

dichloro derivatives, which, with lithium diisopropylamide, provided monochloro derivatives of **2** (**18** and **19**). Syntheses of **2** have thus far proceeded only in low yields and difficulties encountered in purification have not allowed us to fully characterize **2**.²⁰ Interestingly, protonation of the **10**-enolate took place at the 9 position, producing an extremely strained compound, **20**, presumably the first example of a methano-bridged cyclodecane in which two trans double bonds are accommodated without benefit of full cyclic conjugation.

Although compound **14** is somewhat air-sensitive, other derivatives such as **11**, **17**, and **18** are stable and can be handled with routine precautions. There is no indication of polymerization even upon heating. Characteristic of the 1,5-methano[10]annulene system is the appearance of ¹H NMR signals due to the methano-protons H11a, 11b at high field as observed for the 1,6-methano series.^{1,20} All the derivatives of **2** thus far obtained exhibit only one set of ¹H and ¹³C NMR signals even at -90 °C. Therefore, if single and double bond switching is proceeding in these molecules, it is not detectable at the present time. The electronic absorption of the present system is shifted toward longer wavelengths compared with that of its 1,6-methano counterpart and extends deeply over the visible region, an observation reminding one of the comparison between azulene and naphthalene. Comments on the crucial problem concerning the transannular electronic interaction demand more information and are being deferred until we have completed an x-ray analysis and photoelectron spectral studies, as well as a theoretical treatment of the system.²¹

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- (21) The authors are grateful to Dr. A. Venot for exploring other approaches prior to this work and the National Research Council of Canada for financial support.

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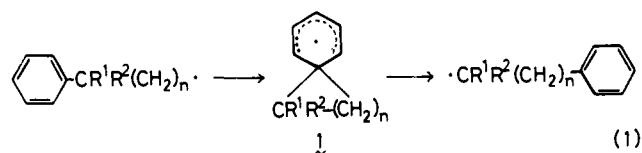
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An Electron Spin Resonance Study on the Spiro Cyclohexadienyl Radicals¹

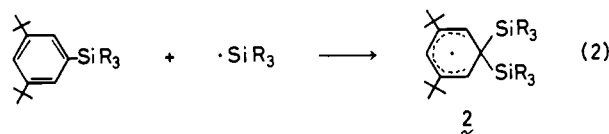
Sir:

The 1,*n*-aryl shift is one of the important homolytic reactions and a spiro (or bridged) cyclohexadienyl radical has been postulated as an intermediate or a model of the transition state.²

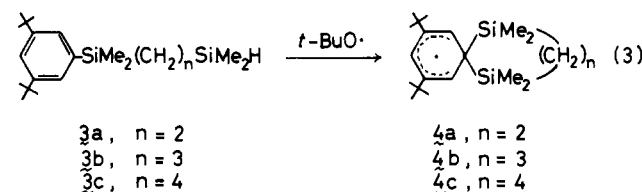


However, no evidence for the spiro radicals such as **1** was obtained by ESR even in the system suitably designed for the homolytic rearrangement,³ although it has been demonstrated chemically that the spiro radical (**1**) can serve as an intermediate.⁴ In the neophyl rearrangement, only ESR spectra of unrearranged and rearranged radicals have been observed before and after the reaction.^{5,6}

Recently, we⁷ have reported ESR spectra of various 2,4-di-*tert*-butyl-6,6-bis(organosilyl)cyclohexadienyl radicals (**2**) arising from the addition of a silyl radical to 3,4-di-*tert*-butylphenylsilanes⁸ and have demonstrated that such a homolytic ipso substitution occurs very efficiently to give the intermediate radicals in high concentration.



In this paper, we report the first ESR spectra of spiro radicals derived from ω -(3,5-di-*tert*-butylphenyl)- α,ω -disilaalkanes. Analysis of the spectra indicates interesting features of the radicals.



Irradiation of a mixture of 1,1,4,4-tetramethyl-4-(3,5-di-*tert*-butylphenyl)-1,4-disilabutane (**3a**)⁹ and di-*tert*-butyl peroxide with a 500W super-high-pressure mercury arc lamp in the cavity of an ESR spectrometer¹⁰ gave a well-resolved spectrum as shown in Figure 1. The spectrum is composed of a doublet (11.83 G) of triplets (7.54 G) with a *g* value of 2.00284 similar to the spectrum of the 2,4-di-*tert*-butyl-6,6-bis(trimethylsilyl)cyclohexadienyl radical (**2**, R = Me),⁷ but each line splits further into small quintets (0.34 G). No spectral

