Anion Radicals of Phenylsilanes[1]

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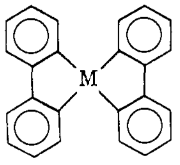
Abstract: The anion radicals of several phenylsilanes containing both hydrogens and methyls attached to silicon have been characterized by electron spin resonance. Many of these anion radicals, especially ones containing silicon–hydrogen bond(s), showed only limited stability and further reduction led to other paramagnetic species. Identification of the anion radicals resulting from further reduction showed that three modes of reaction are possible: (a) para coupling with the formation of 1,4-bis(disilyl)benzene anion radicals and then formation of tetraphenylsilane anion radical; (b) formation of biphenyl anion radical from diphenylsilanes; or (c) reaction with DME to form phenyltrimethylsilane anion radical. Conflicting previous reports for some of these phenylsilane anion radicals were due to the observation of the paramagnetic products of further reduction rather than to the anion radicals of the starting phenylsilanes.

The synthetic importance of silylmetal compounds is reflected by the large number of investigations which have been carried out since their independent discovery by Benkeser[2] and Gilman.[3] These reagents, especially triarylsilylmetal compounds, have been employed extensively in organosilicon syntheses.[4] The intermediate presence of anion radicals in the alkali metal reduction of organosilanes to organosilyl anions has often been implied.[5-8] Recently, anion radicals for a wide variety of organosilanes have been characterized. The greatest share of these silicon-containing anion radicals contains one or more trialkylsilyl groups attached to a single aromatic moiety.[9-14] Interpretation of the hyperfine couplings and the total line widths of some of these anion radicals has led to the conclusion that the free electron interacts with silicon's 3d orbitals.[9,13,14]

Organosilyl anion radicals with more than one aromatic moiety attached to silicon have been reported.[11,15-17] Townsend prepared the anion radical of tetraphenylsilane.[15] The narrowness of the spectrum compared to other aromatic anion radicals and the appearance of an *odd* number of lines led to the conclusion that the electron was delocalized into all rings through silicon. Similarly, Cowell, Urry, and Weissman prepared the anion radical of bis(2,2′-biphenylene)silane (Ia) and compared its total line width to that for the anion radical of its carbon analog, bis(2,2′-biphenylene)methane (Ib).[16] The narrower line width of Ia was used as evidence for the spin density residing in the five-membered silicon-containing rings.



Ia, M = Si; 11.5 G
b, M = C; 21 G

The reductions of diphenyldialkylsilanes,[11,17] triphenylalkylsilanes,[18] and tetraphenylsilane with potassium metal in 1,2-dimethoxyethane (DME) were recently investigated. It was claimed that the anion radicals of the parent organosilanes were observed and that the esr spectra could be interpreted as resulting from the free electron being restricted to one aryl ring. These results are surprising when compared to the results for Ia and to the earlier report of Townsend for the anion radical or tetraphenylsilane.

There have been few reports of anion radicals containing silicon–hydrogen bond(s).[11,12,18,19] In two of these reports, the silicon–hydrogen hyperfine coupling was assigned widely differing values (0.81 G[12] and 6.0 G[11]). The anion radicals of diphenylsilane,[11] triphenylsilane,[18] and 1,2-disilaacenaphthene[19] have been reported but no silicon–hydrogen hyperfine couplings were assigned.

Results and Discussion

We wish to report the preparation and esr characterization of four arylsilane anion radicals which contain silicon–hydrogen bonds ($PhSiH_3\cdot^-$, $PhSiMeH_2\cdot^-$, $PhSiMe_2H\cdot^-$, and p-$Me_2HSiPhSiHMe_2\cdot^-$) and the anion radicals of two phenylmethylsilanes ($Ph_2SiMe_2\cdot^-$ and

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[1] Abstracted from the Ph.D. dissertation of Y.-P. W., Texas A & M University, 1971.

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[3] H. Gilman and T. C. Wu, *ibid.*, 73, 4031 (1951).

[4] C. Eaborn and R. W. Bott, "Organometallic Compounds of the Group IV Elements," Vol. 1, Part 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, pp 180–187.

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[17] A. N. Pravednikov, V. A. Sharpatyo, N. V. Eliseeva, N. V. Zakatova, and V. I. Frants, *Zh. Fiz. Khim.*, 41, 118 (1967).

[18] I. G. Makarov and V. M. Kazakova, *Zh. Strukt. Khim.*, 9, 996 (1968).

[19] I. G. Makarov, V. M. Kazakova, N. G. Tolstikova, and E. A. Chernyshev, *J. Struct. Chem.* (*USSR*), 10, 495 (1969).

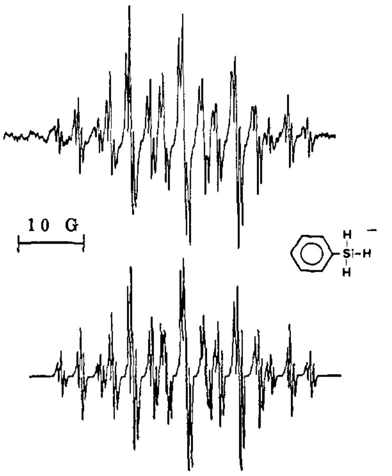

Figure 1. The anion radical of phenylsilane: upper spectrum, experimental; lower spectrum, computer simulated.

