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CHEMISTRY OF ALKALI METAL-UNSATURATED HYDROCARBON ADDUCTS

XI *. ESR MONITORING OF TRANSIENT RADICAL-ANIONS FROM UNSATURATED ORGANOSILANES **

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Summary

By the potassium-metal reduction of a series of α,β-unsaturated organosilanes at low temperatures, radical-anionic intermediates were generated. Both the detailed structure of such radical-anions and their chemical transformations were studied by a combination of ESR spectroscopy and chemical characterization. Relatively stable radical-anions were obtained from the methyl(phenyl)silanes, tetraphenylsilane and hexaphenyldisilane, but even these decomposed eventually through cleavage and coupling processes. More labile radical-anions arose from organosilanes of the type, Ph_3SiE, where E was chloro, cyclopropyl, substituted biphenyl, vinyl, 1-propenyl and 1-propynyl. In several cases, the transient parent radical-anion could be measured with ESR spectroscopy by working at low temperatures in the presence of HMPT. As an aid to deciding among several possible structural assignments of an ESR spectrum, the actual chemical products obtained from such reductions were scrutinized. The conclusion reached from these studies is that that part of the organosilane molecule bearing the highest free electron spin density in the radical-anion is the site of highest chemical reactivity. Sites of radical-coupling, chemical reduction, isomerization and carbon–silicon bond cleavage can be predicted from such ESR data.

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* For part X, see ref. 11.

** This work is dedicated to Professor Makoto Kumada whose many splendid contributions to organosilicon chemistry and superb scientific leadership serve to inspire his colleagues throughout the world. His good offices enabled the senior author to visit Japan and experience firsthand, not only the vigor of modern Japanese science, but also the serene beauty of an ancient culture.

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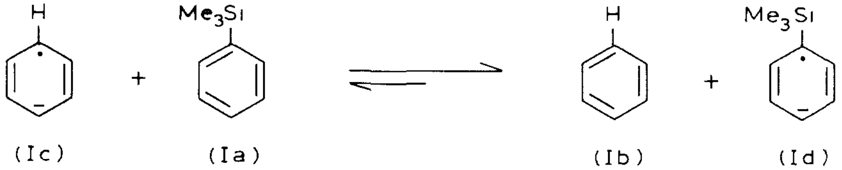
Introduction

Replacement of a hydrogen attached to an unsaturated carbon–carbon linkage (Ib) by a triorganosilyl group (Ia) markedly increases the electron affinity of the molecule ($K_{eq} > 1$ in eq. 1). This conclusion is based upon various lines of chemical and physical evidence. First, not only is $K_{eq} > 1$ in eq. 1, but the greatest electron spin density is on C(1) and C(4) (*para*-hydrogen hyperfine coupling constant is 8.13 G [1]) and considerable spin density is delocalized onto the silicon (thus narrowing the total spectral width from 22.50 for Ib to 18.63 G for Id [2,3]). Second, vinylsilanes undergo additions of electrons to the C=C linkage, either by alkali metals [4] or by electrochemical reduction [5], more readily than vinylmethanes ($R_3SiCH=CH_2$ vs. $R_3CCH=CH_2$). Third, α,β-unsaturated organosilanes react with alkali metals to undergo diverse isomerizations [6], carbon–silicon bond cleavages [7], reductions [8–11] and reductive dimerizations [4,11]. In all these chemical transformations, there is strong preliminary, circumstantial evidence that radical-anions are formed as key transient intermediates, whose chemical decomposition determines the ultimate reaction products [10,11].



(1)

Although ESR studies on relatively stable radicals derived from organosilanes have been the topic of an extensive series of publications [12–14], little attention has been given to the chemical behavior of the more short-lived radical-anions. Our goal has been to generate reactive radical-anions from organosilanes and to monitor their chemical transformations, where possible, by ESR spectroscopy. Finally, in order to corroborate our assignment of an observed ESR spectrum to a given radical-anion, we have examined the nature of the ultimate reaction products obtained by hydrolysis. Guided by the reaction products actually observed, we have been able, in certain cases, to choose with reasonable confidence between two different possible radical-anionic intermediates. Because of the similar magnitudes of proton hyperfine coupling constants (*a* for aromatic C–H ranges from 1.0 to 9.0 G; *a* for silane Si–H ranges from 1.0 to 8.0 G [14]), the ability to simulate an observed ESR spectrum by some choice of *a*-values gives no assurance that the spectrum is uniquely assigned or properly identified. For reactions having this ambiguity, a knowledge of the kinds of reaction products is essential in choosing the most likely intermediate radical-anion.

Results

The radical-anions of the organosilanes were generated, in most cases, by allowing solutions of the substrate in 1,2-dimethoxyethane (DME) or in tetrahydrofuran (THF) to come in contact with potassium metal mirrors for brief periods at −70 °C. The apparatus permitted the resulting colored solutions, which were thereafter not in contact with potassium, to be promptly examined by ESR spectroscopy. In a number of cases, the color of the solution and the ESR signal thereby obtained depended on: (a) the concentration of the initial solution in DME; (b) the time of contact of such solutions with the potassium mirror; (c) the time lapse between contact with the potassium mirror and measurement of the ESR signal; and (d) the temperature at which the radical-anionic solution was kept until the ESR measurement.

A number of arylsilanes, which give relatively stable radical-anions whose hyperfine coupling constants have previously been reported [1,2,14], were examined, in order to verify our calibration of the spectrometer. These compounds were trimethyl(phenyl)silane (I), dimethyl(diphenyl)silane (II), methyl(triphenyl)silane (III) and tetraphenylsilane (IV). Other silanes, such as hexaphenyldisilane (V), chloro(triphenyl)silane (VI), cyclopropyl(triphenyl)silane (VII), 4,4′-bis[cyclopropyl-(diphenyl)silyl]biphenyl (VIII), triphenyl(vinyl)silane (IX), triphenyl(*trans*-1-propenyl)silane (X), diphenyl(divinyl)silane (XI) and triphenyl(1-propynyl)silane (XII), were shown to form transient radical-anions, whose lifetimes were very sensitive to temperature and to lapsed time from exposure to the potassium mirror.

Silanes of the type, $Me_nPh_{4-n}Si$*, where* $n = 0$*–*3

The ESR spectra obtained from the phenylsilanes I–IV were generally in good or excellent agreement with literature values reported for the proton hyperfine coupling constants. Trimethyl(phenyl)silane (I) yielded a radical-anion whose free spin was principally on C(4) (cf. Id, eq. 1), since a_p is 8.10 G, much greater than a_o (2.65 G), a_m (1.06 G) or a_{Me} (0.30 G). With time, Id is destroyed and is replaced by the benzene ion Ic, showing that the phenyl–silicon bond of Id is cleaved (Table 1).

