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Multinuclear NMR study of chlorinated vinylsilanes

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Abstract

Silylethylenes of the types $(CH_3)_{3-n}X_nSiCH{=}CHCl$ (I = *trans*, II = *cis*), $(CH_3)_{3-n}X_nSiCH{=}CCl_2$ (III), $(CH_3)_{3-n}X_nSiCCl{=}CCl_2$ (IV) and $(CH_3)_{3-n}X_nSi$-$CH{=}CHSiX_n(CH_3)_{3-n}$ (V) ($n = 0$–3, X = Cl, OEt, OMe), were studied by ^1H, ^{13}C, ^{29}Si and ^{17}O NMR methods. A comparison of the ^{13}C chemical shifts in I–V with those in the corresponding vinylsilanes reveals that the sensitivity of α, β-olefinic carbon resonances to electronic effects of the Si substituents diminishes in the sequence: I > III > II ≈ IV.

Various possible coupling constants in I–V were measured. A linear correlation between $^1J(CC)$ coupling in I–IV and the sum of the electronegativities of the Si substituents was obtained. The different correlations between $^1J(^{29}Si-^{13}C)$ and $^2J(^{29}Si-C-^1H)$ involving X = Cl or OR substituents is explained within the framework of the $(p-d)_\pi$ hypothesis.

Introduction

^1H, ^{13}C and ^{29}Si NMR spectral analyses carried out earlier for bis(trimethylsilyl)ethylenes [1–3] and some types of vinylsilanes [4–8] indicates an interaction between the vacant *d*-orbitals on the silicon atom and the π-electron system of the vinyl group. In an effort to broaden these notions and in continuation of previous studies concerned with the influence of electronic effects of silicon and vinyl substituents on the chemical shifts as well as the coupling constants we obtained the ^1H, ^{13}C, ^{29}Si and ^{17}O NMR spectra for the following chlorinated silylethylenes (I–IV) and 1,2-disilylethylenes (V):

$(CH_3)_{3-n}X_nSiCH{=}CHCl$ (I = *trans*, II = *cis*)
$(CH_3)_{3-n}X_nSiCH{=}CCl_2$ (III)
$(CH_3)_{3-n}X_nSiCCl{=}CCl_2$ (IV)
$(CH_3)_{3-n}X_nSiCH{=}CHSiX_n(CH_3)_{3-n}$ (V) ($n = 0$–3, X = Cl, OC_2H_5, OCH_3)

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Table 1

^1H NMR spectral parameters for silylethylenes in $CDCl_3$ at 303 K

Compounds	X	n	Chemical shifts ($\delta(^1H)$(ppm))			$^3J(H_\alpha H_\beta)$, Hz
			CH_α	CH_β	CH_3/others	
Ia	Cl	0	6.15	6.29	0.12	15.35
Ib	Cl	1	6.21	6.59	0.53	15.40
Ic	Cl	2	6.25	6.84	0.91	15.40
Id	Cl	3	6.31	7.11	–	15.43
Ie	OC_2H_5	1	6.13	6.46	0.23 3.65(OCH_2) 1.23(CH_3)	15.49
If	OC_2H_5	2	6.01	6.58	0.21 3.79(OCH_2) 1.23(CH_3)	15.55
Ig	OC_2H_5	3	5.91	6.63	3.85(OCH_2); 1.24(CH_3)	15.55
Ih	OCH_3	3	5.89	6.69	3.59	15.50
IIa	Cl	0	5.89	6.74	0.21	9.2
IIb	Cl	1	6.03	6.84	0.64	9.4
IIc	Cl	2	6.11	6.97	1.05	9.5
IId	Cl	3	6.15	7.11	–	9.7
IIe	OC_2H_5	1	5.93	6.80	0.33 3.70(OCH_2); 1.21(CH_3)	9.5
IIf	OC_2H_5	2	5.87	6.85	0.35 3.82(OCH_2); 1.25(CH_3)	9.5
IIg	OC_2H_5	3	5.79	6.89	3.90(OCH_2); 1.26(CH_3)	9.5
IIh	OCH_3	3	5.77	6.93	3.62	9.6
IIIa	Cl	0	5.97		0.20	–
IIIb	Cl	1	6.09	–	0.63	–
IIIc	Cl	2	6.17	–	1.01	–
IIId	Cl	3	6.23	–	–	–
IIIf	OC_2H_5	2	5.95	–	0.33; 3.83(OCH_2); 1.25(CH_3)	–
IIIg	OC_2H_5	3	5.87	–	3.90(OCH_2); 1.26(CH_3)	–
IVa	Cl	0	–	–	0.34	–
IVb	Cl	1	–	–	0.75	–
IVc	Cl	2	–	–	1.12	–
IVf	OC_2H_5	2	–	–	0.41; 3.88(OCH_2); 1.26(CH_3)	–
IVg	OC_2H_5	3	–	–	3.94(OCH_2); 1.27(CH_3)	–
Va	Cl	0	6.59		0.06	–
Vb	Cl	1	6.78	0.51	–	
Vc	Cl	2	6.93		0.90	–
Vd	Cl	3	7.03		–	–
Ve	OC_2H_5	3	6.67		3.84(OCH_2); 1.23(CH_3)	–

