

Preliminary communication**Chemistry of alkali metal-unsaturated hydrocarbon adducts
VIII*: ESR detection of radical-anion intermediates derived from α,β -unsaturated organosilanes**

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The remarkably efficient bimolecular reduction of both triphenyl(vinyl)silane¹ and cyclopropyl(triphenyl)silane² by means of alkali metals strongly implies the intermediate formation of radical anions. However, although stable radical anions of various arylsilanes have been detected by electron spin resonance spectroscopy^{3,4}, no such ESR studies have been made on those organosilanes that have also been shown to undergo subsequent bimolecular reduction or silicon-carbon bond cleavage reactions. The latter organosilanes would be of particular interest, since their study might permit a test of the possible connection between the sites of high free-spin density in the ground states of the radical anions and the sites of chemical reaction. In this Communication we wish to report ESR data for a series of α,β -unsaturated organosilanes whose chemical behavior toward alkali metals has also been carefully examined. By choosing phenylsilanes that also contained 1-alkenyl, 1-alkynyl or cyclopropyl groups we hoped to assess the intramolecular electron affinities or organic groups attached to silicon. For this purpose the radical anions were generated from the following silanes dissolved in donor solvents by contact with potassium mirrors at -70° or lower: triphenyl(vinyl)silane, diphenyl-(divinyl)silane, triphenyl(*trans*-1-propenyl)silane, triphenyl(1-propynyl)silane, methyl-(triphenyl)silane and cyclopropyl(triphenyl)silane. Typical, reproducible ESR spectra of the radical anions formed from some of these substances as 10^{-3} – 10^{-4} M solutions in 1,2-dimethoxyethanehexamethylphosphoric triamide (HMPT) are offered in Fig. 1–4**.

* For Part VII see ref. 2.

** Standard vacuum-line technique was used for preparing and diluting the solution samples contained in 1–3 mm I.D. quartz tubes. ESR spectra were recorded with a Varian V-4502 spectrometer operating nominally at 9.5 GHz (X-band) with 100 kHz field modulation. Spectra were calculated by use of the computational scheme described by Stone and Maki⁵ and were simulated with a CALCOMP plotter, after the program was adapted for a Univac 1108 computer.

The inclusion of 2% of HMPT generally led to ESR spectra that were reproducible over longer periods of time.

Calculated spectra could be obtained for cyclopropyl(triphenyl)silane (I) and methyl(triphenyl)silane (II) that were superimposable with the experimental spectra (Fig. 1) and with each other. The proton hyperfine splitting constants [a in gauss(G)] and the multiplicities are in complete accord with the conclusion that the free-spin density is delocalized (or exchanged) over all three phenyl rings and is maximized at the *para* positions (since $a \propto$ free-spin density⁶). Also, there is considerable spin density at silicon, since the overall spectral width is 16 G*; but there is very little on the methyl or cyclopropyl group, since $a(\text{CH}_3)$ or $a(\text{CH})$ is <0.2 G.

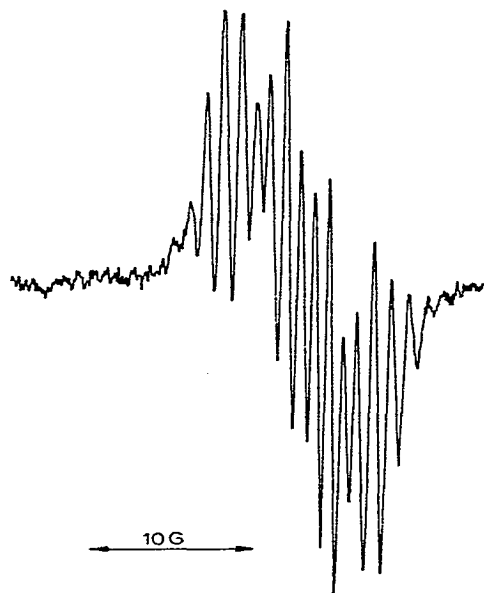


Fig. 1. ESR spectrum arising from cyclopropyl(triphenyl)silane, ascribable to splitting by three (2.80 G) six (1.15 G) and six (1.05 G) protons, respectively.

Detection of the parent radical anions of triphenyl(1-propynyl)silane (III) and of diphenyl(divinyl)silane (IV) failed, but the observation of radical intermediates did permit us to correlate the ESR species with the known chemical reactions. The ESR intermediate from III (Fig. 2) is a stable radical having a spectral width of 33 G and a splitting corresponding to three protons with $a = 9.52$ G and one proton with $a = 4.96$ G. The spectrum from IV (Fig. 3) is explicable in terms of splitting by one ($a = 7.1$ G), two (1.95 G) and two (1.55 G) protons, respectively. Now, the preparation metal reductions at -78° of III lead to triphenyl(*trans*-1-propenyl)silane; similar treat-

* By the McConnell relationship⁶ a radical anion of a benzene derivative having no exocyclic electron delocalization is expected to have a total spectral width of ca. 22.5 G.