The radical-anion of dimethyl(diphenyl)silane (II) in DME solution containing some hexamethylphosphorus triamide (HMPT) was analyzable in terms of equivalent phenyl rings undergoing rapid exchange of the free electron (Fig. 1). The a_p value, 4.21 G was about one-half that shown by I. In the absence of HMPT, the ESR spectrum was analyzable only if the a_p of each ring was given a different value: a_p 4.21 and $a_{p'}$ 4.10 G. This observation suggests that on the time-scale of the ESR measurement the potassium ion is more closely associated with one ring than the other (eq. 2, Fig. 2).

(2)

The removal of this ring inequivalency by the HMPT can be ascribed to the disruption of the contact ion-pairing shown in eq. 2. The presence of HMPT not only favors solvent-separated ion-pairing [15], but was found to enhance the kinetic stability of the radical-anions generated in this study.

Methyl(triphenyl)silane (III) in DME alone, for example, upon contact with potassium rapidly gave rise to a red solution whose ESR spectrum resembled that of the radical anion of II (cf. infra). Shortly thereafter, the unmistakable ESR spectrum of the biphenyl radical-anion emerged from the hyperfine pattern. In contrast, the ESR spectrum of III's radical-anion in a DME/HMPT mixture was relatively stable even at 25 °C and was analyzable in terms of rapid exchange of the electron among the three phenyl rings. Consistent with this view, the largest coupling constant, a_p

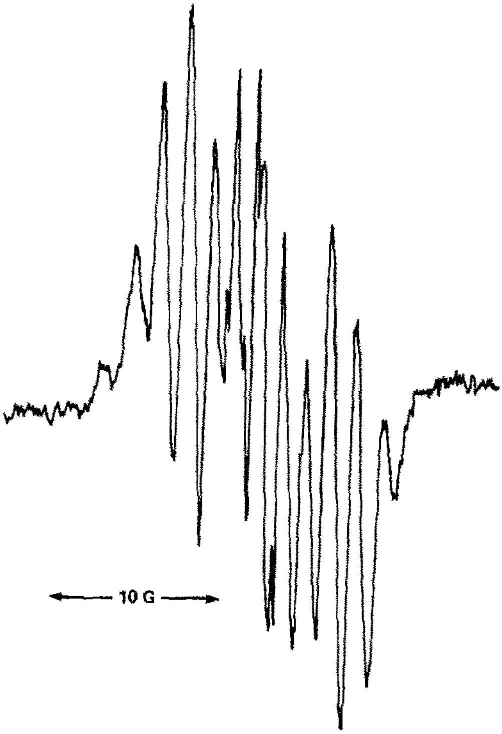


Fig. 1. ESR spectrum of the dimethyl(diphenyl)silane radical-anion at −70 °C in DME with 2% of HMPT.

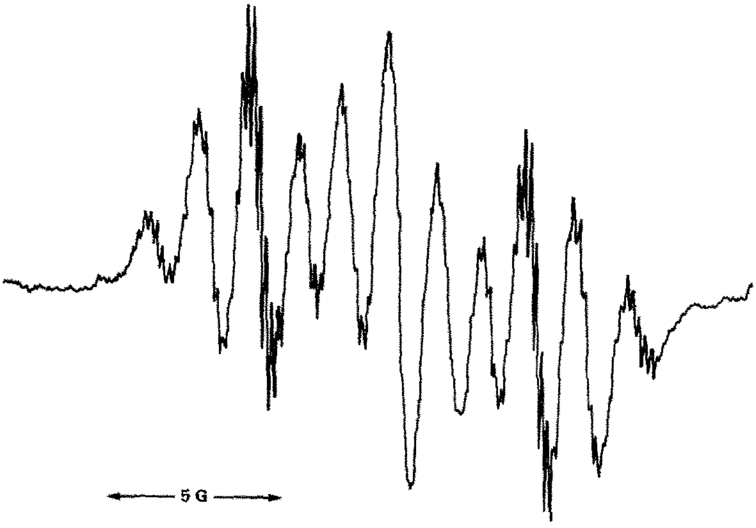


Fig. 2. ESR spectrum of the dimethyl(diphenyl)silane radical-anion in DME at −70 °C.

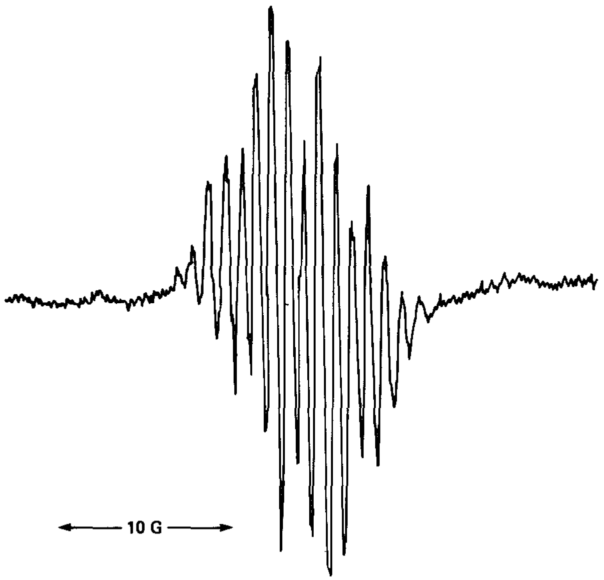


Fig. 3. ESR spectrum of the methyl(triphenyl)silane radical-anion at −70 °C in DME with 2% of HMPT.

2.80 G, was approximately one-third that observed with I (Fig. 3).

The ESR spectra obtained from tetraphenylsilane (IV) and hexaphenyldisilane (V) probably do not represent the maximum hyperfine splitting attainable [14,16]. However, the reproducibility of the spectra and their obliteration at higher temperatures with the formation of benzene and biphenyl suggest that the observed spectra arise from unchanged IV and V, respectively. From the total spectra width (14.1–17.2 G), it can be concluded that the free electron is exchanging with at least two rings in each radical anion (a_p 4.20 G in V) (Fig. 4).