Table 1 (continued)

Compounds	X	n	Chemical shifts ($\delta(^1H)$(ppm))			$^3J(H_\alpha H_\beta)$, Hz
			CH_α	CH_β	CH_3/others	
VI	$Me_3SiCH{=}CHBr$	*trans*	6.49	6.57	0.12	15.4
	cis	6.52	6.97	0.23	9.0	
VII	$Et_3SiCH{=}CHCOOEt$	*trans*	6.29	7.24	4.23(OCH_2); 1.32(CH_3) 0.69(CH_2); 0.97(CH_3)	19.1

Results and discussion

The parameters measured in the ^1H, ^{13}C, ^{29}Si and ^{17}O NMR spectra are summarized in Tables 1–5.

The ^1H chemical shifts for $SiCH_3$ groups are shifted to lower fields with increasing number of electronegative substituents X attached to the silicon atom. At the same time, the downfield shift of the $SiCH_3$ signal for $X = Cl$ is more pronounced than in the case of $X = OR$. The same phenomenon is observed for $C^\beta H$ protons in the vinyl group. In conformity with refs. 6 and 9, this suggests that the electronegativity of the silicon atom also rises with increasing number of chlorine atoms attached. The ^1H chemical shift of the $C^\alpha H$ proton is obviously greatly affected by the Si–X bond anisotropy, because opposite tendencies are found for the chemical shift changes of substituents $X = Cl$ and $X = OR$ with increasing number n (Table 1). The total diamagnetic shift of the vinyl proton resonances in the molecules of ethoxysilylethylenes (Ie–g, IIe–g and IIIf,g in Table 1) compared with chloro derivatives (Ia–d, IIa–d and IIa–d in Table 1) has been explained earlier by the predominance of the $(p-d)_\pi$ effect over the inductive properties of oxygen in the Si–X bond as opposed to those of the chlorine atom [4].

The ^{13}C resonances of $SiCH_3$ groups ($X = Cl$) are shifted downfield in the row $n = 0 < 1 < 2$, whereas in the case of $X = OR$ they undergo an upfield shift in the same sequence. These facts can also be explained by a stronger $(p-d)_\pi$ interaction in the Si–O bond in comparison with the Si–Cl bond. At the same time, satisfactory linear correlations were found between the ^{13}C and ^1H chemical shifts of the $SiCH_3$ groups:

I $\delta(^{13}C) = -4.83 + 11.37\delta(^1H)$ $n = 5$ $r = 0.92$ (1)

II $\delta(^{13}C) = -5.27 + 11.30\delta(^1H)$ $n = 5$ $r = 0.92$ (2)

III $\delta(^{13}C) = -5.62 + 11.36\delta(^1H)$ $n = 4$ $r = 0.91$ (3)

IV $\delta(^{13}C) = -7.06 + 12.29\delta(^1H)$ $n = 4$ $r = 0.93$ (4)

V $\delta(^{13}C) = -2.15 + 7.55\delta(^1H)$ $n = 3$ $r = 0.99$ (5)

Replacement of the $SiCH_3$ group in compounds I–V by a chlorine atom leads to a diagmagnetic shift of the α-carbon ^{13}C resonance and to a paramagnetic shift of the vinyl C^β carbon. Analogous shifts found in the ^{13}C NMR spectra of unsubstituted vinylsilanes [6–9] have been explained with the help of π-electron polarization in the double bond under the influence of the electric field of the $SiX_n(CH_3)_{3-n}$

Table 2

^{13}C, ^{29}Si and ^{17}O chemical shifts for silylethylenes in $CDCl_3$ at 303 K

Compounds	X	*n*	δ(^{13}C) (ppm)				δ(^{29}Si) (ppm)	δ(^{17}O) (ppm)	Δν (Hz)
			C_α	C_β	C_X	CH_3/others			
Ia	Cl	0	133.26	129.03	–	−1.54	−6.34		
Ib	Cl	1	128.87	133.42	–	1.85	16.31		
Ic	Cl	2	127.27	137.43	–	5.48	13.64		
Id	Cl	3	125.65	140.69	–	–	−6.69		
Ie	OC_2H_5	1	130.67	131.07	56.81(OCH_2) 17.29(CH_3)	−2.58	3.85	13.3	160
If	OC_2H_5	2	127.56	133.23	57.91(OCH_2) 17.75(CH_3)	−4.66	−22.10	25.7	250
Ig	OC_2H_5	3	123.51	134.85	57.24(OCH_2) 17.61(CH_3)	–	−61.94	21.6	280
Ih	OCH_3	3	122.03	135.23	49.73	–	−58.4	−16.6	160
IIa	Cl	0	130.91	132.93	–	−1.02	−7.57	–	
IIb	Cl	1	128.62	134.88	–	2.63	15.96	–	
IIc	Cl	2	126.40	–	6.68	12.33	–		
IId	Cl	3	124.40	140.97	–	–	−9.56		
IIe	OC_2H_5	1	128.48	133.20	58.08(OCH_2) 17.30(CH_3)	−1.72	4.11	–	
IIf	OC_2H_5	2	126.19	134.58	57.91(OCH_2) 17.75(CH_3)	−3.79	−21.98	–	
IIg	OC_2H_5	3	122.62	135.80	58.13(OCH_2) 17.58(CH_3)	–	−62.58	–	
IIh	OCH_3	3	121.16	136.20	49.60	–	−58.80		–
IIIa	Cl	0	129.83	129.83	–	−1.47	−6.07		–
IIIb	Cl	1	127.26	133.10	–	2.14	14.80		–
IIIc	Cl	2	125.08	137.06	–	5.95	10.15		–
IIId	Cl	3	122.93	141.14	–	–	−11.72		–
IIIf	OC_2H_5	2	125.48	132.66	58.27(OCH_2) 17.88(CH_3)	−4.36	−23.99	27.0	240