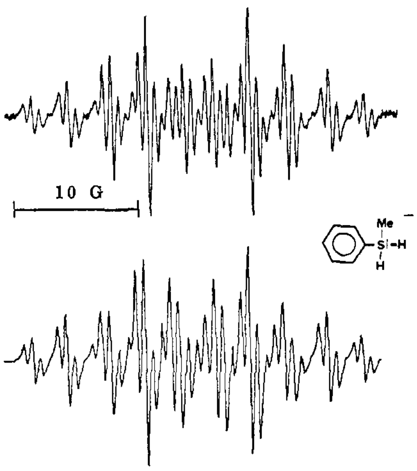

Figure 2. The anion radical of phenylmethylsilane: upper spectrum, experimental; lower spectrum, computer simulated.

$Ph_3SiMe\cdot^-$). The hyperfine couplings of several of these were found to differ markedly from the previously reported values. A better resolved spectrum was obtained for the tetraphenylsilane anion radical than previously reported[15] and it was possible to assign all the hyperfine couplings. The anion radical of phenyltrimethylsilane, which has been previously characterized, was prepared for comparison purposes. The preparation of the anion radicals of diphenylsilane, diphenylmethylsilane, and triphenylsilane was also attempted. However, spectra due to the anion radicals of the original organosilanes were not observed.

The anion radicals were generated at low temperatures electrolytically or by potassium reduction in either THF or DME. In general, the anion radicals were not stable for long periods even at temperatures below −80°. Further reactions were noted through the appearance of new paramagnetic species. By comparing the esr spectra of the anion radicals formed in these subsequent reactions, it is possible to qualitatively follow the stepwise reduction of arylsilanes. The results presented here offer an explanation for the conflicting reports which have appeared in the literature.

A. Anion Radicals of Phenylsilane, Phenylmethylsilane, and Phenyldimethylsilane. Electrolytic reduction of phenylsilane in THF or DME at −76° gave a well-resolved spectrum of the anion radical (Figure 1). This spectrum features a large doublet splitting due to the para hydrogen (8.46 G) and a large quartet splitting due to the hydrogens on silicon (8.04 G). The apparent broadening of the central portion of the spectrum is due to the close values of these two couplings. Smaller couplings are observed for the ortho and meta hydrogens.

Electrolytic or potassium reduction of phenylmethylsilane in DME at −76° gave a green-yellow solution which displayed the esr spectrum shown in Figure 2. The spectrum consists of a large doublet splitting due to the para hydrogen (8.40 G), a triplet due to the hydrogens on silicon (6.33 G), and smaller splittings from the ortho and meta hydrogens. Couplings due to the methyl hydrogens were too small to be resolved.

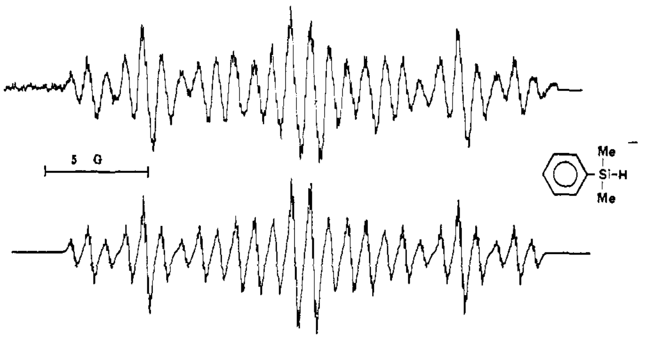

Figure 3. The anion radical of phenyldimethylsilane: upper spectrum, experimental; lower spectrum, computer simulated.

The reduction of phenyldimethylsilane electrolytically or with potassium in THF or DME at −76° gave a yellow solution which displayed the esr spectrum shown in Figure 3. This spectrum consists of a doublet of doublets due to the para hydrogen (8.15 G) and the silicon hydrogen (7.20 G). Smaller couplings due to the ortho, meta, and methyl hydrogens were also resolved.

It is important to stress the key role that the esr spectrum of phenyldimethylsilane anion radical played in the present investigation. In identifying anion radicals with couplings to several different hydrogens, it is essential to assign a specific coupling to each. This becomes particularly important when the anion radicals are subject to the formation of other paramagnetic species as the result of further reaction(s), as was true with the phenylsilanes. The anion radical of phenyldimethylsilane displayed a spectrum in which all of the couplings were sufficiently nonoverlapping that all were easily assigned (Figure 3). This spectrum served as a guide for the size of the various couplings for the other organosilane anion radicals.

The hyperfine coupling constants for these three organosilane anion radicals are collected in Table I along with two previous reports for phenylsilane and phenyldimethylsilane anion radicals. Using the values presented in Table I, the computer-simulated spectra agree well with the experimental spectra. The significance of the size of the silicon–hydrogen coupling with regard to spin density at silicon has been discussed elsewhere.[20] It appears that the previous reports were in error, most probably because these investigators were

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(20) H. Sipe, *Diss. Abstr.*, No. 3706 (1970).