Silanes of the type, Ph_3SiR, where R is a readily cleavable group (Table 1)

On contact with potassium, chloro(triphenyl)silane (VI) in DME underwent a

TABLE 1

ESR COUPLING CONSTANTS, a_H (nH), OBSERVED FOR THE RADICAL-ANIONS GENERATED FROM UNSATURATED ORGANOSILANES AND POTASSIUM IN DME AT −70 °C

Organosilane	a_H (nH), (G)			
$PhSiMe_3$ (I)	a_p 8.10 (H)	a_o 2.65 (2H)	a_m 1.06 (2H)	a_{Me} 0.30 (9H)
Ph_2SiMe_2 (II) [a]	a_p 4.21 (2H)	a_o 1.50 (4H)	a_m < 0.2 (4H) [c]	a_{Me} 0.20 (6H)
Ph_3SiMe (III) [a]	a_p 2.80 (3H)	a_o 1.15 (6H)	a_m 1.05 (6H)	a_{Me} < 0.20 (3H) [c]
$Ph_3SiSiPh_3$ (V)	a_p 4.20 (2H)	a_o 1.65 (4H)	–	–
Ph_3SiCl (VI)	Spectrum of I,then of III			
$Ph_3Si\text{-}c\text{-}C_3H_5$ (VII)	a_p 2.80 (3H)	a_o 1.15 (6H)	a_m 1.05 (6H)	$a_{c\text{-}CH}$ < 0.2 (H) [c]
$Ph_3SiCH{=}CH_2$ (IX) [a]	a_H 5.02 (2H)	$a_{H'}$ 1.60 (4H)		
$Ph_3SiCH{=}CHMe$ (X) [a]	a_H 5.0 (H)	$a_{H'}$ 1.4 (H)	$a_{H''}$ 1.8 (3H)	$a_{H'''}$ 0.8 (3H)
$Ph_2Si(CH{=}CH_2)_2$ (XI) [b]	a_p 7.10 (H)	a_o 1.95 (2H)	a_m 1.55 (2H)	
$Ph_3SiC{\equiv}CMe$ (XII)	a_H 9.52 (3H)	$a_{H'}$ 4.96 (H)		

[a] In DME containing 2% of HMPT. [b] Only in highly dilute (10^{-5} M) DME. [c] Not observed.

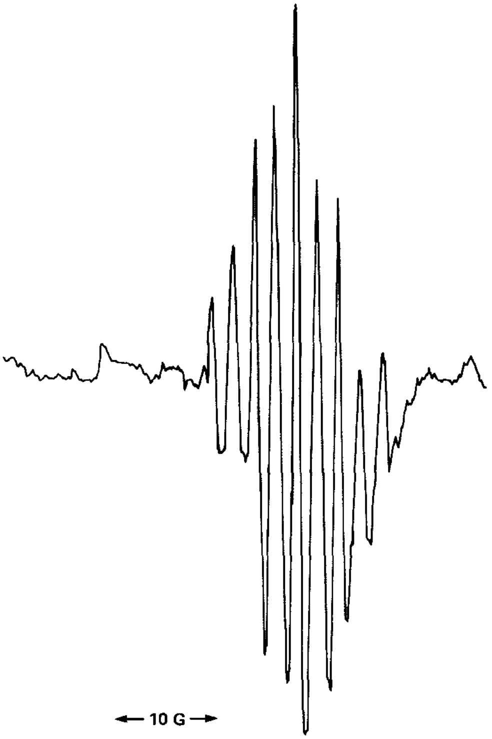


Fig. 4. ESR spectrum of the radical-anion from hexaphenyldisilane in DME at −70 °C.

remarkable series of reactions. Against expectations, the radical-anion derived from hexaphenyldisilane was not observed, but the radical-anions of trimethyl(phenyl)silane (I), benzene and methyl(triphenyl)silane appeared in succession as the temperature of the sample was gradually increased. The methylated silanes arose from reactions of silylpotassium intermediates with the DME (cf. infra) (Fig. 5).

Cyclopropyl(triphenyl)silane (VII) in DME/HMPT formed a radical-anion whose ESR spectrum was identical with that from methyl(triphenyl)silane (III). This indicates that the hyperfine coupling constants of the methyl protons in III and methyne proton in VII are very small (< 0.10 G). Again, as with III, the spin density in the radical anion from VII is maximum at the C(4) position and is spread evenly among the three phenyl rings.

Although the radical anions from III and VII were stable for long periods at −50 °C, that from 4,4′-bis[cyclopropyl(diphenyl)silyl]biphenyl promptly decomposed at −70 °C to form biphenyl. With time, phenyl–silicon bonds were also cleaved to yield benzene.

Triphenyl(vinyl)silane (IX) in DME underwent cleavage and coupling reaction upon contact with potassium and both benzene and biphenyl were eventually produced. Longer contact times eventually generated the radical anion of trimethyl(phenyl)silane (I), which stemmed from phenyl–silicon bond cleavage and methylation by the DME.

In DME/HMPT, however, vinylsilane IX did give a reproducible, rather broad-lined spectrum that can be simulated by a two-proton coupling of 5.02 G and a

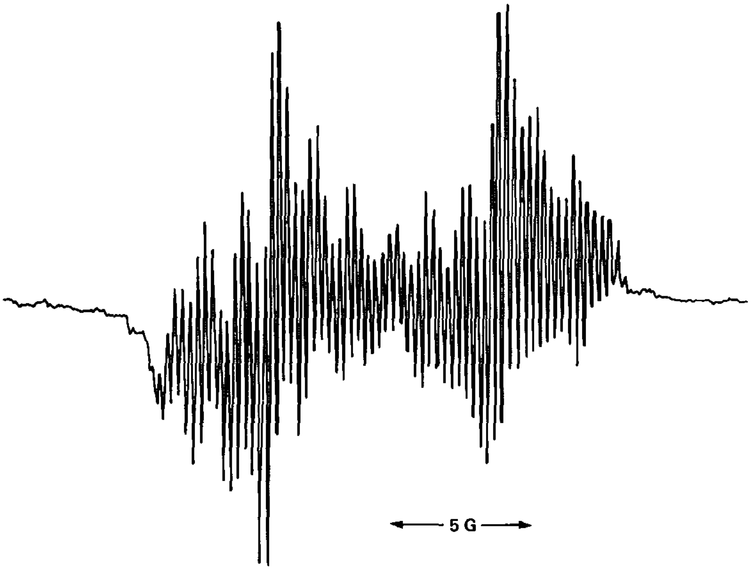
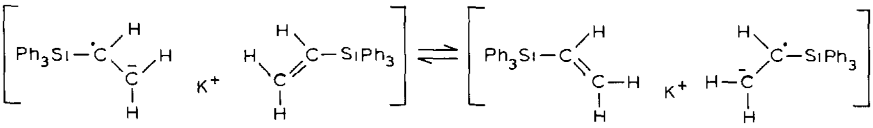


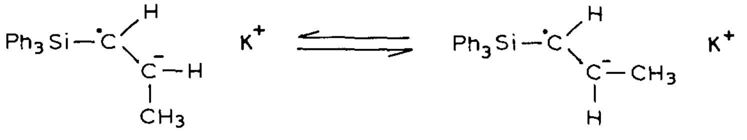
Fig. 5. ESR spectrum of the radical-anion of trimethyl(phenyl)silane derived from chloro(triphenyl)silane and potassium in DME at −70 °C.

four-proton coupling of 1.60 G. A structure most consistent with the known chemical products of such metal reactions with IX would be a 1 : 1 complex of IX with its radical-anion (eq. 3):



(3)

Support for the formulation in eq. 3 was gained by examining the response of triphenyl(*trans*-1-propenyl)silane (X) in DME to contact with potassium. As with IX, only decomposition and ultimately the ESR spectrum of I were observed. In DME/HMPT, however, a broad-lined reproducible spectrum was generated at −70 °C, whose hyperfine pattern could be simulated by two different three-proton splittings (*a* 0.8 and 1.8 G) and two different one-proton splittings (*a* 1.4 and 5.0 G). Such a spectrum could arise from a *cis*, *trans*-mixture of radical-anions Xa and Xb (eq. 4, Fig. 6).