IIIg	OC_2H_5	3	121.98	133.78	58.37(OCH_2) 17.55(CH_3)	–	–65.61	22.7	280
IVa	Cl	0	133.34	126.48	–	–1.00	3.40	–	
IVb	Cl	1	129.34	129.96	–	2.74	17.87	–	
IVc	Cl	2	126.46	132.99	–	6.62	9.46	–	
IVd	Cl	3	124.34	135.88	–	–	–13.04	–	
IVf	OC_2H_5	2	129.53	128.61	58.91(OCH_2) 17.69(CH_3)	–4.34	–28.92	27.7	240
IVg	OC_2H_5	3	126.46	130.02	59.29(OCH_2)	–	–71.82	23.0	300
Va	Cl	0	150.60		–	–1.59	–7.76	–	
Vb	Cl	1	148.77	–	1.46	16.80	–		
Vc	Cl	2	147.26		4.77	14.58	–		
Vd	Cl	3	146.07	–	–	–5.89	–		
Vg	OC_2H_5	3	145.96	58.67(OCH_2) 18.39(CH_3)	–	–61.45	–		
VI	$Me_3SiCH{=}CHBr$		*trans*						
			138.87	116.87	–	–1.58	–5.09	–	
			cis						
			135.52	122.16	–	–1.12	–5.95	–	
VII	$Et_3SiCH{=}CHCOOEt$		145.32	135.07	164.71(COO) 59.56(OCH_2) 13.53(CH_3)	2.44(CH_2) 6.41(CH_3)	0.09	–	
VIIIa [a]	Cl	0	139.69 [b]	130.34 [b]	–	–	–7.0		
VIIIb [a]	Cl	1	135.99 [b]	133.89 [b]	–	–	16.7 [c]	–	
VIIIc [b]	Cl	2	133.84	137.27	5.55	–	16.40	–	
VIVd [a]	Cl	3	131.72	139.57	–	–	–3.22	–	
VIIIe [a]	OC_2H_5	1	137.46 [b]	132.72 [b]	–	–	2.7 [c]	–	
VIIIf [a]	OC_2H_5	2	133.79 [b]	134.83 [b]	–	–	–	–	
VIVg [b]	OC_2H_5	3	130.05	135.06	–	–	–60.3 [c]	–	

[a] VIII: $(CH_3)_{3-n}X_nSiCH{=}CH_2$. [b] [7]. [c] [6].

Table 3

Sum of the vinylic ^{13}C chemical shifts in silyl- and halogenethylenes

Compounds	$\Sigma\delta(C_{\alpha,\beta})$(ppm)
$CH_2{=}CH_2$	246.6
$CH_2{=}CHCl$	243.3
$CH_2{=}CCl_2$	240.4
$CHCl{=}CCl_2$	242.7
$CCl_2{=}CCl_2$	242.6
$CCl_2{=}CClSiMe_3$	259.8
$CCl_2{=}CClSiClMe_2$	259.3
$CCl_2{=}CClSiCl_2Me$	259.9
$CCl_2{=}CClSiCl_3$	260.2
$CCl_2{=}CHSiMe_3$	259.7
$CCl_2{=}CHSiClMe_2$	260.4
$CCl_2{=}CHSiCl_2Me$	262.1
$CCl_2{=}CHSiCl_3$	264.1
$Me_3SiCH{=}CHSiMe_3$	301.2
$Me_2ClSiCH{=}CHSiClMe_2$	297.5
$MeCl_2SiCH{=}CHSiCl_2Me$	294.5
$Cl_3SiCH{=}CHSiCl_3$	292.1

substituent. For the carbon analogue of IV (1,1,2-trichloropropene-1-$CCl_2{=}CClCH_3$), however, gradual chlorination of the methyl group causes a paramagnetic shift of the ^{13}C resonance signal for the olefinic α-carbon, whereas the β-carbon $\delta(^{13}C)$ changes irregularly [10,11]. In compound IVa, both the C^{α}- and the C^{β}-carbon ^{13}C resonances are shifted to lower fields as compared with the model compound 1,1,2-trichloroethylene-$C^{\alpha}HCl{=}C^{\beta}Cl_2$ ($\delta(^{13}C_{\alpha}) = 117.6$ ppm, $\delta(^{13}C_{\beta}) = 125.1$ ppm [12]). At the same time, the relationship $\delta(^{13}C_{\alpha}) < \delta(^{13}C_{\beta})$ holds true. Gradual introduction of chlorine atoms into the trimethylsilyl group (compounds IVb,c) leads to opposite shifts for both olefinic carbon ^{13}C resonances, and so the relationship $\delta(^{13}C_{\beta}) < \delta(^{13}C_{\alpha})$ is observed (Table 2). This can be explained by a symbatic influence of both the $(-I)$ and the $(p\text{-}d)_{\pi}$ effects of the $SiCl_3$ substituent on the π-system of the double bond. In the case of the $Si(CH_3)_3$ substituent, these two effects act in opposite directions [9].