Table I. Anion Radicals of Phenylsilanes Containing Silicon–Hydrogen Bonds

Anion radical	Hyperfine coupling[a] a_{SiH}	a_p	a_o	a_m	a_{CH_3}	Conditions[b]	Ref
$PhSiH_3\cdot^-$	8.04 (4)	8.46 (2)	3.08 (3)	0.52 (3)		e⁻; THF, DME; −76	*c*
$PhSiMeH_2\cdot^-$	6.33 (3)	8.40 (2)	2.76 (3)	0.64 (3)	<0.20 (4)	e⁻; THF, DME; −76 K; DME; −76	*c*
$PhSiMe_2H\cdot^-$	7.20 (2)	8.15 (2)	2.72 (3)	0.86 (3)	0.11 (7)	e⁻, K; THF, DME; −76	*c*
$PhSiH_3\cdot^-$	6.0 (4)	6.0 (2)	1.9 (3)	0.9 (3)		K; THF, DME; −70	*d*
$PhSiMe_2H\cdot^-$	0.81 (2)	8.12 (2)	2.70 (3)	0.97 (3)	0.13 (7)	Na; DME; −80	*e*

[a] Couplings in gauss; figures in parentheses represent multiplicity. [b] Conditions: method of reduction (e⁻ = electrolytic reduction), solvent(s) used, temperature of reduction (°C). [c] This work. [d] Reference 11. [e] Reference 12; the anion radical was formed through further reduction of $PhSiMe_2SiMe_3$.

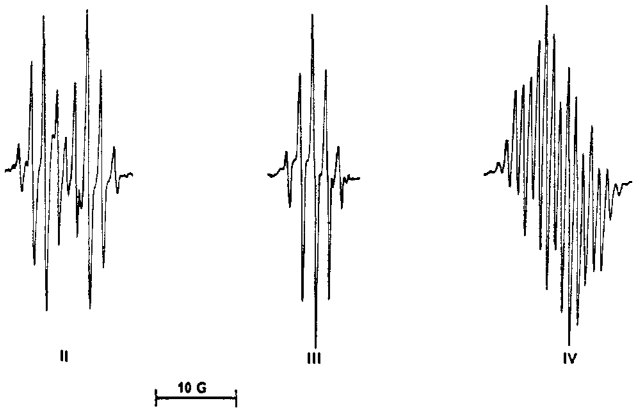


Figure 4. Anion radicals formed in the further reduction of phenylsilane.

observing paramagnetic species resulting from the further reduction of the parent anion radical.[11,12]

Stability, as measured qualitatively by the length of time that the anion radical persisted, among these three anion radicals appeared to increase as methyls replaced hydrogen on silicon. This order is reflected by the conditions under which the anion radicals could be produced (Table I). All three anion radicals were formed when electrolytic reduction was employed. Electrolytic reduction is inherently a milder method compared to metallic reduction. A continuous range of reduction potentials is available and the amount of substrate reduced is probably extremely small. In the present work, the low concentration of anion radicals produced electrolytically effectively eliminated either reaction of the anion radical with unreduced silane or further reduction. In contrast, much less control over the extent of reaction was possible with metallic mirrors. The least stable anion radical, that of phenylsilane, could not be observed with metallic reduction. The most stable, that of phenyldimethylsilane, could be prepared by potassium reduction in THF or DME.

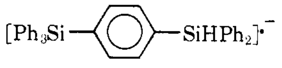
B. Formation of *p*-Bis(disilyl)benzene Anion Radicals. We now wish to describe the several paramagnetic species observed for the metallic reduction of phenylsilanes either after longer reaction time or at higher temperatures. The appearance and identification of these species allow a qualitative picture of the stepwise reduction of phenylsilanes to emerge.

Triphenylsilane. Numerous attempts were made to obtain the esr spectrum of the anion radical of triphenylsilane. Anion radicals were observed but none that could be associated with the expected spectral pattern (2 × 4 × 7 × 7). The most reasonable explanation for the failure to observe this anion radical lies in the ease with which it is reduced to the triphenylsilyl anion (eq 1).

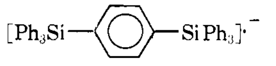
$$Ph_3SiH \xrightarrow{K} [Ph_3SiH\cdot^-]K^+ \xrightarrow{K} Ph_3Si:^-K^+ + KH \qquad (1)$$

Reduction of triphenylsilane with potassium in THF (but *not* DME, see section D) gave three different esr spectra (Figure 4). The length of time that the solution of triphenylsilane was allowed to remain in contact with the metallic mirror at −76° determined which pattern was observed. Patterns II and III appeared after very short contact times. It was possible to interchange these two patterns by allowing the solution to come in contact with the mirror again and frequently one spectrum was superimposed upon the other. Species IV appeared when the reduction was carried out over longer periods at low temperatures (−76°, ~6 hr) and somewhat more rapidly at higher temperatures (>−20°).