(4)

(Xa) (Xb)

Attempts to generate radical-anions from diphenyl(divinyl)silane (XI) in concentrated solutions of DME led only to polymerization, as sharp viscosity increases made evident. Very dilute solutions gave a satisfactory, reproducible spectrum that could be simulated as arising from two different two-proton splittings (*a* 1.55 and

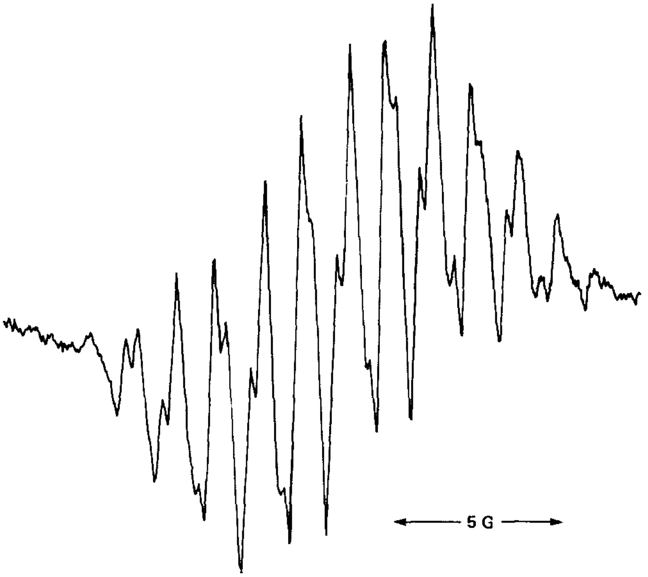
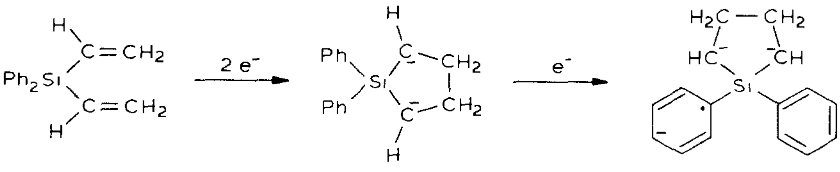


Fig. 6. ESR spectrum of the radical-anion of triphenyl(*trans*-1-propenyl)silane at −70 °C in DME with 2% of HMPT.

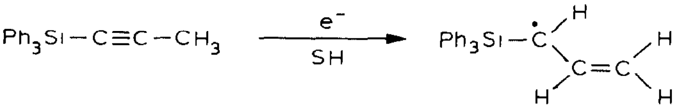
1.95 G) and one one-proton splitting of 7.10 G. Since chemical reduction of XI in dilute solution leads to 1,1-diphenylsilacyclopentane (XIII) [11], the ESR signal is ascribed to the radical-anion of XIII or, more likely, of an anionic derivative, XIIIb (eq. 5):



(XI) (XIIIa) (XIIIb) (5)

The localization of the electron in one phenyl ring (i.e., a_p 7.10 and not 3.55 G) may be due to the carbanionic charges at C(2) and C(5) of the five-membered ring.

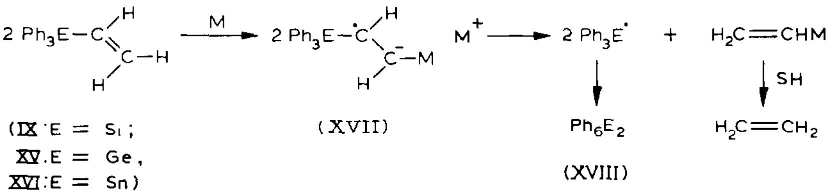
Finally, the strong, reproducible hyperfine ESR signal obtained from triphenyl(1-propynyl)silane (XII) can be simulated excellently by a three-proton splitting of 9.52 and a one-proton splitting of 4.96 G. Since the chemical reduction of XII leads to the formation of triphenyl(*trans*-1-propenyl)silane (X), together with its *cis* isomer, the radical-anion derived from XII clearly involves the propynyl group, not the phenyl group. For reasons discussed below and because of the magnitudes of the coupling constants, the observed ESR spectrum is assigned to the 1-triphenylsilylallyl radical (XIV, eq. 6):



(XII) (XIV) (6)

Cleavage of vinylmetallics of the type, $Ph_3ECH{=}CH_2$, where E = Si, Ge and Sn

Bringing solutions of individual vinylmetallics in DME or THF into brief contact with sodium or potassium at low temperatures generates radical-anions, but only with triphenyl(vinyl)silane (IX) is the signal ascribable to the parent compound. Triphenyl(vinyl)germane (XV) and triphenyl(vinyl)tin (XVI) produce, as the only detectable radical-anions, those of benzene and biphenyl. However, all three vinylmetallics yield greater or lesser amounts of the hexaphenyldimetallic (XVIII) and ethylene upon treatment with an alkali metal. This reaction is consistent with the generation and direct decomposition of a vinylmetallic radical-anion (XVII, eq. 7):

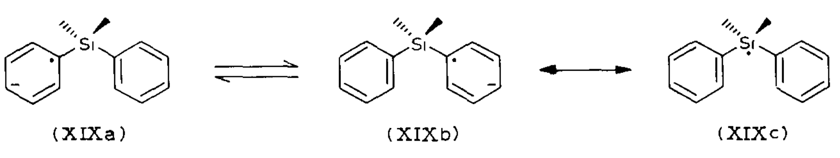


(7)

Discussion

Parent radical-anions of organosilanes bearing only aryl and saturated hydrocarbon groups

In 1,2-dimethoxyethane containing hexamethylphosphorus triamide the phenylsilanes of this type all generated radical-anions with potassium, whose ESR spectra were completely consistent with the presence of the parent radical-anion at −70 °C. With the series of trimethyl(phenyl)silane (I), dimethyl(diphenyl)silane (II) and methyl(triphenyl)silane (III), the added electron is accommodated in the symmetric antibonding molecular orbital and hence free spin is maximized at C(1) and C(4) of the phenyl group [2]. But the successive decrease in the hyperfine coupling constant $a_{C(4)}$ for I (8.10 G), II (4.21 G) and III (2.80 G) shows that the electron is rapidly being exchanged between the rings in II and III (since a is proportional to free spin density) [3] (Table 1) (XIXc). Since in all three cases the total ESR spectral width of I–III was less (16–18 G) than that expected for the benzene radical-anion (22.5 G) [3], there is considerable spin density on silicon (XIXc, eq. 8). Furthermore, the simulation of the observed spectra for II and III and the observation of identical spectra for III and for cyclopropyl(triphenyl)silane (VII) demonstrate that there is little free spin density on the CH_3 of III or the cyclopropyl of VII (< 0.10 G).