The role of chlorine atoms in shielding ^{13}C nuclei in the vinyl group of vinylsilane molecules was estimated by comparing the ^{13}C chemical shifts of C^{α} and C^{β} carbons in compounds I–IV with those in silanes VIII unsubstituted in the vinyl group [7]:

$$\text{I}\quad \delta(^{13}C_{\alpha}) = 6.3 + 0.91\delta(^{13}C_{\alpha})\ \text{VIII} \qquad r = 0.998 \qquad (6)$$

$$n = 7$$

$$\delta(^{13}C_{\beta}) = -39.6 + 1.29\delta(^{13}C_{\beta})\ \text{VIII} \qquad r = 0.970 \qquad (7)$$

$$\text{II}\quad \delta(^{13}C_{\alpha}) = 24.0 + 0.76\delta(^{13}C_{\alpha})\ \text{VIII} \qquad r = 0.988 \qquad (8)$$

$$n = 7$$

$$\delta(^{13}C_{\beta}) = 16.4 + 0.88\delta(^{13}C_{\beta})\ \text{VIII} \qquad r = 0.92 \qquad (9)$$

$$\text{III}\quad \delta(^{13}C_{\alpha}) = 18.5 + 0.79\delta(^{13}C_{\alpha})\ \text{VIII} \qquad r = 0.995 \qquad (10)$$

$$n = 6$$

$$\delta(^{13}C_{\beta}) = -27.0 + 1.20\delta(^{13}C_{\beta})\ \text{VIII} \qquad r = 0.92 \qquad (11)$$

$$\text{IV}\quad \delta\left({}^{13}\mathrm{C}_{\alpha}\right) = 25.2 + 0.77\delta\left({}^{13}\mathrm{C}_{\alpha}\right)\ \text{VIII} \qquad r = 0.887 \qquad (12)$$

$$n = 6$$

$$\delta\left({}^{13}\mathrm{C}_{\beta}\right) = -4.07 + 0.99\delta\left({}^{13}\mathrm{C}_{\beta}\right)\ \text{VIII} \qquad r = 0.91 \qquad (13)$$

Judging from the slope coefficients in eqs. 6–13, the C^{β}-carbon resonances are always more sensitive to the electronic influence of Si-substituents than those of the C^{α}-carbon atoms. At the same time, the slope coefficients for both the C^{α}- and C^{β}-carbon atoms tend to decrease with increasing number or chlorine atoms in the vinyl group. For compounds I and III, the β-chlorine atom in the vinyl group amplifies the electronic effects of Si substituents at β-carbons, whereas the same effects for α-carbon are less pronounced (eqs. 6, 7, 10, 11). Equations 8 and 9 are characterized by significantly lower slope coefficients in the case of *cis*-isomers II, as compared with those in eqs. 6 and 7 for the *trans*-isomers I. These differences can be possibly attributed to local changes in the mean excitation energy or to different electron densities on the corresponding carbons [13]. A comparison of the sums of the ^{13}C chemical shifts for α,β-olefinic carbons in compounds I–IV with those in unsubstituted ethylenes [12] shows (Table 3) that ethylene chlorination leads to an insignificant increase in the π-electronic density on the double bond. Introduction of a silyl substituent at the double bond decreases the π-charge (Table 3), which is in keeping with the suggested acceptor character of the $SiX_n(CH_3)_{3-n}$ substituent with respect to the double bond.

The ^{29}Si chemical shift depend in a non-linear manner on the charge at the silicon atom, which considerably complicates their exact interpretation [14]. The ^{29}Si chemical shift values for compounds I–V (Table 2) show that ethylene chlorination has little effect on the general tendency of ^{29}Si resonance changes as compared to vinylsilanes unsubstituted in the vinyl group [6]. An opposite trend is noted for the ^{29}Si chemical shifts of trimethylsilyl and trichlorosilyl derivatives with increasing number of chlorine atoms in the vinyl group. For the former compounds (Ia–IVa, Table 2), a transition from the unsubstituted vinyl to the trichlorovinyl group causes a gradual downfield shift of the ^{29}Si resonance. For $SiCl_3$ derivatives (Id–IVd, Table 2), the same transition leads to an upfield shift of the ^{29}Si resonance signal. These facts are obviously connected with the parabolic dependence between the ^{29}Si chemical shift and the electronic charge on this atom [14]: $Si(CH_3)_3$ derivatives are located on the right arm of the parabola. Therefore, an increase in the acceptor properties of the vinyl group causes opposite shifts of the ^{29}Si resonance signals in the ^{29}Si NMR spectra.