Species II is a doublet of quintets. The size of the doublet splitting (6.10 G) when compared to couplings for phenylsilanes containing silicon–hydrogen bonds allows it to be assigned to a *single* silicon hydrogen. III is a quintet with the same coupling as the quintet of II (a = 1.86 G). Quintet splittings with couplings of about 1.8 G have been found to be characteristic of the four hydrogens on the phenyl bridge in 1,4-bis(disilyl)benzene anion radicals.[11-13] Remembering that II and II are formed in the reduction of triphenylsilane, they may be tentatively assigned to the anion radicals of *p*-(diphenylsilyl)triphenylsilylbenzene and *p*-bis(triphenylsilyl)benzene, respectively. Unlike Ia and methylphenylsilane anion radicals (section D), the electron is localized in the bridging phenyl in 1,4-bis(disilyl)benzene anion radicals.



II



III

Evidence supporting these assignments was found in the similar spectra observed after initial formation of the anion radicals of phenylmethylsilane and phenyldimethylsilane. Further reaction of phenylmethylsilane resulted in the observation of a 15-line spectrum ($3a_{SiH} \times 5a_{aryl}$) while phenyldimethylsilane displayed two spectra ($2a_{SiH} \times 5a_{aryl}$ and $3a_{SiH} \times 5a_{aryl}$). The multiplicities of the larger silicon–hydrogen couplings were used to make probable structural assignments. The spectral characteristics of these intermediate anion radicals are summarized in Table II along with the couplings of previously reported 1,4-bis(trialkylsilyl)benzene anion radicals.

Table II. Anion Radicals Formed by Reduction and Para Coupling of Phenylsilanes

Starting phenylsilane	Anion radical $[R{\equiv}SiPhSi{\equiv}R']\cdot^-$ R	R′	Hyperfine coupling[a] a_{SiH}	a_{aryl}	Ref
Ph_3SiH	Ph_3	HPh_2	6.10 (2)	1.86 (5)	*b*, II, *c*
	Ph_3	Ph_3		1.86 (5)	*b*, III, *c*
$PhSiMe_2H$	MePhH	HMe_2	7.02 (3)	1.80 (5)	*b*, *c*
	Me_2Ph	HMe_2	6.28 (2)	1.88 (5)	*b*, *c*
$Me_2SiHC_6H_4SiHMe_2$	Me_2H	HMe_2	7.28 (3)	1.78 (5)	*b*
$PhSiMeH_2$	MePhH	HPhMe	6.67 (3)	1.78 (5)	*b*, *c*
$R_3SiC_6H_4SiR_3$ (R = Ph, Et, or Me)	R_3	R_3		2.1 (5)–1.9 (5)	*d*
$Me_3SiC_6H_4SiMe_3$	Me_3	Me_3		1.76 (5)	*e*
				1.83 (5)	*f*

[a] Coupling in gauss; figures in parentheses represent multiplicity. [b] This work. [c] Tentative structural assignment (see text). [d] Reference 11. [e] Reference 12. [f] Reference 13.

As a model for these intermediate anion radicals, 1,4-bis(dimethylsilyl)benzene was reduced. Electrolytic or potassium reduction in THF resulted in the immediate appearance of an anion radical characterized by a spectrum with a large triplet splitting due to the silicon hydrogens (a_{SiH} = 7.28 G) and a smaller quintet splitting from the aryl bridge hydrogens (a = 1.78 G).

Species IV was obtained in the reduction of triphenylsilane when the solution was allowed to remain in contact with the metal mirror for long periods at low temperatures or if the reduction was carried out at room temperature. Species IV also appeared as the last one observed after long reduction times in THF for other phenylsilanes. These included phenylsilane, phenylmethylsilane, phenyldimethylsilane, triphenylchlorosilane, and triphenylvinylsilane. When tetraphenylsilane was reduced with potassium in THF, IV was the *only* anion radical observed (Figure 5, section D). It consisted of 19 relatively broad lines compared to the 17 lines observed by Townsend.[15] The computer-simulated spectrum was obtained with the largest coupling due to the four para hydrogens (a_p = 2.12 G) and smaller couplings due to the ortho and meta hydrogens (Table III). It is therefore concluded that IV is the anion radical of tetraphenylsilane.

The formation of tetraphenylsilane from phenylsilanes containing fewer phenyls attached to silicon has been previously observed in preparative scale reactions by metal reduction under somewhat more strenuous conditions.[21,22] Benkeser and Foster obtained tetraphenylsilane in 68, 80, and 62% yield from phenylsilane, diphenylsilane, and triphenylsilane by sodium–potassium reduction. To account for the formation of more highly phenylated silanes, these authors proposed that phenyls are reductively cleaved from silicon with the formation of phenylpotassium. Phenylpotassium then couples with unreduced phenylsilane to form a new phenyl–silicon bond. Repetition of this sequence eventually leads to tetraphenylsilane (eq 2).

$$\begin{aligned} PhSiH_3 + Na\text{-}K &\longrightarrow Ph^-K^+ + H_3Si^-K^+ \\ Ph^-K^+ + PhSiH_3 &\longrightarrow Ph_2SiH_2 + KH \\ Ph^-K^+ + Ph_2SiH_2 &\longrightarrow Ph_3SiH + KH \\ Ph^-K^+ + Ph_3SiH &\longrightarrow Ph_4Si + KH \end{aligned} \tag{2}$$

In these reactions, it should be noted that alkyl–silicon bonds remain intact. For example, only triphenylmethylsilane is formed from diphenylmethylsilane.