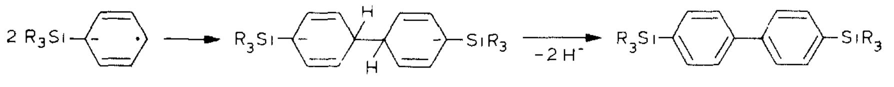


(8)

In the absence of HMPT, the electron exchange depicted in eq. 8 was slower so that the phenyl rings were no longer equivalent (eq. 2).

Similar electron exchange between the phenyl rings was also observed for the parent radical-anions of tetraphenylsilane (IV) and hexaphenyldisilane (V). The observed broad splitting is consistent with electron exchange between at least two phenyl rings and the narrowing of the spectral width (17.2 for IV and 14.1 G for V) indicate considerable spin density on silicon. Further resolution of these spectra was precluded by irreversible chemical change.

Indeed, all the foregoing radical-anions decomposed with increasing time and temperature, although inclusion of some HMPT in the DME enhanced the kinetic stability of the ESR-active intermediates. The methyl(phenyl)silanes decomposed to form radical-anions of benzene and biphenyl. Such products can readily be explained by: (a) the scission of XIX into a phenyl anion and an $R_3Si\cdot$ radical, after which benzene arises by proton abstraction from the DME, and (b) the *para* coupling of two XIX radical-anions to give hydrobiphenyl derivatives that aromatize by hydride loss (eq. 9):



(9)

(XX) (XXI) (VIII)

As was shown in this study, a compound of type VIII, 4,4′-bis[cyclopropyl(diphenyl)silyl]biphenyl, promptly undergoes cleavage with potassium and DME at −70 °C to yield biphenyl. Also, the coupling of XX to XXI is well precedented and has been realized on a preparative scale for R_3Si = cyclopropyl(diphenyl)silyl [11].

Such cleavage reactions also give rise to silylpotassium intermediates, R_3SiK, which then were methylated by the DME. In this manner, III eventually reacted with potassium to form II (cf. infra).

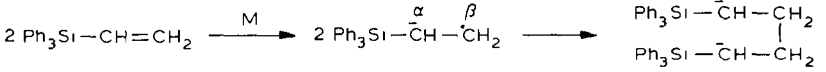
Radical-anions from phenylsilanes bearing a readily cleavable group

Chloro(triphenyl)silane (VI) reacted with potassium, not by dimerizing to the disilane V, but rather by forming triphenylsilylpotassium (eq. 10). In a known reaction with DME [14,17], this then produced III, which by a series of phenyl–silicon bond cleavages and methylation by DME led to I:

$$Ph_3SiCl \xrightarrow{K} Ph_3SiK \xrightarrow{DME} \underset{(III)}{Ph_3SiMe} \xrightarrow[2\ DME]{1\ K} \underset{(I)}{PhSiMe_3} \tag{10}$$

Despite the tendency of cyclopropyl rings attached to aryl groups to be cleaved by alkali metals [18], no such cleavage was observed with cyclopropylsilanes. In fact, with alkali metals cyclopropyl(triphenyl)silane(VII) underwent cleavage of a phenyl group preferentially. This unexpected stability of the strained C(3) ring could be rationalized from the lack of any significant free spin in the radical anion (< 0.10 G). The spin is principally in the phenyl ring and that is the site of the observed chemistry: both carbon–silicon bond cleavage and reductive dimerization (eqs. 9 and 11).

With phenylsilanes bearing vinyl or acetylenic groups, unstable radical-anions can be observed whose hyperfine coupling constants accord with the free spin being on the vinyl or acetylenic group, rather than on the phenyl group. The similar ESR spectra generated from triphenyl(vinyl)silane (IX) and triphenyl(*trans*-1-propenyl)silane (X) reinforce the conclusion that each is due to the parent radical-anion *. For IX the observed splitting rules out major phenyl ring involvement. As with other Ph_3SiR types, such as III and VII, one would expect a three-proton splitting with a 2.80 G. Since IX is known to undergo a facile alkali metal-induced dimerization through the radical-anion (XXII, eq. 11), we suggest that the ESR



$$2\,Ph_3Si{-}CH{=}CH_2 \xrightarrow{M} 2\,Ph_3Si{-}\overset{\alpha}{\bar{C}H}{-}\overset{\beta}{\dot{C}H_2} \longrightarrow \begin{array}{l} Ph_3Si{-}\bar{C}H{-}CH_2 \\ \qquad\qquad\quad | \\ Ph_3Si{-}\bar{C}H{-}CH_2 \end{array} \qquad (11)$$

(IX) (XXII)

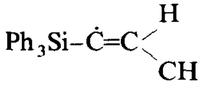
hyperfine pattern arising from IX is due to the exchange of the electron between XXII and IX in a complex (eq. 3). The observed values of $a_{\alpha\text{-H}}$ and $a_{\beta\text{-H}}$, 5.02 and 1.60 G, would be about half of a values for protons α to silicon (9.05 G) and β to silicon (3.2 G), in non-exchanging radical-anions [1].

The observed spectrum of the propenyl X is in best accord with the presence of *cis*- and *trans*-radical-anions (eq. 4). The two different three-proton splittings are difficult to rationalize in any other way. The magnitude of vinyl proton a-values are somewhat low for non-exchanging sites, but the inductive effect of the methyl group may lower the total spin density on the vinylic group. As has been shown in preparative-scale reactions, *cis*-X undergoes dimerization much less readily than IX but readily isomerizes to the *trans*-isomer of X.

All three vinylsilanes examined, IX, X and diphenyl(divinyl)silane (XI), showed a tendency with alkali metals to give decomposition products that involved chemical reaction at the vinyl group (eq. 5). ESR studies on IX and X demonstrate that the vinyl group is the primary site of free elecron spin in the radical-anion.