The ^{17}O chemical shifts (Ie–f, IIIf,g, IVf,g, Table 2) measured fall within the range characteristic of other alkoxysilanes [15]. An increase in the number of chlorine atoms in the vinyl group results in a slight downfield shift of the ^{17}O resonances.

So far, coupling constants, including ^{13}C and ^{29}Si nuclei, in silylethylenes have been studied only occasionally [5,8,10,16–20]. These types of coupling constants for chlorinated silylethylenes have not been explored either.

A rise in $^{1}J(^{13}C,H)$ in the $SiCH_3$ as well as in the vinyl group with increasing number n (Table 4) is obviously caused by the greater inductive effect of the chlorine atom or the OR group as compared to the methyl one. The same dependence has been found earlier in the case of chloromethanes [13].

(continued on p. 196)

Table 4

$^{13}C-^{13}C$ and $^{13}C-^{1}H$ spin–spin coupling constants (Hz) in silylethylenes

Compound	X	*n*	$^{13}C{=}^{13}C$	$^{13}C_\alpha{=}C_\beta-^{1}H$	$^{13}C_\beta{=}C_\alpha-^{1}H$	$^{1}H_3C\text{-}Si\text{-}^{13}C_\alpha$	$^{13}C-^{1}H_3$	$H_3{}^{13}C\text{-}Si\text{-}\overset{^{1}H}{\overset{\|}{C_\alpha}}$	$^{13}C-^{1}H$	$^{1}H_3CSi-^{13}CH_3$
Ia	Cl	0	65.53	11.72	13.77	1.99	119.38	1.10	141.25($C_\alpha H$) 197.30($C_\beta H$)	2.09
Ib	Cl	1	67.04	10.35	10.57	1.63	121.73	0.73	146.16($C_\alpha H$) 195.20($C_\beta H$)	1.61
Ic	Cl	2	–	9.22	11.25	0.25	128.83	1.11	151.02($C_\alpha H$) 196.57($C_\beta H$)	–
Id	Cl	3	69.69	8.29	11.17	–	–	–	155.23($C_\alpha H$) 196.92($C_\beta H$)	–
Ie	OC_2H_5	1	65.13	11.35	10.01	1.43	119.27	1.60	142.10($C_\alpha H$) 194.07($C_\beta H$)	1.00
If	OC_2H_5	2	64.87	10.64	11.90	0	119.21	0.91	143.52($C_\beta H$) 197.25($C_\beta H$)	–
Ig	OC_2H_5	3	65.42	10.20	12.17	–	–	–	144.98($C_\alpha H$) 198.14($C_\beta H$)	–
Ih	OCH_3	3	65.43	10.25	12.30	–	–	–	145.47($C_\alpha H$) 198.30($C_\beta H$)	–
IIa	Cl	0	70.90	4.16	1.73	2.08	119.53	1.25	137.05($C_\alpha H$) 197.13($C_\beta H$)	2.16
IIb	Cl	1	71.06	4.63	1.20	1.63	121.97	1.12	143.65($C_\alpha H$)	1.61
IIc	Cl	2	–	4.98	0.74	1.51	124.41	0.92	148.62($C_\alpha H$) 199.15($C_\beta H$)	–
IId	Cl	3	72.33	5.77	0.20	–	–	–	151.99($C_\beta H$) 198.72($C_\beta H$)	–
IIe	OC_2H_5	1	70.90	4.29	1.34	1.34	119.47	1.80	137.62($C_\alpha H$) 198.17($C_\beta H$)	1.00
IIf	OC_2H_5	2	70.34	4.33	1.21	0.80	119.87	0.66	138.87($C_\alpha H$) 197.67($C_\beta H$)	–
IIg	OC_2H_5	3	70.79	4.65	0.72	–	–	–	140.15($C_\alpha H$) 197.51($C_\beta H$)	–