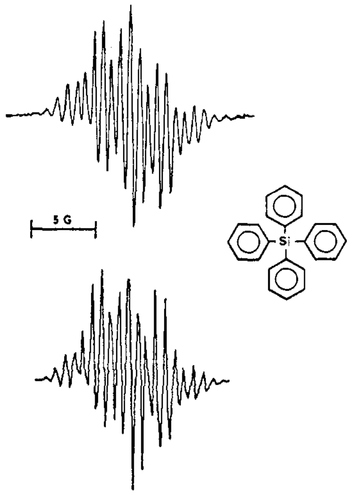


Figure 5. The anion radical of tetraphenylsilane: upper spectrum, experimental; lower spectrum, computer simulated.

In the present work, the appearance of 1,4-bis(disilyl)benzene anion radicals in the early stages of the reduction of phenylsilanes (II, III, and Table II) and the final appearance of tetraphenylsilane anion radical from a variety of precursors suggest a slightly different sequence. This sequence involves: (a) reduction of the phenylsilane to a phenylsilyl anion through silicon–hydrogen cleavage rather than silicon–phenyl cleavage; (b) para coupling with unreduced phenylsilane to form a 1,4-bis(disilyl)benzene moiety;[23] and (c) reductive cleavage of a silicon–aryl bond to form tetraphenylsilane (eq 3). It must be stressed that this reaction scheme is tentative at best because of the limitations of esr in obtaining a detailed picture of a complex reaction. Electron spin resonance "sees" only paramagnetic species and such species may reflect the most stable anion formed rather than the major pathway of reaction. Further, in comparing the esr results to previous preparative scale reactions, inconsistencies may be due to the substantial differences in concentration, solvent, and temperature. The inconsistencies between the esr results and the previous results[21,22] are exemplified by the formation of tetraphenylsilane anion

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(21) R. A. Benkeser and D. J. Foster, *J. Amer. Chem. Soc.*, **74**, 4200 (1952).

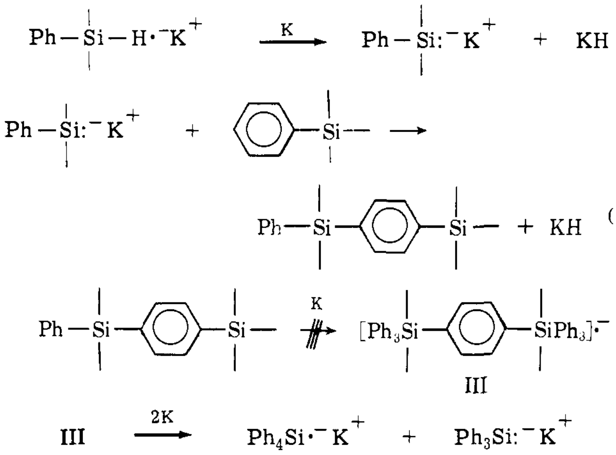
(22) R. A. Benkeser and D. J. Foster, *ibid.*, **74**, 5314 (1952).

(23) For other examples of para coupling in the reduction of organosilanes, see (a) D. R. Weyenberg, L. H. Toporcher, and A. Bey, *J. Org. Chem.*, **30**, 4096 (1965); (b) A. E. Bey and D. R. Weyenberg, *ibid.*, **30**, 2436 (1965); (c) ref 11 and 18.

Table III. Anion Radicals of Phenylmethylsilanes

Anion radical	Hyperfine coupling[a] a_p	a_o	a_m	a_{CH_3}	Conditions	Notes and ref
$PhSiMe_3\cdot^-$	8.06 (2)	2.61 (3)	1.05 (3)	0.26 (10)	K; THF, DME	17.72,[b] *c*
$Ph_2SiMe_2\cdot^-$	4.15 (3)	1.44 (5)	0.34 (5)	0.17 (7)	K; THF, DME	16.44,[b] *c*
$Ph_3SiMe\cdot^-$	2.76 (4)	1.01 (7)	0.19 (7)	0.10 (4)	K; THF, DME	15.48,[b] *c*
$Ph_4Si\cdot^-$	2.12 (5)	0.80 (9)	<0.10 (9)		K; THF, DME	14.88,[b] *c*
$PhSiMe_3\cdot^-$	8.13 (2)	2.66 (3)	1.06 (3)	0.40 (10)	Li; THF	*d*, *e*
$Ph_2SiMe_2\cdot^-$	8.1 (2)	2.6 (3)	nr[i]	nr[i]	K; DME	*f*, $PhSiMe_3\cdot^-$ [g]
$Ph_2SiEt_2\cdot^-$	8.5 (2)	3.4 (3)	1.7 (3)	nr[i]	K; DME	*f*, $PhSiEt_2Me\cdot^-$ [g]
$Ph_3SiMe\cdot^-$	8.4 (2)	2.8 (3)	1.2 (3)	nr[i]	K; DME	*h*, $PhSiMe_3\cdot^-$ [g]
$Ph_3SiH\cdot^-$	8.2 (2)	2.9 (3)	1.1 (3)		K; DME	*h*, $PhSiMe_3\cdot^-$ [g]
$Ph_4Si\cdot^-$	8.0 (2)	3.0 (3)	1.0 (3)		K; DME	*h*, $PhSiMe_3\cdot^-$ [g]

[a] Couplings in gauss; figures in parentheses represent multiplicity. [b] Total line width in gauss. [c] This work. [d] Reference 10. [e] Reference 12. [f] Reference 11. [g] Anion radical probably observed (see text). [h] Reference 18. [i] nr = not reported.



