CHEMISTRY LETTERS, pp. 129-134, 1976. Published by the Chemical Society of Japan

SILYL RADICALS XVI.
AN ELECTRON SPIN RESONANCE STUDY ON THE HOMOLYTIC AROMATIC SILYLATION [1]

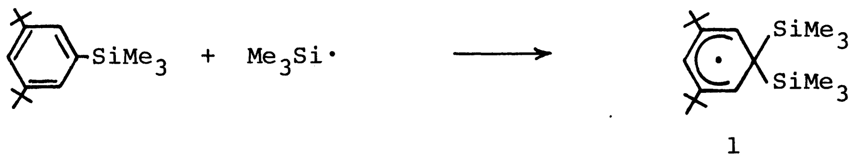
Hideki SAKURAI, Ikuo NOZUE, and Akira HOSOMI
Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980

Seven 2,4-di-*t*-butyl-6,6-bis(organosilyl)cyclohexadienyl and two 2,4-di-*t*-butyl-6-organosilylcyclohexadienyl radicals, the intermediate radicals in homolytic *ipso*-substitution and silylation, respectively, are generated and characterized by esr spectroscopy. Spectral features, especially the large ^{29}Si coupling constants are discussed.

In homolytic aromatic substitution a substituted cyclohexadienyl radical, arising from the addition of a free radical to an aromatic compound, is generally thought to be the key intermediate.[2] We have previously discussed the structure and reactivity of homolytic aromatic silylations in detail, where such silyl-substituted cyclohexadienyl radicals were also postulated as the intermediates.[3] However because of their high reactivity, intermediate cyclohexadienyl radicals have been detected by esr only in solid matrices and no solution esr spectrum was reported except for hydroxycyclohexadienyl radicals produced in aqueous solutions by the flow method.[4,5] We have now generated several silyl substituted cyclohexadienyl radicals in di-*t*-butyl peroxide solution which were fairly stable and hence gave well-resolved intence esr spectra. After we have completed the present study,[6] we received a paper of Ingold et al.[7] who described esr spectra of similar cyclohexadienyl-type radicals generated by the addition of certain carbon, silicon, oxygen, and phosphorous centered radicals to several sterically hindered aromatic compounds for the purpose of generating the persistent cyclohexadienyl-type radicals. However, our attention has been directed to the mechanistic study on the homolytic aromatic silylation and actually all radicals reported in both studies do not overlap each other except for one case.

Irradiation of a mixture of 3,5-di-*t*-butylphenyltrimethylsilane, trimethylsilane, and excess di-*t*-butyl peroxide with a 500W super-high-pressure mercury arc lamp in the cavity of an esr spectrometer[8] at -10°C gave the 2,4-di-*t*-butyl-6,6-bis(trimethylsilyl)cyclohexadienyl radical (**1**).

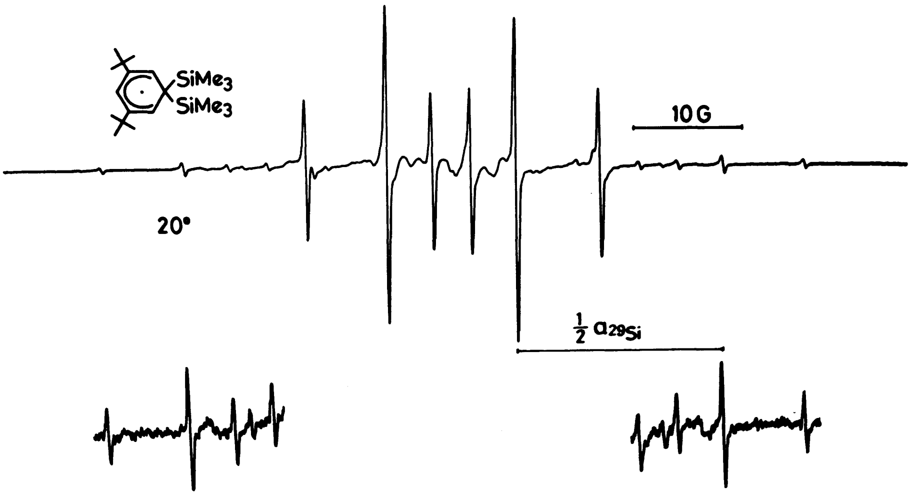
$$Me_3SiH + t\text{-}BuO\cdot \longrightarrow Me_3Si\cdot + t\text{-}BuOH$$