IIh	OCH_3	3	70.74	4.70	0	–	–	–	140.65($C_\alpha H$) 197.54($C_\beta H$)	–
IIIa	Cl	0	–	–	6.86	2.15	119.87	1.21	141.80($C_\alpha H$)	2.12
IIb	Cl	1	79.53	–	6.77	1.62	122.27	0.98	147.34($C_\alpha H$)	1.61
IIIc	Cl	2	80.68	–	7.02	0	124.56	1.03	151.78($C_\alpha H$)	–
IIId	Cl	3	82.53	–	6.92	–	–	–	155.00($C_\alpha H$)	–
IIIf	OC_2H_5	2	78.20	–	7.35	0.67	120.02	0.59	143.57($C_\alpha H$)	–
IIIg	OC_2H_5	3	79.60	–	7.55	–	–	–	144.51($C_\alpha H$) 143.03(OCH) 126.02(CH_3)	–
UVa	Cl	0	82.41	–	–	1.00	125.29	–	–	–
IVb	Cl	1	–	–	–	1.00	125.29	–	–	–
IVc	Cl	2	88.10	–	–	1.00	125.29	–	–	–
IVd	Cl	3	90.05	–	–	–	–	–	–	–
IVf	OC_2H_5	2	–	–	–	0.44	120.67	–	142.73(OCH_2) 126.10(CH_3)	–
IVg	OC_2H_5	3	84.55	–	–	–	–	–	126.17(CH_3)	
Va	Cl	0	–	–	–	–	118.92	–	139.38(CH)	–
Ib	Cl	1	–	7.55	–	1.46	121.56	–	145.56(CH)	1.74
Vc	Cl	2	–	7.66	–	–	123.96	–	151.64(CH)	–
Vd	Cl	3	–	7.90	–	–	–	–	156.99(CH)	–
Vg	OC_2H_5	3	–	8.10	–	–	–	–	144.68(CH)	–
VI	$Me_3SiCH{=}CHBr$	*trans*	64.48	8.37	13.45	1.97	119.43	0.80	145.53($C_\alpha H$) 198.86($C_\beta H$)	2.05
		cis	69.94	3.77	2.30	2.13	119.58	0.32	135.52($C_\alpha H$) 198.69($C_\beta H$)	2.05
VII	$Et_3SiCH{=}CHCOOEt$		65.33	1.79	8.59	–	–	–	138.00($C_\alpha H$) 162.88($C_\beta H$)	
VIIIa [a]	Cl	0	58.25	–	–	–	–	–	–	–
VIIIc [a]	Cl	2	60.30	–	–	–	–	–	–	–
VIII [a]	Cl	3	61.33	–	–	–	–	–	–	–

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[a] VIII: $(CH_3)_{3-n}X_nSiCH{=}CH_2$.

Table 5

^{29}Si–^{13}C and ^{29}Si–^{1}H spin–spin coupling constants (Hz) in silylethylenes

Compounds	X	n	^{29}Si–^{13}CH$_3$	^{29}Si–^{13}C$_\alpha$	^{29}Si–^{13}C$_\beta$	^{29}Si–C–^{1}H$_3$	^{29}Si–C$_\alpha$–^{1}H	^{29}Si–C$_\alpha$=C$_\beta$–^{1}H
Ia	Cl	0	53.33	59.32	5.76	6.81	4.25	2.34
Ib	Cl	1	60.69	69.87	7.42	7.14	5.71	4.76
Ic	Cl	2	73.00	86.11	9.03	7.93	6.75	6.81
Id	Cl	3	–	111.86	11.54	–	8.22	8.50
Ie	OC_2H_5	1	62.64	68.20	7.06	6.81	2.83	4.75
If	OC_2H_5	2	78.38	86.90	7.01	7.40	3.02	4.30
Ig	OC_2H_5	3	–	114.56	7.79	–	3.22	5.06
Ih	OCH_3	3	–	115.68	8.05	3.76(^3J(SiOCH))	3.03	5.13
IIa	Cl	0	53.49	61.82	–	6.85	–	–
IIb	Cl	1	60.49	73.02	–	7.31	2.17	13.40
IIc	Cl	2	72.28	89.62	–	8.10	3.25	17.23
IId	Cl	3	–	115.58	–	–	7.69	21.76
IIe	OC_2H_5	1	62.64	71.24	–	6.92	1.48	11.76
IIf	OC_2H_5	2	78.54	89.68	–	7.51	1.20	13.25
IIg	OC_2H_5	3	–	117.08	–	–	0.4	15.32
IIh	OCH_3	3	–	116.74	–	3.95(^3J(SiOCH))	1.03	15.53
IIIa	Cl	0	54.24	58.60	–	6.85	1.46	–
IIIb	Cl	1	61.77	70.19	–	7.25	1.10	–
IIIc	Cl	2	74.37	87.81	–	8.17	1.60	–
IIId	Cl	3	–	114.62	–	–	5.13	–
IIIf	OC_2H_5	2	81.19	87.35	–	7.58	1.13	–
IIIg	OC_2H_5	3	–	115.67	–	–	0.81	–

IVa	Cl	0	55.49	60.81	6.07	6.89	–	–
IVb	Cl	1	63.82	74.80	8.08	7.36	–	–
IVc	Cl	2	77.58	96.77	10.72	8.39	–	–
IVd	Cl	3	–	130.77	13.42	–	–	–
IVf	OC_2H_5	2	84.34	91.30	8.64	7.73	–	–
IVg	OC_2H_5	3	–	127.28	9.75	–	–	–
Va	Cl	0	51.89	63.34		6.63	–	–
Vb	Cl	1	59.30	71.11		7.07	–	7.55
Vc	Cl	2	71.01	84.42		7.74	–	7.66
Vd	Cl	3	–	107.46		–	–	7.90
Vg	OC_2H_5	3	–	115.96		–	–	8.10
VI	$Me_3SiCH=CHBr$	*trans*	53.05	57.10	4.91	6.77	–	–
		cis	53.48	62.19	–	6.85	0.70	10.93
VII	$Et_3SiCH=CHCOOEt$		53.48($SiCH_2$)	57.86	8.28	8.00($SiCH_2$) 6.60($SiCH_3$)	4.30	6.00
VIIIa [a]	Cl	0	52.25	64.16	–	–	6.19	15.12(SiH_2) 8.17(SiH_3)
b [a]	Cl	1	–	–	–	–	6.42 [b]	15.26 [b] 8.59 [b]
c [a]	Cl	2	70.40	89.70	–	–	11.80	23.81(SiH_2) 12.53(SiH_3)
d [a]	Cl	3	–	112.40	–	–	15.44	30.61(SiH_2) 15.54(SiH_3)

