyl radical site.

Although silyl radicals have been observed by esr spectra in several systems,[1-3] no datum on the bridgehead silyl radical was reported. It seemed interesting to compare the esr data of such bridgehead silyl radicals with those of bridgehead carbinyl radicals such as bicyclo[2. 2. 2]-octyl (I) and 1-adamantyl (II) radicals, which have been reported recently by Krusic, Rettig, and Schleyer,[4] since the stereochemistry at the silyl radical site studied by esr has been a subject of controversy in recent years.[5, 6]

Irradiation of a solution of bicyclo[2. 2. 2] - 1-silaoctane[7] dissolved in di-t-butyl peroxide in a quartz tube in an esr cavity afforded an esr spectrum of the bicyclo[2. 2. 2]- 1-silaoctyl radical (III).



(III)

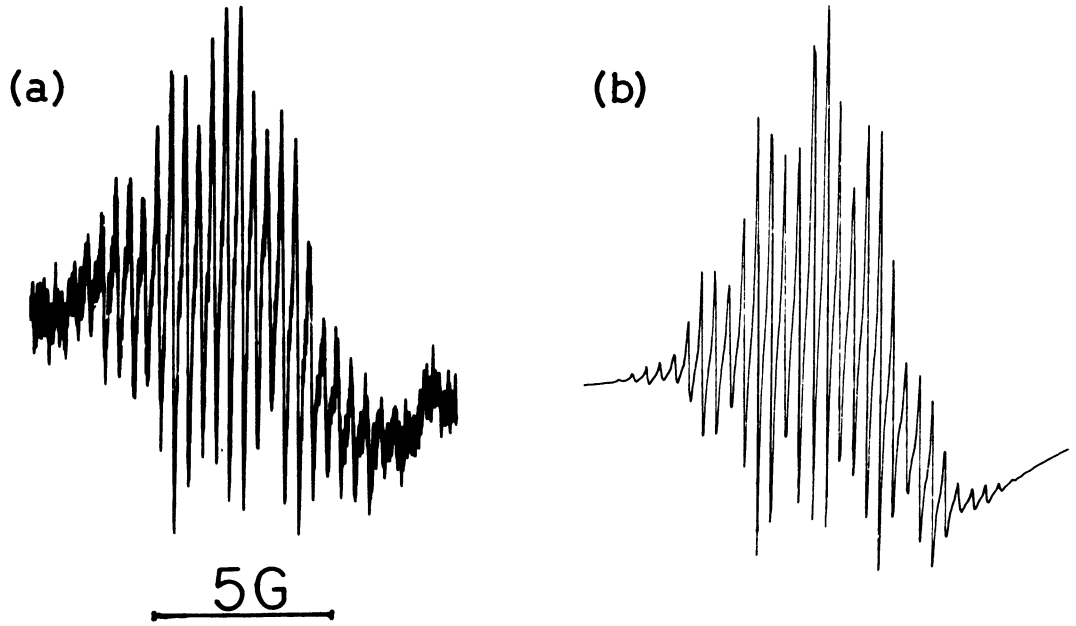
No temperature dependence in the spectra was observed in the temperature range between -100 and -30°. In spite of repeated experiments, (III) was not obtained free from contamination with unidentified radicals, and the ^{29}Si coupling constant was not obtained due to the limited signal to noise ratio. However the spectrum of (III) was clear enough to determine the coupling constant of each hydrogen. These coupling constants assessed by a first-order analysis were tested by computer simulation (Figure 1). Table 1 lists these coupling constants together with those values of other pertinent radicals.

Obviously, the pyramidal structure at the bridgehead silyl radical site resulted in the small β-hydrogen coupling constant (1. 53 G). It is worthwhile to draw attention to the fact that the ratio of $a_{\beta\text{-H}}$(III) to $a_{\beta\text{-H}}$(I) (0. 24) is very close to the corresponding ratio of $a_{\beta\text{-H}}(Me_3Si\cdot)$ to $a_{\beta\text{-H}}(Me_3C\cdot)$ (0. 28). Similarly to (I), large γ- and δ-hydrogen coupling constants of (III) should be noticeable. Structure and stereochemistry of silyl radicals will be discussed in detail in a forthcoming paper.

Table 1. Esr spectral data of some radicals

Radical	Coupling constants (G)			Reference
	β-H	γ-H	δ-H	
(III)	1.53	0.37	0.37	this work
(I)	6.64	0.89	2.69	4
$(CH_3)_3Si\cdot$	6.28			1
$(CH_3)_3C\cdot$	22.72			8
$(CH_3CH_2)_3Si\cdot$	5.69	0.16		1

Figure 1. Esr spectra of the bicyclo[2. 2. 2]-1-silaoctyl radical: (a) experimental; (b) computer simulated using Lorentzian line shapes and a line width of 0.068 G.



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