ment of IV leads to polymerization or to 1,1-diphenylsilacyclopentane⁷. Thus, it seems most reasonable to ascribe the foregoing ESR spectra to the triphenylsilylallyl radical (V) and to the radical anion (VI), respectively:

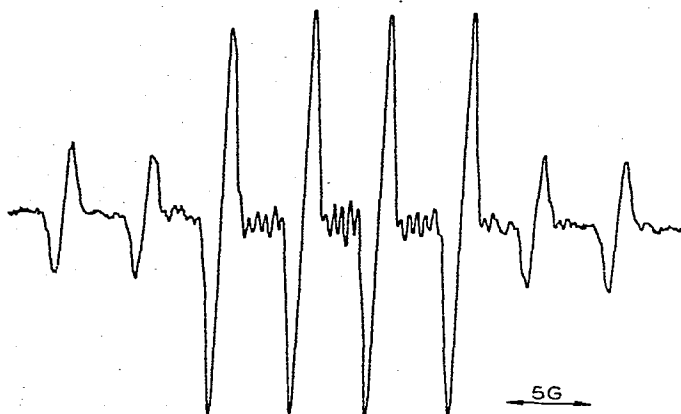
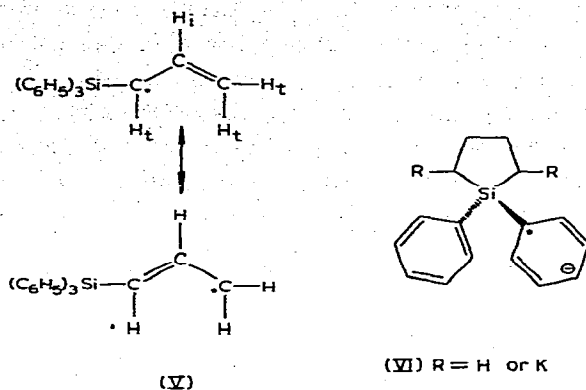


Fig. 2. ESR spectrum arising from triphenyl(1-propynyl)silane, ascribable to splitting by one (4.96 G) and three (9.52 G) protons, respectively.

In a fluid medium under our spectral resolution the terminal allylic protons of V would be expected to be equivalent⁸; and the magnitudes of a_t and a_i are more consistent with known allylic values^{8,9} (a_t 14–15 G and a_i 4.1 G) than with purely vinylic or alkyl coupling constants^{9*}. The ESR splitting observed from IV is in best accord with VI, where the radical anion is confined to one ring. The somewhat smaller a_{para} (which is usually ca. 8 G) may stem from the anionic charge on the silacyclopentane arising from its mode of formation¹. Such charge may also be responsible for the lack of electron exchange between

* Although a neutral radical, such as V, might well be expected to undergo ready reduction to an ESR-inactive anion, when in contact with a metallic mirror, note that V is a derived species, not again brought in contact with the metallic mirror.

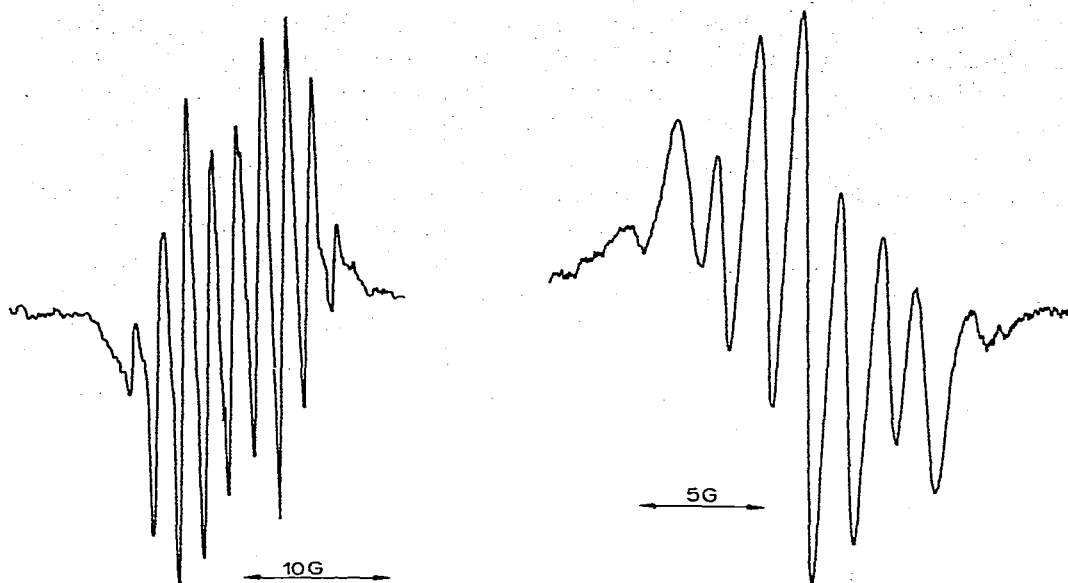
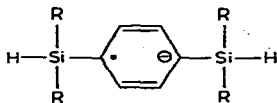


Fig. 3. ESR spectrum arising from diphenyl(divinyl)silane, ascribable to splitting by one (7.1 G), two (1.95 G) and two (1.55 G) protons, respectively.