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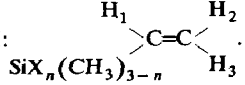
[a] VIII:

$(H_1)(SiX_n(CH_3)_{3-n})C=C(H_2)(H_3)$. [b] [25].

Linear correlations (eqs. 14–21) were found between the $^{13}\mathrm{C}^{\alpha}$-H CC and the ^{1}H or ^{13}C chemical shifts:

I $\quad ^{1}J(^{13}\mathrm{C}_{\alpha},\mathrm{H}) = 381.4 - 1.81\delta(^{13}\mathrm{C}_{\alpha}) \quad n = 4;\ r = 0.993 \quad (14)$

$\quad ^{1}J(^{13}\mathrm{C}_{\alpha},\mathrm{H}) = -408.4 + 89.4\delta(^{1}\mathrm{H}) \quad n = 4;\ r = 0.995 \quad (15)$

II, III $\quad ^{1}J(^{13}\mathrm{C}_{\alpha},\mathrm{H}) = 419.9 - 2.15\delta(^{13}\mathrm{C}_{\alpha}) \quad n = 8;\ r = 0.989 \quad (16)$

$\quad ^{1}J(^{13}\mathrm{C}_{\alpha},\mathrm{H}) = -177.0 + 53.3\delta(^{1}\mathrm{H}) \quad n = 8;\ r = 0.994 \quad (17)$

$\mathrm{X} = \mathrm{OR}$

II $\quad ^{1}J(^{13}\mathrm{C}_{\alpha},\mathrm{H}) = 187.2 - 0.38\delta(^{13}\mathrm{C}_{\alpha}) \quad n = 5;\ r = 0.995 \quad (18)$

$\quad ^{1}J(^{13}\mathrm{C}_{\alpha},\mathrm{H}) = 263.5 - 21.3\delta(^{1}\mathrm{H}) \quad n = 5;\ r = 0.929 \quad (19)$

I, III $\quad ^{1}J(^{13}\mathrm{C}_{\alpha},\mathrm{H}) = 186.4 - 0.34\delta(^{13}\mathrm{C}_{\alpha}) \quad n = 7;\ r = 0.968 \quad (20)$

$\quad ^{1}J(^{13}\mathrm{C}_{\alpha},\mathrm{H}) = 219.9 - 12.7\delta(^{1}\mathrm{H}) \quad n = 7;\ r = 0.950 \quad (21)$

These correlations indicate that changes in the *s*-character of the C^{α}–H bond are connected with electronic density alterations both on the H^{α} proton and on the C^{α} carbon of the vinyl group. At the same time, the lack of a general correlation of the 14–17 type for all the substituents at silicon suggests additional contributions selectively transmitted via the silicon atom to the C^{α}–H bond. It should be noted that vinylic $^{1}J(^{13}\mathrm{C}_{\alpha},\mathrm{H})$ is more sensitive than $^{1}J(^{13}\mathrm{C},\mathrm{H})$ in the SiCH_3 group to CH_3 substitution by a chlorine atom. Consequently, the electronic effects of chlorine attached to the silicon atom affect the *s*-character of the C^{α}–H more essentially than that of the $^{13}\mathrm{C}$–H_3 bond. This may be associated with different $\mathrm{H}_3\mathrm{C}$–Si and C^{α}–Si, as well as C–H_3 and C^{α}–H, bond lenghts.

The geminal ^{13}C–H coupling constants are smaller than those over one bond (Table 4) and are essentially different in *cis,trans*-isomers: $^{2}J(^{13}\mathrm{C}_{\alpha} = \mathrm{C}_{\beta}\text{–}\mathrm{H})_{trans} > {}^{2}J(^{13}\mathrm{C}_{\alpha} = \mathrm{C}_{\beta}\text{–}\mathrm{H})_{cis}$. In the *trans*-isomers (I), changes in $^{2}J(^{13}\mathrm{C}_{\beta} = \mathrm{C}_{\alpha}\text{–}\mathrm{H})$ are negligibly small, whereas $^{2}J(^{13}\mathrm{C}_{\alpha} = \mathrm{C}_{\beta}\text{–}\mathrm{H})$ decreases considerably when n increases. On the contrary, in *cis*-isomers the latter coupling constant increases but $^{2}J(^{13}\mathrm{C}_{\beta} = \mathrm{C}_{\alpha}\text{–}\mathrm{H})$ decreases with increasing n.