With triphenyl(1-propynyl)silane (XII), no parent radical-anion could be detected. The observed ESR spectrum cannot be ascribed to radical-anion XXIII, for

$Ph_3Si{-}\dot{C}{=}\bar{C}{-}CH_3$
(XXIII)



$$Ph_3Si{-}\dot{C}{=}C\begin{array}{l} H \\ CH_3 \end{array}$$

(XXIV)

an a-value of 9.52 G is improbably high for a methyl group in such a system. Moreover, even if such a value were accepted, XXIII would not account for the one-proton splitting of 4.96 G. Vinyl radical XXIV would require much larger a-values than were observed. The 1-methylvinyl radical, for example, displays a methyl a of 19.48 G and vinyl a-values of 32.9 and 57.9 G [19]. On the other hand, the allyl radical has coupling constants of 13.93 and 14.83 G for the terminal protons and 4.06 G for the central proton [20]. With the reasonable expectation that the terminal protons might well give an average a-value in XIV, the ESR signal is best ascribed to the 1-triphenylsilylallyl radical.

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* In a preliminary report [10] our studies had led only to ESR spectra of decomposition products (strong doublet of a 8.5–9.5 G) or a spectrum derived from IX (a 5.02, 2H; a 1.60 G, 4H) that we had ascribed to a radical-anion from a 1,4-bis[hydrido(diorgano)silyl]benzene. Our subsequent failure to detect any such hydride in preparative-scale runs and the similarity of the improved ESR spectra obtained from IX and X has caused us to abandon our former interpretation.

Radical-anion intermediates in organosilane reactions

As is evident from the foregoing discussion, the site of maximum free spin density, either on a group or on an atom, in the parent organosilicon radical-anion determines the sites of subsequent cleavage, coupling, isomerization or reduction processes. This study clearly demonstrates that radical-anions are the key reactive intermediates in the reactions of organosilanes with alkali metals. That ligand to which an electron is preferentially transferred is the one that undergoes subsequent reaction.

But a further question can be raised: Does the radical-anion react directly or does it react through a subsequent dianion (XXV)? Although the relative roles of XXII

$$\underset{(\text{XXII: E = Si, Ge, Sn})}{\text{Ph}_3\text{E–}\dot{\text{C}}\text{H–}\bar{\text{C}}\text{H}_2} \xrightarrow[?]{+e^-} \underset{(\text{XXV})}{\text{Ph}_3\text{E–}\bar{\text{C}}\text{H–}\bar{\text{C}}\text{H}_2} \rightarrow \text{reactions} \qquad (12)$$

and XXV undoubtedly vary with the given reaction, there seems little question that radical-anions are the immediate precursors in electron-transfer (eqs. 2, 3, 8), isomerization (eq. 4) and coupling (eqs. 5, 9, 10) processes. Finally, since all the vinyl(triphenyl)metallics (IX, XV, XVI) react with alkali metals to yield some hexaphenyldimetallics (5–90%), radical-anions must be able to cleave directly to CH_2=CH–M and Ph_3E . Only in this way could the requisite $Ph_3E^{\cdot}$ radicals arise readily.

Experimental

Starting materials

Chloro(triphenyl)silane, tetraphenylsilane, trimethyl(phenyl)silane and triphenyl(vinyl)silane were obtained from commercial sources and then recrystallized, until their melting points and ^{1}H NMR spectra accorded with literature data. Similarly, commercial samples of trimethyl(vinyl)silane (b.p. 55–56 °C), benzyl(trimethyl)silane (b.p. 191–192 °C) and diphenyl(divinyl)silane (b.p. 108–110 °C/0.07 mmHg) were carefully fractionated in an apparatus free of silicone grease, until GC criteria of purity were met. Analytical samples of triphenyl(*trans*-1-propenyl)silane, triphenyl(1-propynyl)silane, cyclopropyl(triphenyl)silane and 4,4′-bis[cyclopropyl(diphenyl)silyl]biphenyl were prepared by Dr. Goutam Gupta of this Laboratory [11].

Finally, methyl(triphenyl)silane was prepared from phenylmagnesium bromide and chloro(methyl)diphenylsilane in ethyl ether and then recrystallized from absolute ethanol, m.p. 67.5–68 °C [21]. Similarly, dimethyl(diphenyl)silane was prepared from methylmagnesium chloride and dichlorodiphenylsilane in tetrahydrofuran. Careful fractional distillation of the crude product gave the pure silane, b.p. 127–129 °C/8 mmHg) [22].

The 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF), which were used as solvents for the organosilicon radical-anions, were dried preliminarily by heating over, and distilling from, sodium metal slices. The solvent was then thoroughly dried and deoxygenated by heating it with potassium metal and some benzophenone under argon at reflux for several days. Then the solvent was distilled under argon into a flask containing a fresh charge of benzophenone and potassium. After being attached to a vacuum line the solvent was stirred magnetically for 2 h (immediate development of blue ketyl color) and then degassed by repeated freeze-thaw cycles.

(The use of $LiAlH_4$ is not recommended because it is less effective in purifying the solvent and can give rise to spurious ESR signals [23]).

Metallic potassium, freshly stripped of its oxide coat, was placed in a large-bore, flat-bottomed tube surmounted by a ground-glass joint. Glass capillary tubes, sealed at one end, were placed on top of the potassium slices with their open ends down. Under reduced pressure the potassium was melted and an atmosphere of argon readmitted to force the molten metal up into the capillaries. Subsequent sealing of the tubes provides a convenient way of handling potassium for radical-anion formation.

Radical-anion formation

The two procedures for generating radical-anions were devised to avoid any possible contamination of the samples by silicone grease from stopcocks or joints. In the first method, the main reaction chamber A was fused, on the one side, to a small tube B, which contained the potassium metal (broken capillary tube). On the other side, A was fused to a glass frit C, beyond which the frit tube was fused to 2 or more glass ESR sample tubes (D). The silane was placed in A and then potassium in B was heated so as to form a metal mirror on the upper part of A. Through a vacuum manifold the solvent was condensed into A. The whole A-B-C unit is sealed, removed from the vacuum and cooled in a bath at −80 °C. By tilting the apparatus the cold solution of the silane could be brought into contact with the potassium mirror. After colors had developed, the apparatus was tilted to filter the radical-anion solution through frit C and into one of the ESR tubes D. The ESR tube was cooled and sealed off with a torch. When dilution of the sample was desired, solvent from A could be condensed into C and thence D.

In the second method, shorter reaction times could be permitted by omitting the glass frit C and side arm tubes D. An ESR tube was fused directly on the bottom of A and the silane with its required solvent introduced directly into the ESR tube. Here again, tilting of the apparatus brought the silane solution into contact with the potassium mirror deposited on the upper wall of A. At the concentrations employed (0.005–0.01 *M*), no metal particles were seen in the resulting radical-anion solution.