Table I. ESR Data of Spirocyclohexadienyl Radicals

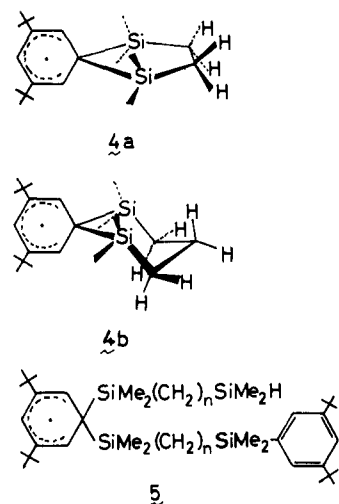
Radical	Temp, °C	Hyperfine Coupling Constants, G				g values
		<i>o</i> -H	<i>p</i> -H	²⁹ Si	H ^a	
3a, <i>n</i> = 2	0	7.54	11.83	35.75	0.34	2.0028 ₄
3b, <i>n</i> = 3	50	7.73	11.96	38.68	0.26	2.0027 ₉
3c, <i>n</i> = 4	-30	7.71	11.91	37.90	<i>b</i>	2.0028 ₁

^a The hyperfine coupling constant of the methylene as quintets, see text. ^b Not observed.

change was observed over a temperature range studied from -50 to 50 °C. Spectral data are summarized in Table I.

Similar irradiation of **3b** (*n* = 3) gave a similar spectrum shown in Figure 2a, but in this case a marked temperature dependence of the spectrum was observed. Thus, the smallest triplets (0.52 G at -50 °C) observed at temperature lower than 0 °C changed to quintets (0.26 G at 50 °C) at higher temperature, as shown in Figure 2b.

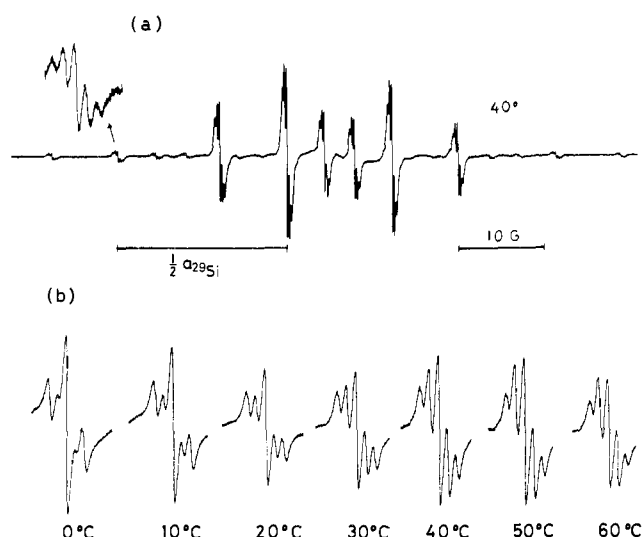
Open bissilyl cyclohexadienyl (**5**) other than the spiro radicals may be formed from **3**. However, spectral data collected in Table I and especially the different temperature-dependent nature between **4a** and **4b**, which should be ascribed to the conformational effect of the spiro radicals, exclude this possibility.



Inspection of molecular models show that the 1,3-disilapentane part of the radical **4a** is quasi-planar, so that four methylene hydrogens are equivalent to give quintets over the temperature range studied, while the 1,3-disilahexane part of **4b** takes a chair form, which inverts rapidly at room temperature, and four hydrogens adjacent to two silicon atoms become indistinguishable in the ESR time scale at an ambient temperature. However, at low temperature, **4b** is frozen to a fixed conformation, two hydrogens of which are only observable as triplets. From a line-shape analysis,¹¹ an activation energy of 4.4 ± 0.5 kcal/mol was obtained for the inversion process of **4b**. This value is similar to the inversion barrier of 1,1-dimethyl-1-silacyclohexane (5.4 kcal/mol) determined by NMR.¹²

A similar ESR spectrum was obtained from **3c** (*n* = 4), which should give a seven-membered ring radical (**4c**). However, the steady-state concentration was rather low in this case. Spectral data are also listed in Table I.

It is remarkable that only the spiro radicals are observed from the reaction of **3**. This means that the spiro radicals are kinetically most stable with the highest steady-state concentration under the reaction condition. Since unrestricted CNDO/2 calculations on the 6-silylcyclohexadienyl radical show the important $\sigma(\text{C-Si})-\pi$ conjugation for stabilization,¹³

Figure 1. ESR spectrum of **4a**.Figure 2. ESR spectra of **3b**: (a) full spectrum at 40 °C; (b) line-shape alteration at various temperatures for $M_1 = 0$ lines.

two C-Si bonds with favorable ring structures and blocking *tert*-butyl groups^{7,8} make **3** relatively long-lived.

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