

is converted stepwise into labeled ubiquinone-10 and rhodoquinone-10 (newly identified as an amino derivative of Q-10<sup>21</sup>), indicating a 10-unit side chain.

Treatment of I with 3,5-dinitrobenzoyl chloride yielded a monobenzoate derivative:  $\nu_{\text{max}}^{\text{film}}$  no OH absorption, 1755 cm.<sup>-1</sup> (carbonyl), 1540 and 1340 cm.<sup>-1</sup> (nitro); n.m.r.,  $\tau$  0.79 (nitro aromatic, 3 H), 2.69–2.85 (phenol aromatic, 4 H), 5.0 (vinyl, 10 H), 6.80 (benzyl, 2 H), and 7.95 and 8.36 (alkyl, ca. 65 H).

2-Decaprenylphenol is the first known precursor to ubiquinone which possesses both the aromatic nucleus and isoprenoid side chain. Studies are in progress on subsequent biosynthetic steps to ubiquinone, and on the syntheses of these new isoprenoid phenols.

**Acknowledgment.** Appreciation is expressed (K. F.) to Dr. Leo P. Vernon of the Charles F. Kettering Research Laboratory, Yellow Springs, Ohio, for a research grant, and to the Muscular Dystrophy Associations of America, Inc., for a research grant.

(21) H. W. Moore and K. Folkers, *J. Am. Chem. Soc.*, **87**, 1409 (1965).

(22) Post-Doctoral Fellow of the Muscular Dystrophy Associations of America, Inc.

(23) Research Career Awardee GMK6993 of the U. S. Public Health Service.

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## The Magnitudes and Relative Signs of Long-Range Silicon-Proton Coupling Constants<sup>1</sup>

Sir:

A knowledge of the signs of spin-spin coupling constants is of considerable importance in checking the theory for these parameters and in sorting out the magnitudes of the terms contributing to the coupling interaction. Sign determinations are of particular interest for couplings extending over more than two intervening bonds where a cancellation of contributing terms can occur.<sup>2</sup> Most of the relative sign determinations reported thus far<sup>3</sup> have been for proton-proton couplings, and these have been related in turn to an assumed positive value for a directly bonded C<sup>13</sup>-H coupling constant.<sup>4</sup> Correlations of this type have been extended recently to P<sup>31</sup>-H and Si<sup>29</sup>-H coupling constants.<sup>5,6</sup> In this communication we wish to report the relative signs for long-range silicon-proton coupling constants in substituted vinylsilanes.

The proton spectra were recorded on a Varian DP-60 spectrometer and H<sup>1</sup>-{H<sup>1</sup>} decoupling measurements were carried out following the procedure of Freeman.<sup>7</sup>

(1) This work was carried out while the author was guest worker at the National Physical Laboratory, Basic Physics Division, Teddington, England, July-Aug. 1964.

(2) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

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(5) (a) S. L. Manatt, G. L. Juvinal, and D. D. Elleman, *ibid.*, **85**, 2664 (1963); (b) G. M. Whitesides, J. L. Beauchamp, and J. D. Roberts, **85**, *ibid.*, 2665 (1963).

(6) S. S. Danyluk, *ibid.*, **86**, 4504 (1964).

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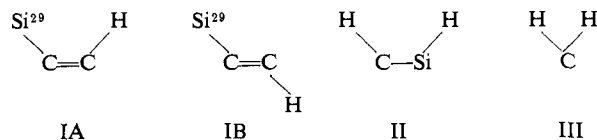
The H<sup>1</sup>-{Si<sup>29</sup>} decoupled spectra were obtained by procedures described previously.<sup>6</sup> A summary of the magnitudes and relative signs for proton-proton and silicon-proton coupling constants for a variety of silicon derivatives is given in Table I. The directly bonded Si<sup>29</sup>-H coupling constants were obtained from the respective Si<sup>29</sup> decoupling frequencies and are somewhat less accurate than the Si<sup>29</sup>C=CH (I) couplings, obtained by an analysis of the Si<sup>29</sup> satellite spectra.