Electron Spin Resonance measurements

The ESR spectra were recorded with a Varian spectrometer, Model V-4502, operating nominally at 9.5 GHz (X-band) with 100 KHz field modulation. The 9-inch electromagnet was equipped with a Fieldial magnetic field regulator. A saturated aqueous solution of potassium peroxylamine disulfonate [24] at 25 °C was used to calibrate the magnet sweep width by using the nitrogen hyperfine splitting of 13.0 G [25]. This calibration was stable ±0.02 G over a period of several months and spectra of several compounds (e.g., biphenyl, trimethyl(phenyl)silane) gave hyperfine splitting constants in close agreement with reported values. To avoid saturation and hence line-broadening, spectra were measured at incident power levels of 30 μW or less. The ESR spectra were recorded in first derivative presentation by modulation and phase detection. Modulation amplitudes were between 0.05 and 0.60 G, with the majority being less than 0.15 G.

The resonant cavity used most frequently was a multipurpose rectangular cavity operating in the TE_{102} mode. This was equipped with a vacuum-jacketed quartz Dewar flask to contain the sample; the flask could be cooled in a stream of cold nitrogen. Most frequently, high-purity quartz tubes of 1 mm I.D. were used for the samples.

Simulation of ESR spectra

The ESR spectra were calculated by using the computational scheme described by Stone and Maki [26]. The program was modified for use with a Univac computer, Model 1108, and a Calcomp plotter. The program as listed requires about 40k locations for data storage and 5k for instructions. A description of the input variables, a program listing, a sample of the printed output and a collation of calculated ESR spectra for the silane studied here have been published in a doctoral dissertation [27]. Experimental spectra obtained from cyclopropyl(triphenyl)silane, triphenyl(1-propynyl)silane, diphenyl(divinyl)silane and triphenyl(vinyl)silane have been previously published [10] and hence will not be repeated here.

ESR spectral observations and data

Trimethyl(phenyl)silane (I). After a 30-s exposure to a potassium mirror at −70 °C, a solution of I in DME turned a dark green, but after 10 min the solution had become a royal blue. This color could be reversibly discharged and then regenerated by alternately warming and cooling the solution. An ESR spectrum of the blue solution could be analyzed very satisfactorily with coupling constants previously reported [1,14]: a_o 2.65; a_m 1.06; a_p 8.10; a_{Me} 0.30 G; with a_{Si} unobserved. After 20 min the methyl splittings were obscured and after 4 h a 7-line spectrum with a 3.71 G and with binomial intensities emerged, signaling the formation of the benzene radical-anion.

Dimethyl(diphenyl)silane (II) A solution of II in a mixture of DME with 2% (v/v) of hexamethylphosphorus triamide (HMPT) gave, on contact with potassium, a dark-red solution, whose ESR spectrum remained unchanged after 5 h at −70 °C. This spectrum could be simulated very closely by assuming the following coupling constants (proton no.): a_p 4.21 (2H); a_o 1.50 (4H); a_{Me} 0.20 G (6H); and a_m unobserved (< 0.2 G).

A solution of II in pure DME turned dark-green immediately on contact with potassium at −70 °C. After 60 s the solution became orange-brown and some solid had deposited. The ESR spectrum had 11 main absorption peaks and exhibited line-width alternation on its principal peaks: the central peak was almost featureless, while its neighboring peaks displayed distinct hyperfine splittings (a_{Me}). The spectrum could be simulated very closely, however, even including the line width alternation, by assuming a slight inequivalence of the rings where $a_p \neq a_{p'}$; a_p 4.21 (1H); $a_{p'}$ 4.1 (2H); a_o 1.50 (4H); a_{Me} 0.20 G (6H); and $a_m < 0.20$ G. When these solutions were warmed above −30 °C, the spectrum broadened markedly until only one diffuse signal remained at 25 °C.

Methyl(triphenyl)silane (III). Contact of a solution of III in DME with a potassium mirror gave at first a dark-red solution, whose ESR spectrum consisted of a 5-line pattern having binomial intensities and a 1.65 G. This signal can be assigned to the formation of a 1,4-bis(triorganosilyl)benzene (XIX) anion or, more likely, that of dimethyl(diphenyl)silane (II).

After 30 min a dark green solution was formed, whose ESR spectrum was stable even at 25 °C and persisted for 22 days. The signal consisted of at least a 5-line, broad pattern whose splittings could be simulated closely by a 4-proton coupling constant of a 2.7 and a 2-proton coupling of a 5.4 G. This signal corresponded well with that of the biphenyl radical-anion, whose wing splittings were obscured.

A solution of III in DME containing 2% of HMPT gave a dark-red solution upon exposure to potassium at $-70\,^{\circ}$C. Its ESR spectrum, which was unchanged even after 48 h at 25 °C, consisted of 20 main peaks and had a total width of 16 G. The pattern could be simulated excellently by assuming these hyperfine splitting constants (proton no.). a_p 2.80 (3H); a_o 1.15 (6H); a_m 1.05 (6H); and $a_{Me} < 0.2$ G.

Tetraphenylsilane (IV). A solution of IV in DME developed a red-brown color after 2 min in contact with potassium at $-70\,^{\circ}$C. This gave rise to a 15-line ESR spectrum having a total width of 17.2 G. As the odd number of lines indicated splitting by an even number of protons, the spectrum suggests electron spin delocalization over two or more phenyl groups. Since the total spectral width was only slightly less than that of $C_6H_5Si(CH_3)_3$, one can conclude that both radical-anions have about the same free spin density on silicon. Further analysis of the spectrum was not warranted in view of its low resolution. After 24 h of contact with potassium at $-70\,^{\circ}$C the solution was dark-green and a broad ESR singlet appeared. This signal disappeared upon warming to 25 °C.

Hexaphenyldisilane (V). Upon contact with a potassium mirror at $-70\,^{\circ}$C a solution of V in DME turned successively lemon-yellow and then deep green, and finally deposited a colorless solid. Thereafter, the solid redissolved to give an orange solution, whose ESR spectrum showed a 9-line pattern with a strong central peak and a total width of 14.1 G. This spectrum, which is consistent with splitting by an even number of protons, can be simulated closely by a two-proton coupling of 4.20 G and four-proton coupling of 1.65 G. The possibility that this spectrum is due to the formation of the radical-anion of 1,4-bis[hydrido(diphenyl)silyl]benzene, namely 1,4-$Ph_2HSiC_6H_4SiHPh_2$, can be ruled out on the basis of known a-values for such systems [14,16]. The a_{SiH} is 6.10–7.28 G and a for the p-phenylene C–H protons is 1.76–2.1 G. The observed spectrum from V accords better with an electron delocalized over two phenyl groups with a_p 4.20 G (2H) and a_o 1.65 G (4H). After standing for 24 h at $-70\,^{\circ}$C, the foregoing spectrum was overshadowed by the characteristic 7-line spectrum of the benzene radical-anion.