(3)

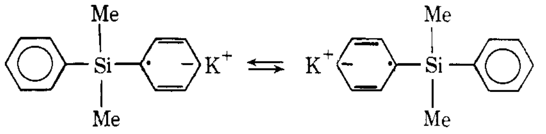
radical even from phenylmethylsilane and phenyldimethylsilane. This apparently requires methyl–silicon cleavage somewhere in the reaction scheme. Also, reduction of diphenylsilanes *did not* lead to tetraphenylsilane anion radical.

C. Attempted Preparation of the Anion Radicals of Diphenylsilane and Diphenylmethylsilane. The electrolytic or metallic reduction of diphenylsilane and diphenylmethylsilane at low temperatures gave only the very rapid formation of the biphenyl anion radical. The formation of biphenyl anion radical from phenylated compounds upon alkali metal reduction appears to be quite general. Its formation has been observed from tetraphenylmethane,[15] triphenylamine,[24] triphenylboron,[25,26] triphenylphosphine oxide,[27,28] and phenyl ethers.[29,30] Several differing mechanisms have been proposed.[17,26,29]

In the present case, the rapid formation of biphenyl anion radical indicates a change in the preferred mode of cleavage in going from monophenylsilanes to diphenylsilanes. For monophenylsilanes, silicon–hydrogen cleavage is favored because the anion formed is stabilized by the phenyl attached to silicon (eq 3). However, for diphenylsilanes, reductive cleavage of a silicon–phenyl bond (and subsequent biphenyl anion radical formation) may be favored because the anion formed is still stabilized by the remaining phenyl.

D. Anion Radicals of Tetraphenylsilane, Triphenylmethylsilane, Diphenyldimethylsilane, and Phenyltrimethylsilane. Reduction of these four phenylsilanes with potassium in THF at −76° gave yellow solutions. These solutions displayed well-resolved esr spectra characterized by a largest coupling due to the para hydrogen(s) and smaller couplings due to the ortho, meta, and methyl hydrogens (Figures 5–8).

The hyperfine couplings for these four anion radicals along with previous literature reports are collected in Table III. The experimental spectra for the anion radicals of diphenyldimethylsilane and triphenylmethylsilane compare well in the wings but are somewhat broader in the central portions than the computer-simulated spectra (Figures 6 and 7). It was initially thought that this broadening might be due to line width alternation associated with the interchange of the position of the potassium ion (eq 4). Line width alternation has recently been reported for the anion radical of tetramethyl-5,10-dihydrosilanthrene, perhaps due to the interchange of the potassium ion between the 3d orbitals of the two silicon atoms.[31] In the present case, examination of these two anion radicals in solvents of different dielectric constant (THF, DME, and 2-methyl-THF) showed no change in the broadening within the accessible temperature range (−80 to −10°). Attempted electrolytic reduction using tetra-*n*-butylammonium perchlorate as supporting electrolyte failed to give any paramagnetic species.



(4)

An alternative and more likely explanation for this broadening is the presence of small concentrations of anion radicals having the same *g* value from the further reduction of the starting silanes. Compared to the anion radicals of phenylsilanes containing silicon–hydrogen bonds, these anion radicals are qualitatively more stable toward further reaction. Their spectra remain unchanged for long periods of time below about −10° when prepared in THF. However, they are eventually replaced by the five-line patterns characteristic of the formation of 1,4-bis(disilyl)benzene anion

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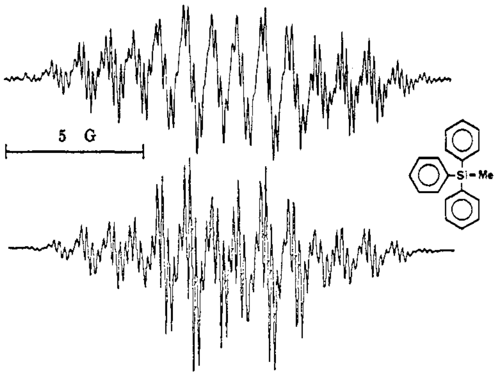

Figure 6. The anion radical or triphenylmethylsilane: upper spectrum, experimental; lower spectrum, computer simulated.

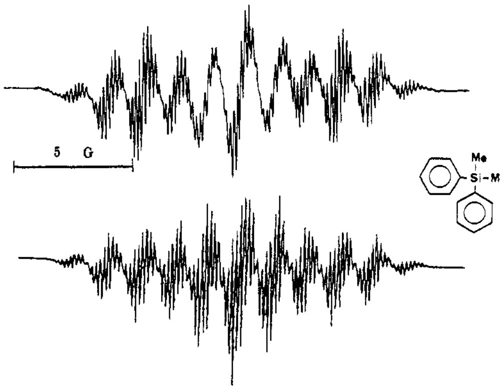

Figure 7. The anion radical of diphenyldimethylsilane: upper spectrum, experimental; lower spectrum, computer simulated.

radicals ($a = \simeq 1.8$ G). The line width of this pattern ($\simeq 7.2$ G) corresponds to the broadened portion of the experimental spectra for the anion radicals of diphenyldimethylsilane and triphenylmethylsilane (Figure 6 and 7).