Table I

Compound	Type of coupling	Magnitude, c.p.s.	Sign of J	Sign of K <sup>a</sup>
CH <sub>3</sub> SiHCl <sub>2</sub>	Si <sup>29</sup> -H	285 ± 10	-	+
	H-C-Si-H	3.7 ± 0.1	+	+
CH <sub>3</sub> SiHBr <sub>2</sub>	Si <sup>29</sup> -H	275 ± 10	-	+
	H-C-Si-H	3.6 ± 0.1	+	+
(CH <sub>3</sub> ) <sub>2</sub> SiHCl <sup>b</sup>	Si <sup>29</sup> -H	227 ± 5	-	+
	H-C-Si-H	3.3 ± 0.1	+	+
(CH <sub>3</sub> ) <sub>2</sub> SiHBr	Si <sup>29</sup> -H	211 ± 10	-	+
	H-C-Si-H	3.5 ± 0.1	+	+
(CH <sub>3</sub> ) <sub>2</sub> SiHI	Si <sup>29</sup> -H	225 ± 5	-	+
	H-C-Si-H	3.6 ± 0.1	+	+
(CH <sub>3</sub> ) <sub>2</sub> Si > C=C < H	H-C-H	1.02 ± 0.03	-	-
	Si <sup>29</sup> -C=C-H	4.36 ± 0.05	-	+
	(cis)			
	Si <sup>29</sup> -C=C-H	10.51 ± 0.05	-	+
Cl <sub>2</sub> Si > C=C < H	H-C-H	2.04 ± 0.03	-	-
	Si <sup>29</sup> -C=C-H	7.48 ± 0.05	-	+
	(cis)			
	Si <sup>29</sup> -C=C-H	21.20 ± 0.05	-	+
	(trans)			
	(trans)			

<sup>a</sup> K<sub>IJ</sub> = (2π/hγ<sub>I</sub>γ<sub>J</sub>)J<sub>IJ</sub>. <sup>b</sup> See ref. 6.

The signs of the reduced coupling constants, K<sub>Si<sup>29</sup>-H</sub> and K<sub>II</sub>, are the same in both the monomethyl- and dimethylsilyl halide derivatives. If K<sub>II</sub> is assumed to be positive, in conformity with the signs for other vicinal couplings,<sup>5,8,9</sup> then the absolute sign of the Si<sup>29</sup>-H



coupling constant is also positive in agreement with earlier results.<sup>6</sup> The magnitudes of J<sub>Si<sup>29</sup>-H</sub> for the dimethylsilyl derivatives are slightly less than the values reported for corresponding monomethylsilyl halides by Ebsworth and Frankiss.<sup>10</sup> No significant change of J<sub>Si<sup>29</sup>-H</sub> with halogen substituent (Cl, Br, I) is noted for the dimethylsilyl halides. On the other hand, replacement of a CH<sub>3</sub> group by a halogen leads to an appreciable increase (more positive) of K<sub>Si<sup>29</sup>-H</sub> (~55 c.p.s.). It is likely that similar observations for corresponding

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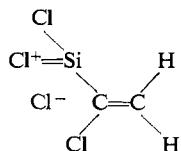
(9) D. P. Evans, S. L. Manatt, and D. D. Elleman, *ibid.*, **85**, 238 (1963).

(10) E. A. V. Ebsworth and S. G. Frankiss, *Trans. Faraday Soc.*, **59**, 1518 (1963).

silyl halides<sup>11</sup> also reflect a trend toward more positive couplings with increasing halogen substituents. These trends can be interpreted semiquantitatively in terms of changes in s-character of the silicon bonding orbitals combined with changes in Si<sup>29</sup>-H bond polarity.<sup>12</sup>

The H<sup>1</sup>-{H<sup>1</sup>} and H<sup>1</sup>-{Si<sup>29</sup>} decoupling results show that the *cis* and *trans* silicon-proton coupling constants and the geminal ( $J_{\text{III}}$ ) coupling constant are all of the same sign in trimethyl- and trichloro- $\alpha$ -chlorovinylsilane. If the reduced Si<sup>29</sup>C=CH (IA) coupling is assumed to be positive, in conformity with the absolute sign determined for *p*-nitrotoluene,<sup>13</sup> then the ratio  $K_{\text{III}}/K_{\text{IA}}$  will be negative ( $J_{\text{IA}}$  is actually negative because of the negative magnetogyric ratio of Si<sup>29</sup>). Therefore  $K_{\text{III}}$  and  $J_{\text{III}}$  are negative in both the  $\alpha$ -chlorovinylsilane derivatives. An opposite sign (assumed to be negative for  $J_{\text{gem}}$  relative to  $J_{\text{cis}}$  (or  $J_{\text{trans}}$ ) has previously been indicated in monosubstituted vinyl compounds with strongly electronegative substituents.<sup>14</sup>