Chloro(triphenyl)silane (VI) Upon contact with potassium at $-70\,^{\circ}$C a solution of VI in DME turned dark orange after 2 min but no ESR signal was observed. After 45 min the solution became dark green and a strong ESR signal developed. The pattern of this spectrum could be simulated closely by using the values of a_p, a_o and a_{Me} for trimethyl(phenyl)silane (I). With time, this signal was obscured by the 7-line signal of the benzene radical-anion.

A sample of VI at a much higher concentration in DME gave again the radical-anions of I and then of benzene. Raising the sample to 25 °C changed the color to light yellow and generated a new 16-line ESR spectrum having a width of 15.4 G (Spectrum A). This spectrum did not resemble that of hexaphenyldisilane but agreed very closely with that of methyl(triphenyl)silane (III). The a-values of III could be used to simulate this spectrum satisfactorily.

Cyclopropyl(triphenyl)silane (VII). In DME containing 2% of HMPT this compound reacted with potassium at $-70\,^{\circ}$C to form a dark orange solution that was identical with that observed with methyl(triphenyl)silane in the same medium. This spectrum could be simulated with excellent congruence by employing the same values of a_p, a_o, a_m and a_{Me} used for III. The spectrum was stable at $-50\,^{\circ}$C but the intensities of the peaks changed irreversibly above −30 °C.

When VII in pure DME was exposed to potassium at −70 °C, the first spectrum observed for the orange solution was a 16-line pattern separated by 0.46 G and having a total width of 15 G. This spectrum was identical with that obtained from a solution of VII in DME2%-HMPT.

4,4′-Bis[cyclopropyl(diphenyl)silyl]biphenyl (VIII). On contact with potassium at −70 °C, a DME solution of VIII gave a dark green solution, whose ESR spectrum was the characteristic nonet of the biphenyl anion (a_p 5.46, a_o 2.73 and a_m 0.43 G). After 24 h at −70 °C, the septet of the benzene anion dominated (a 3.76 G).

Triphenyl(vinyl)silane (IX). Low concentrations of IX in DME (10^{-5} M) gave the ESR spectrum of the benzene anion (7-lines of binomial intensity with a 3.75 G) upon contact with potassium at −70 °C. Higher concentrations gave yellow-orange colors after 3 min but no ESR spectrum; after 30 min a dark green color developed and strong broad two-peaked ESR spectra were exhibited (a 8.0–9.0 G).

In a 2%-HMPT/DME solution IX gave a dark red color after 20 min and exhibited a reproducible, broad-lined spectrum: 9-lines analyzable as generated by 2 protons of a 5.02 and 4 protons of a 1.60 G, with a width of 21 G. Upon longer contact with potassium, solutions of IX in DME developed dark green colors and an ESR spectrum of the biphenyl anion.

Triphenyl(trans-1-propenyl)silane (X). Like IX, solutions of X in DME did not give reproducible ESR spectra upon reaction with potassium at −70 °C. The one consistent feature of such spectra was a major doublet splitting of 8.5 ± 0.1 G. In 2% HMPT/DME X gave orange-red colors and complex, broad-lined spectra with a width of 16.0 G, which were reproducible. A set of coupling constants that can simulate the observed spectrum fairly well are: a 5.0 (1H); a 1.8 (3H); a 1.4 (1H); and a 0.8 G (3H).

Diphenyl(divinyl)silane (XI). Potassium caused polymerization of XI in concentrated DME solutions. In high dilution (10^{-5} M) an 11-line spectrum with a width of 20 G was observed in the orange solution. The spectrum could be simulated closely by assuming a 1-proton, a 2-proton and another 2-proton splitting with a values of 7.10, 1.95 and 1.55 G, respectively.

Triphenyl(1-propynyl)silane (XII). Solutions of XII that were 0.02 M in DME gave upon contact with potassium an 8-line major spectrum with much more splitting of 0.45 G between the major peaks. With time, this smaller splitting was obliterated. The total width of the spectrum was over 33 G. This spectrum can be simulated to account for the 8 major peaks by assuming splitting by 3 protons with a 9.52 and by 1 proton with a 4.96 G.

Solvent blanks. Blank runs were made by allowing the pure solvents to react with a potassium mirror, both at −70 and at 25 °C for extended periods. Runs were also made using solutions of stopcock grease. In no case did a detectable ESR signal arise.

Cleavage reactions by metals

Triphenyl(vinyl) derivatives

(a) Triphenyl(vinyl)silane (IX). A solution of 14.3 g (50 mmol) of IX in 250 ml of DME was stirred at 25 °C with 1.15 g (50 mg-atoms) of freshly cut sodium slices until a red-orange color developed. The solution was cooled to −80 °C for 18 h. The

dark red solution was hydrolyzed with deoxygenated 1*N*-aqueous HCl at −80 °C under argon. Separated and dried over anhydrous $MgSO_4$, the organic layer was evaporated to yield 13.3 g of organic product. By ^1H NMR and IR spectroscopy, no detectable amounts of bis-1,4-triphenylsilylbutane were observed. The IR spectrum appeared to be identical with that of IX, but the NMR spectrum revealed some changes in the aromatic protons (no SiH peak was observed). By distillation the bulk of IX was removed and the residue extracted to yield insoluble hexaphenyldisilane, (10%), as verified by a mixture m.p. and IR spectroscopy.

A solution of lithium naphthalenide (50 mmol) in 100 ml of DME was allowed to react with 50 mmol of IX in 100 ml of DME at −70 °C. After 4 h a work-up showed that the triphenyl(vinyl)silane was unchanged.

(b) Triphenyl(vinyl)germane (XV). In a similar manner, a solution of 50 mmol of XV in 250 ml of DME was stirred with fresh potassium slices at −80 °C for 18 h. Usual work-up and column chromatography on alumina gave much recovered XV and about 5% of hexaphenyldigermane, as verified by mixture m.p. and IR spectroscopy.

(c) Triphenyl(vinyl)tin (XVI). A solution of 47 mg (0.122 mmol) of XVI in 5 ml of DME was allowed to react with a potassium mirror at −70 °C. Hydrolysis gave a colorless, insoluble solid that was recrystallized from petroleum ether. The resulting crystals melted at 231–231.5 °C and represented a 91% yield of hexaphenylditin. A mixture m.p. and an IR spectral comparison verified its identity.

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