Despite this broadening due to the probable presence of small amounts of 1,4-bis(disilyl)benzene anion radicals, the major features of these four spectra are quite clear: $\mathrm{PhSiMe_3}\cdot^-$, 2×3; $\mathrm{Ph_2SiMe_2}\cdot^-$, 3×5; $\mathrm{Ph_3SiMe}\cdot^-$, 4×7; and $\mathrm{Ph_4Si}\cdot^-$, 5×9. These multiplicities show that the free electron is associated with *all* of the phenyls attached to silicon. Further, the size of the para and ortho couplings and the total line widths show a regular decrease as methyls are replaced by phenyls (Table III). These line widths are substantially narrower than those of similar aromatic anion radicals.

The last five entries in Table III present previous reports for the characteristics of anion radicals of organosilanes containing more than one phenyl attached to silicon. For these, it was claimed that the free electron resided in only *one* ring.[11,18] The most reasonable explanation lies in the further reaction of the initially formed anion radicals with the solvent and the eventual observation of phenyltrialkylsilane anion radicals.

In the present investigation, all three phenylsilanes ($\mathrm{Ph_2SiMe_2}$, $\mathrm{Ph_3SiMe}$, and $\mathrm{Ph_4Si}$) eventually formed the anion radical of phenyltrimethylsilane *when the reductions were carried out in DME.* Phenyltrimethylsilane anion radical appears to be the most stable paramagnetic species formed from these three and a number of other phenylsilanes. Similar behavior was also observed for phenylsilane, phenylmethylsilane, phenyldimethylsilane, and triphenylsilane for metallic reduction in DME. The facile formation of phenyltrimethylsilane anion radical can be pictured as the formation of the anion radical, reductive cleavage of a silicon–phenyl (or silicon–hydrogen) bond, and reaction of the resulting silyl anion with DME (eq 5). Repetition of this process eventually results in the formation of phenyltrimethylsilane anion radical. Similar preparative scale reactions of silyl anions with methyl ethers have been previously reported. For example, triphenylsilyllithium reacts with DME to give an 84.5% yield of triphenylmethylsilane and with anisole to give a 64.2% yield of triphenylmethylsilane.[32,33]

$$\mathrm{PhSiR_3} \xrightarrow{\mathrm{K}} [\mathrm{PhSiR_3}]\cdot^-$$

$$\mathrm{R = H\ or\ Ph}$$

$$[\mathrm{PhSiR_3}]\cdot^- \xrightarrow{\mathrm{K}} \mathrm{KR} + \mathrm{PhR_2Si}\!:^- \qquad (5)$$

$$\mathrm{PhR_2Si}\!:^- \xrightarrow{\mathrm{DME}} \mathrm{PhR_2SiMe}$$

$$\mathrm{PhR_2SiMe} \xrightarrow[\mathrm{DME}]{\mathrm{K}} [\mathrm{PhSiMe_3}]\cdot^-$$

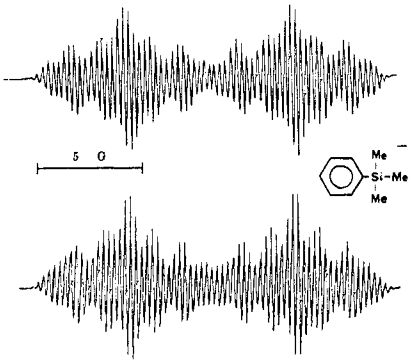

Figure 8. The anion radical of phenyltrimethylsilane: upper spectrum, experimental; lower spectrum, computer simulated.

Experimental Section

Materials. Solvents (THF, DME, and 2-methyl-THF) were twice distilled from potassium metal before storing in bulbs over sodium–potassium alloy on the vacuum line. The solvent in the storage bulbs was stirred and degassed until the characteristic blue color of the solvated electron appeared. Then the solvent was bulb-to-bulb distilled into the sample cell.

All the organosilanes used for the preparation of anion radicals or for syntheses were obtained from Peninsular ChemResearch, Inc. Phenyldimethylsilane and diphenylsilane were distilled before use. Triphenylsilane was recrystallized twice from petroleum ether. Tetraphenylsilane was recrystallized twice from benzene.

Syntheses. Phenylsilane was prepared by the lithium aluminum hydride reduction of phenyltrichlorosilane in ether. Purification by fractional distillation gave phenylsilane, 78% yield, bp 119.0–119.5° (740 mm) [lit.[34] 119.5–120.0° (757 mm)]. Phenylmethylsilane was prepared by the lithium aluminum hydride reduction of phenylmethyldichlorosilane in ether. Purification by fractional distillation gave phenylmethylsilane, 89% yield, bp 141–142° (750 mm) [lit.[35] 139.5–140.0° (760 mm)].