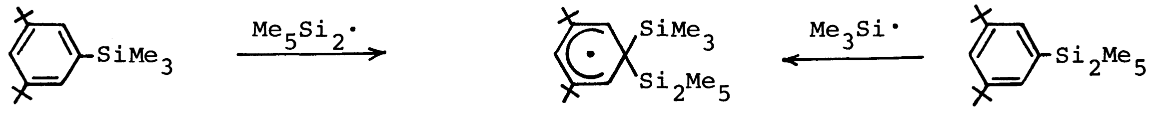
1

The spectrum of **1** (Fig.1) is composed of a doublet (12.06 G) of triplets (7.89G) with a g value of 2.00283 and is so intense that well resolved satelites due to ^{29}Si

Figure 1. Esr spectra of 1. Expanded spectra show the satelites due to ^{29}Si.

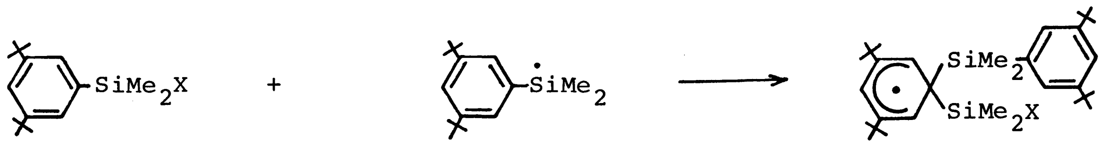


(39.15 G) can also be observed. The esr data are consistent with **1** in which coupling would be expected with one para and two ortho protons on the phenyl ring and one of the two equivalent silicon atoms. Our assignments for the radical **1** may receive further support from the similarity of the coupling constants of the reported cyclohexadienyl radicals (Table 1). Moreover, the radical **2** with two different ^{29}Si coupling constants (Table 1), was obtained by the following two reactions. This fact clearly indicates the intermediate radical **2** in both reactions.



2

These radicals are intermediates in the homolytic <u>ipso</u>-substitution and we have discussed previously the role of such radicals in several reactions.[9] Nelson, Angelotti, and Weyenberg also postulated this sort of radicals as intermediates in the radical-induced redistribution reaction of phenylsilanes at 160°C.[10] A more direct intermediate in such radical-induced redistributions was obtained with 3,5-di-*t*-butylphenyldimethylsilane which gave the radical **3** on photolysis with di-*t*-butyl peroxide.



3a, X=H
b, X=D

The esr spectrum of 3a is similar to that of 1 with additional small doublets (1.30 G) due to Si-H, which disappears in the spectrum of the deuterated radical 3b. In the case of 3a and 3b, two different ^{29}Si satelites can also be recognized as shown in Fig. 2 and 3. Spectral data are also summarized in Table 1.

Figure 2. Esr spectra of 3a. Expanded spectra show two different ^{29}Si couplings.

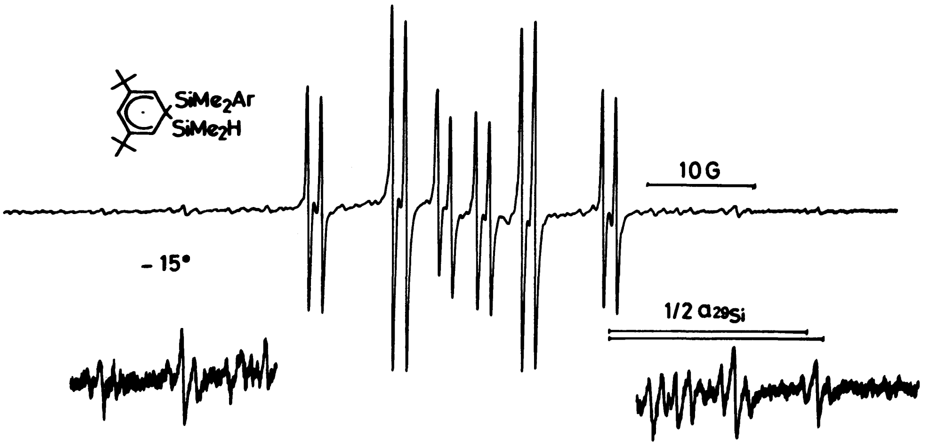


Figure 3. Esr spectra of 3b.