The larger (more negative) value of  $J_{\text{gem}}$  for the more electronegative trichloro substituent group follows the trends noted for other vinyl compounds.<sup>14</sup> In contrast the magnitudes of the long-range Si<sup>29</sup>C=CH couplings appear to be anomalous; from electronegativity considerations both the *cis* and *trans* couplings in the trimethyl compound would be expected to have a larger magnitude (more positive) than the corresponding couplings in the trichloro compound, as has, in fact, been observed for the proton-proton coupling constants in trimethyl- and trichlorovinylsilanes.<sup>15</sup> Although a variety of factors can affect the magnitude of long-range coupling constants,<sup>2,16</sup> it is probable that the "anomalous" silicon couplings arise primarily from hybridization changes of the Si bonding orbitals in much the same manner as for the halosilanes. The magnitude of  $K_{\text{IA}}$  is therefore sensitive to any change in s-character,  $\alpha_c^2$ , of the Si-C bond and since the chloro groups will undoubtedly increase  $\alpha_c^2$ , compared with CH<sub>3</sub> groups,  $K_{\text{IA}}$  will be larger (more positive) in the trichloro derivative. Additional contributions from resonance structures such as



and  $\pi$ -bond interaction between Si and C would also act to increase  $J_{\text{I}}$ . The present results indicate that the major contribution to  $J_{\text{IA}}$  and  $J_{\text{IB}}$  is the contact interaction term and additional contributions from electron-dipole and spin-orbital interactions are not important.<sup>5b</sup>

**Acknowledgments.** The author is indebted to Drs. D. H. Whiffen, K. A. McLauchlan, and A. D. Cohen for many helpful discussions and is very grateful to Dr. E. A. V. Ebsworth for kindly providing the mono- and dimethylsilanes. This paper is published with the

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permission of the Director of the National Physical Laboratory, Teddington, Middlesex, England.

(17) Argonne National Laboratory, Argonne, Ill.

Steven S. Danyluk<sup>17</sup>

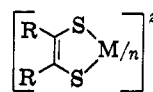
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Received March 6, 1965

## New Systems of Complexes Related by Electron-Transfer Reactions

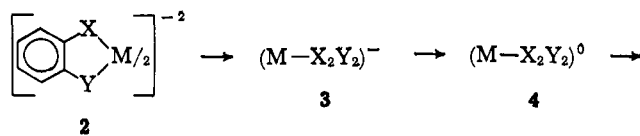
Sir:

Recent investigations in these laboratories have clearly demonstrated that complexes of general type **1** ( $R = \text{CN}, \text{CF}_3, \text{C}_6\text{H}_5$ ;  $n = 2, 3$ ) undergo relatively facile one-electron-transfer reactions which can be effected chemically or electrochemically for complexes with  $M = \text{Cu}, \text{Ni}, \text{Co}, \text{Pd}, \text{Pt}$  ( $n = 2$ ),<sup>1a,b</sup> and  $\text{V}, \text{Cr}, \text{Mo}, \text{W}$  ( $n = 3$ )<sup>1c,d</sup> to yield species with total charge  $z = 0, -1, -2$  ( $n = 2$ ), and  $0, -1, -2, -3$  ( $n = 3$ ).<sup>2</sup> For series of bis complexes the existence of electron-transfer reactions has heretofore been confined to those species having the M-S<sub>4</sub> coordination unit. We are investigating the scope of these reactions in bis complexes and report certain results for M-N<sub>4</sub>, M-N<sub>2</sub>S<sub>2</sub>, M-O<sub>2</sub>S<sub>2</sub>, and M-O<sub>4</sub> complexes which indicate that electron-transfer reactions have a reasonably general occurrence and that oxidative stabilities of complexes of the same general composition and charge type have a marked dependence on the nature of the donor atoms.



**1**

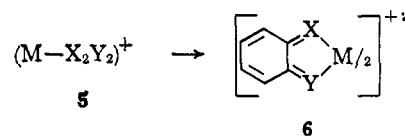
Previous studies have revealed the existence of three-membered electron-transfer series of bis complexes. The present investigation deals with systems in which the metal and, in some cases, the ligand may be oxidized or reduced, thereby generating a five-membered series of complexes represented as



**2**

**3**

**4**



**5**

**6**

Reaction of Ni<sup>+2</sup> and *o*-phenylenediamine in concentrated aqueous ammonia leads to a violet neutral complex,<sup>3</sup> diamagnetic and identical with the reaction

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(2) Bis complexes with  $R = \text{C}_6\text{H}_5$ ,  $M = \text{Ni}$ , and  $z = 0, -1, -2$  have also been isolated by others: cf. G. N. Schrauzer and V. Mayweg, *Z. Naturforsch.*, **19b**, 192 (1964); the existence of tris complexes with  $R = \text{C}_6\text{H}_5$ ,  $M = \text{Cr}, \text{Mo}, \text{W}$ ,  $z = 0, -1$  has been demonstrated by J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *J. Am. Chem. Soc.*, **86**, 4198 (1964).

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