Diphenylmethylsilane was prepared by the reaction of phenylmagnesium bromide with methyldichlorosilane. Purification by

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fractional distillation under vacuum gave diphenylmethylsilane, 45% yield, bp 93–95° (0.35 mm) [lit.[22] 82° (0.15 mm)]. Diphenyldimethylsilane was prepared by the reaction of diphenyldichlorosilane with methylmagnesium iodide in ether. Fractional distillation under vacuum gave diphenyldimethylsilane, 82% yield, bp 115–118° (4.5 mm) [lit.[36] 113–115° (4 mm)]. Triphenylmethylsilane was prepared by the reaction of phenyllithium with methyltrichlorosilane in ether. Recrystallization of the crude product twice from benzene gave triphenylmethylsilane, 68% yield, mp 67–68° (lit.[37] 68.5–69.0°).

1,4-Bis(dimethylsilyl)benzene was prepared by the *in situ* reaction of dimethyldichlorosilane, 1,4-dibromobenzene, and magnesium in ether followed by lithium aluminum hydride reduction. A solution of dimethyldichlorosilane (219 g, 0.59 mol) and 1,4-dibromobenzene (134 g, 0.57 mol) in 200 ml of anhydrous ether containing magnesium turnings (42 g, 1.75 g-atoms) was refluxed for 12 hr. The reaction mixture was then distilled under vacuum and the distillate up to 92° (2 mm) was collected. This distillate was added slowly to a solution of an excess of lithium aluminum hydride dissolved in 300 ml of ether. Fractional distillation under vacuum gave 1,4-bis(dimethylsilyl)benzene: 69 g, 0.54 mol, 91% yield, bp 77–78° (8 mm) [lit.[38] 118° (35 mm)].

Preparation of Anion Radicals. Metallic reductions were carried out *in vacuo* by allowing $\sim 10^{-3}$ *M* solutions of the appropriate phenylsilane dissolved in THF, DME, or 2-methyl-THF at −76° to react with a potassium mirror. Esr spectra were recorded with the resulting solutions of anion radicals contained in side-arm sample tubes out of contact with the metallic mirror.

Electrolyte reductions were performed using a sample cell containing two platinum electrodes. Anion radicals were generated directly in the esr cavity using a Heath Model EUW-16 voltage reference source. The variable dc voltage source was increased until an esr spectrum appeared. No reference electrode was employed. Polarographic grade tetra-*n*-butylammonium perchlorate ($\sim 10^{-2}$ *M*) was used as supporting electrolyte. This simple technique complemented the preparation of anion radicals by metallic reduction, allowing the characterization of three phenylsilane anion radicals that were subject to rapid further reduction in contact with a potassium mirror. No differences were noted in the hyperfine couplings for anion radicals which could be generated both metallically and electrolytically (Table I).

Electron Spin Resonance Measurements. Esr spectra were recorded on a Varian V-4502-15 esr spectrometer using the X-band and a V4560 100-KHz field modulation unit. The temperature was controlled within ±1° using a Varian V-4557 variable-temperature controller. The controller was periodically calibrated with a copper–constantan thermocouple. Both the recorder and the sweep dial were calibrated using the resonance of the cyclooctatetraene anion radical in THF.[39]

Coupling constants were measured directly from the strip chart recorder. Computer simulated spectra were obtained from a "Cal-Comp" adaptation to the IBM 360 computer. Spectra were simulated by the systematic variation of the coupling constants and the line widths until agreement between the calculated and experimental spectra was obtained.

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The Electron Paramagnetic Resonance Spectra of 4-Cyclopropylnitrobenzene Anion Radical and Related Compounds. Spin and Electron Density Distribution in the Cyclopropyl Group[1]

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Abstract: The epr spectra of nitrobenzene anion radicals with 4-vinyl, 4-cyclopropyl, *syn*-4-(*cis*-2,3-dimethylcyclopropyl), *anti*-4-(*cis*-2,3-dimethylcyclopropyl), and 3,5-dimethyl-4-cyclopropyl groups and radicals prepared from 5-nitroindan, 5-nitro-1,1-dimethylindan, 5-nitrospiro(cyclopentane-1,1′-indan), 5-nitrospiro(cyclopropane-1,1′-indan), and 6-nitro-3′,4′-dihydrospiro(cyclopropane-1,1′(2*H*′)-naphthalene) are reported. The coupling constants for the β (methine) hydrogen atoms of the cyclopropane ring establish the conformational preference of the ring and the constants for the γ (methylene) and δ (methyl) hydrogen atoms indicate the extent of spin delocalization. These long-range interactions exhibit a distinctive stereochemical dependence which is compatible with the predictions of the INDO formulation and with an important role for caron–carbon hyperconjugation.

Cyclopropane chemistry often reflects the intriguing interactions between electron-deficient p orbitals in carbonium ions and carbon radicals and neighboring p-rich carbon–carbon bonds. Recently, cyclopropylcarbinyl radical, its derivatives, and related anion and cation radicals have been investigated by epr spectroscopy.[3–5] This work established that the cyclopropyl group often preferentially adopts the bisected confor-

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