Fig. 4. ESR spectrum arising from triphenyl(vinyl)silane, ascribable to splitting by two (5.02 G) and four (1.60 G) protons, respectively.

the phenyl rings, for the radical anion of dimethyl(diphenyl)silane itself does undergo such intramolecular electron exchange under the same conditions^{10,11}★.

No parent radical anions of either triphenyl(vinyl)silane (VII) or triphenyl(*trans*-1-propenyl)silane (VIII) could be detected with certainty. The rapid changes in the signal and the samples' color showed that irreversible reactions had occurred. The first, relatively stable signal from either VII or VIII had a strong doublet ($a = 8.5$ – 9.5 G) superimposed on a complex pattern. In DME–HMPT VII eventually yielded a spectrum (Fig. 4) ascribable to splitting by two ($a = 5.02$ G) and four ($a = 1.60$ G) protons, respectively. Based upon previous ESR studies of related systems^{11,13}★★, this signal is assigned to structure IX.



(IX)

With $R = \text{CH}_3$ or C_6H_5 , IX could easily arise from devinylation², *para*-coupling^{2,14} and attack of R_3SiK on the solvent¹⁵.

★ Cf. ref. 12 for a report on the temperature dependence of this exchange under certain conditions.

★★ With different solvent systems and $R = \text{CH}_3$ and C_6H_5 , Si–H and aromatic C–H coupling constants for radical anions of type IX have been suggested to be 6.10–7.28 G and 1.75–1.9 G, respectively. (refs. 11 and 13).

From the direct observation of the parent radical anion from cyclopropyl(tri-phenyl)silane, it is clear that the R-group of greatest free-spin density in RR_3Si is the one in which bimolecular reduction and cleavage by alkali metals preferentially occur². Further, the site of greatest spin density within that group (*para*) is the preferred site of coupling². The ESR behavior of triphenyl(1-propynyl)silane toward alkali metal serves to show that electron uptake occurs preferentially at the triple bond, rather than at the phenyl group. Since only derivative radical anions were obtained from vinylsilanes, IV, VII and VIII, we can conclude that here electron-uptake and chemical reaction occur at the vinyl group in preference to the phenyl group. In light of these results, the electron affinities of these groups attached to silicon decrease in the series: $C\equiv C-R$ and $CH=CHR > C_6H_5 > CH_3$ and cyclo- C_3H_5 . If such a variation is ascribed to a lessening $d_{\pi-p\pi}$ conjugating effect with silicon¹, one can further conclude that the cyclopropyl group has no olefin-like conjugating ability toward silicon.

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REFERENCES

- 1 J.J. Eisch and R.J. Buehler, *J. Org. Chem.*, 28 (1963) 2876
- 2 J.J. Eisch and G. Gupta, *J. Organometal. Chem.*, 20 (1969) P9.
- 3 G. Urry in E.T. Kaiser and L. Kevan (Eds.), *Radical Ions*, Interscience, New York, N.Y., 1968, p. 275-299.
- 4 F. Gerson, J. Heinzer, H. Bock, H. Alt and H. Seidl, *Helv. Chim. Acta*, 51 (1968) 707.
- 5 E.W. Stone and A.H. Maki, *J. Chem. Phys.*, 38 (1963) 1999.
- 6 (a) H.M. McConnell, *J. Chem. Phys.* 24 (1956) 764;
(b) H.M. McConnell and D.B. Chestnut, *J. Chem. Phys.*, 28 (1958) 107.
- 7 J.J. Eisch and G. Gupta, unpublished studies.
- 8 C. Heller and T. Cole, *J. Chem. Phys.*, 37 (1962) 243.
- 9 R.W. Fessenden and R.H. Schuler, *J. Chem. Phys.*, 39 (1963) 2147.
- 10 L.E. Smith, *Doctoral Dissertation*, May, 1972, The Catholic University of America.
- 11 Y.-P. Wan, D.H. O'Brien and F.J. Smentowski, *J. Amer. Chem. Soc.*, 94 (1972) 7680.
- 12 E.S. Kean, K. Fisher and R. West, *J. Amer. Chem. Soc.*, 94 (1972) 3246.
- 13 (a) I.G. Makarov, F.M. Kozakova and Y.K. Syrkin, *Zh. Strukt. Khim.*, 8 (1967) 164;
(b) I.G. Makarov and F.M. Kozakova, *Zh. Strukt. Khim.*, 9 (1968) 996.
- 14 D.R. Weyenberg and L.H. Toporcer, *J. Amer. Chem. Soc.*, 84 (1962) 2843.
- 15 H. Gilman and H.J.S. Winkler in H. Zeiss (Ed.), *Organometallic Chemistry*, Reinhold, N.Y., 1960, p. 270-345.