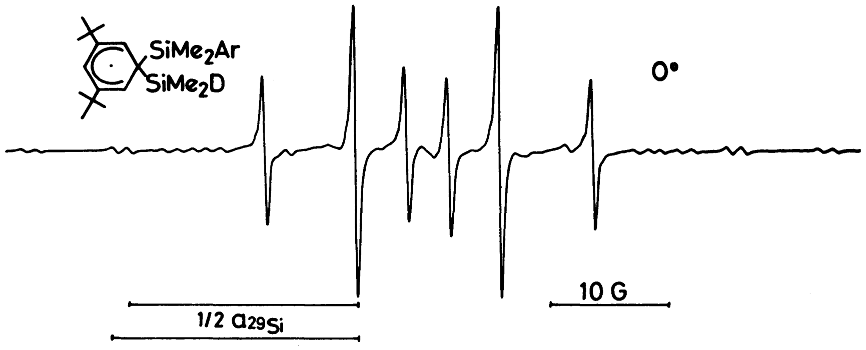
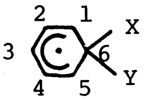
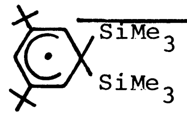
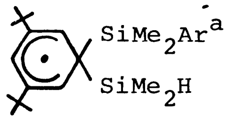
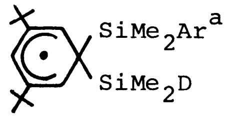
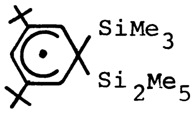
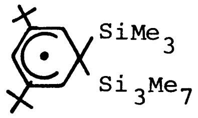
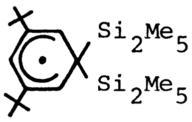
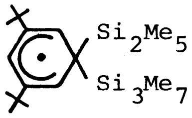
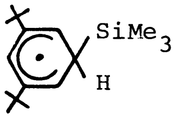
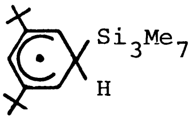
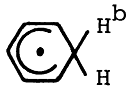
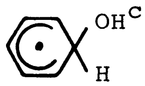


Table 1

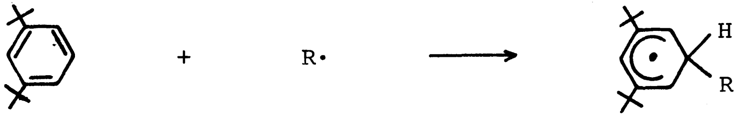
Esr Parameters for Cyclohexadienyl Radicals 

in Solution

Radical	Temp.(°C)	g	Coupling Constants (G)					
			H_1	H_2	H_3	H_6	^{29}Si	other
	- 10	2.0028	7.89		12.06		39.15	
	- 10	2.0028	7.88		12.00		38.83 41.40	1.30 (Si-H)
	0	2.0028	7.86		11.99		38.78 41.23	
	- 20	——[d]	7.80		11.93		37.18 42.98	
	- 60	——[d]	7.79		12.04		——[d]	
	- 40	——[d]	7.74		12.08		——[d]	
	- 50	——[d]	7.23		11.98		——[d]	
	- 30 (24	2.0028 2.0028	8.02 8.06		12.03 12.29	34.15 34.60)[e]	——[d]	
	- 30	2.0028_2	8.00		11.80	35.35	——[d]	
	- 30	2.0025	8.99	2.65	13.04	47.71		
			9.2	2.8	13.4	36.0		

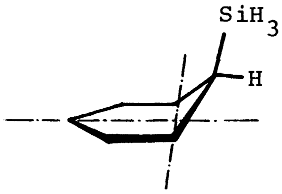
[a] Ar=3,5-di-t-butylphenyl [b] Ref.5 [c] Ref.4a [d] Not determined [e] Ref.7

Two t-butyl groups located in the meta positions undoubtedly contribute to the stability of cyclohexadienyl radicals.[7,11] In this context, we thought that 1,3-di-t-butylbenzene would be a promissing substrate for obtaining persistent intermediate cyclohexadienyl radicals. Advantageously, these cyclohexadienyl radicals have unblocked ortho and para positions where the most of the spin resides.



This expectation has been realized in the related homolytic aromatic silylation. We list spectral data of two such radicals in Table 1. The Table also contains two representative cyclohexadienyl radicals in solution for comparison.

Several interesting features can be seen in the Table 1. Noteworthy is the larger ^{29}Si coupling constants than the corresponding value (37.4 G)[12] reported for $\cdot CH_2CH_2SiEt_3$. This fact indicates an ideal conformation of the cyclohexadienyl radicals for the maximum σ-π conjugation.[13] Actually, unrestricted CNDO/2 calculations on the 6-silylcyclohexadienyl radical show a bent structure (4) for the energy minimum of the radical with maximum σ(C-Si)-π conjugation.[14] Related works are in progress.



(4)

Acknowledgment. We thank Toshiba Silicone Co., Ltd., for a gift of chlorosilanes.

References and footnotes

1) Chemistry of Organosilicon Compounds 87.
2) For a current review, see M. J. Perkins, in "Free Radicals" Vol.2, J. K. Kochi ed., Wiley, New York, N. Y., Chapt. 16 (1973).
3) H. Sakurai and A. Hosomi, J. Amer. Chem. Soc., 93, 1709 (1971).
4) Inter alia,
   (a) W. T. Dixon and R. O. C. Norman, J. Chem. Soc., 4858 (1964);
   (b) C. R. E. Jefcoate and R. O. C. Norman, J. Chem. Soc. (B), 48 (1968);
   (c) T. Shiga, T. Kishimoto, and E. Tomita, J. Phys. Chem., 77, 330 (1973).
5) R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 39, 2147 (1963), prepared the cyclohexadienyl radical in liquid 1,4-cyclohexadiene during continuous electron irradiation. See also, K. Eiben and R. W. Fessenden, J. Phys. Chem., 75, 1186 for radicals in aqueous solution.
6) I. Nozue, A. Hosomi, and H. Sakurai, the 14th Symposium on ESR Spectroscopy, Tokyo, Oct., 1975; Abstracts, p.4.
7) D. Griller, K. Dimroth, T. M. Fyles, and K. U. Ingold, J. Amer. Chem. Soc., 97, 5526 (1975).
8) A Varian Associates E-12 spectrometer was used with a 9.5 GHz microwave bridge.
9) (a) H. Sakurai, I. Nozue, and A. Hosomi, J. Organometal. Chem., 80, 71 (1974);
   (b) H. Sakurai, A. Hosomi, and I. Nozue, the 20th Symposium on Organometallic Chemistry, Kyoto, Oct., 1972; Abstracts, p.29.
10) L. E. Nelson, N. C. Angelotti, and D. R. Weyenberg, J. Amer. Chem. Soc., 85, 2662 (1963).
11) G. D. Mendenhall, D. Griller, and K. U. Ingold, Chem. Brit., 248 (1974).
12) P. J. Krusic and J. K. Kochi, J. Amer. Chem. Soc., 91, 6161 (1969).
13) (a) P. J. Krusic and J. K. Kochi, J. Amer. Chem. Soc., 93, 846 (1971);
   (b) T. Kawamura, P. Meakin, and J. K. Kochi, ibid., 94, 8065
   (c) T. Kawamura and J. K. Kochi, ibid., 94, 649 (1972);
   (d) A. R. Lyons and M. C. R. Symons, J. C. S. Chem. Comm., 1068 (1971);
   (e) M. C. R. Symons, J. Amer. Chem. Soc., 94, 8589 (1972);
   (f) idem, Tetrahedron Lett., 793 (1975);
   (g) D. Griller and K. U. Ingold, J. Amer. Chem. Soc., 95, 6459 (1973);
   (h) idem, ibid., 96, 6715 (1974);
   (i) H. Sakurai, T. Uchida, and M. Kira, J. Organometal. Chem., in press.
14) M. Kira and H. Sakurai, unpublished results.

(Received December 1, 1975)