The $^{13}\mathrm{C} = {}^{13}\mathrm{C}$ coupling constant is very sensitive to the nature of the carbon atoms constituting the bond and mainly depends on the *s*-character of the hybrid orbitals directed towards the two carbons [13,21]. As in the case of ethylene [17,21], the $^{1}J(\mathrm{CC})$ coupling constant measured in compounds I–IV (Table 4) increased in a linear manner with increasing total electronegativity (ΣE [22]) of the substituent $\mathrm{Si(CH_3)_{3-\mathit{n}}X_{\mathit{n}}}$, when $\mathrm{X} = \mathrm{Cl}, \mathrm{OC_2H_5}, \mathrm{OCH_3}$; $n = 0$–3 (Fig. 1). The same dependence has been noted earlier for the carbon analogues $\mathrm{CCl_2 = CClCH_{3-\mathit{n}}Cl_{\mathit{n}}}$; $n = 0$–3 [10]. It can be deduced from Fig. 1 that an increase in the number of chlorine atoms in the vinyl group leads to increased $^{1}J(\mathrm{CC})$ values; furthermore, $^{1}J(\mathrm{OC})_{cis\text{-isomer}} > {}^{1}J(\mathrm{CC})_{trans\text{-isomer}}$.

The $^{1}J(^{29}\mathrm{Si},\mathrm{C})$ coupling constants of I–IV increase with increasing number of substituents X in the molecules. According to Bent's hypothesis [13,23], the value of this coupling depends on the *s*-character of both silicon and carbon. This is supported by the fact that $^{1}J(^{29}\mathrm{Si},\mathrm{C}_{\alpha}) > {}^{1}J(^{29}\mathrm{Si},\mathrm{CH}_3)$ (Table 5). Almost linear correlations were found between the $^{1}J(^{29}\mathrm{Si},\mathrm{C}_{\alpha})$ coupling constants and the sum of

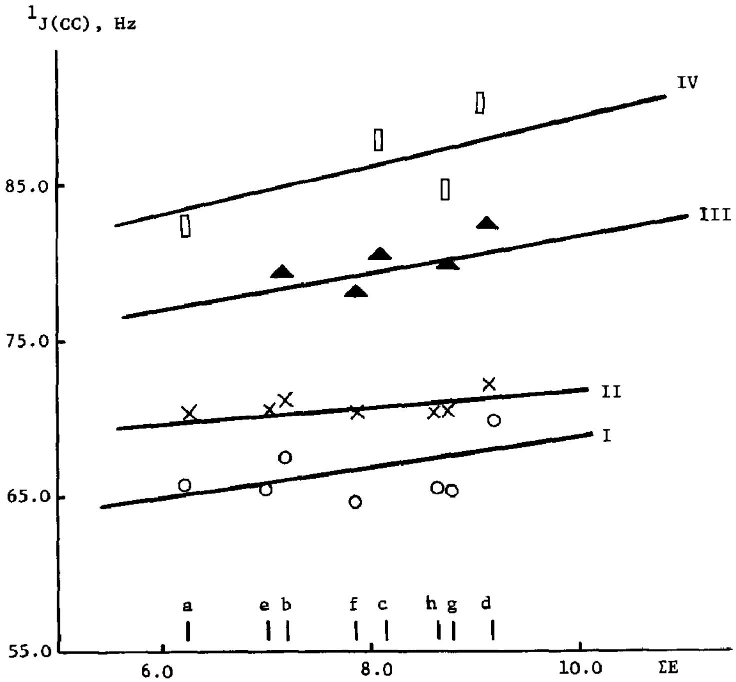


Fig. 1. Correlation between ^1J(C–C) coupling constants and total Si-substituent electronegativity in silylethylenes. Numbering of compounds as in Table 1.

the electronegativities of substituents attached to the silicon atom (ΣE):

$$\text{I} \quad {}^1J(^{29}\text{Si},\text{C}_\alpha) = -71.0 + 20.2\Sigma E \quad n = 8; \quad r = 0.964 \qquad (22)$$

$$\text{II} \quad {}^1J(^{29}\text{Si},\text{C}_\alpha) = -69.6 + 20.4\Sigma E \quad n = 8; \quad r = 0.969 \qquad (23)$$

$$\text{III} \quad {}^1J(^{29}\text{Si},\text{C}_\alpha) = -62.2 + 19.0\Sigma E \quad n = 6; \quad r = 0.984 \qquad (24)$$

$$\text{IV} \quad {}^1J(^{29}\text{Si},\text{C}_\alpha) = -89.7 + 23.5\Sigma E \quad n = 6; \quad r = 0.978 \qquad (25)$$

These equations suggest the predominant role of positive charge in determining $^1J(^{29}\text{Si},\text{C}_\alpha)$ coupling constants.

The long-range coupling constants $^nJ(^{29}\text{Si},\text{H})$ in vinylsilanes have scarcely been studied [8,9,24,25]. Therefore, we measured these coupling constants in compounds I–V (Table 5). There is a certain decrease in the geminal $^2J(^{29}\text{Si},\text{C}_\alpha,\text{H})$ coupling constants in I–III as compared to $(CH_3)_3SiC^\alpha H{=}CH_2$($^2J(^{29}\text{Si},\text{C}_\alpha,\text{H})$ 6.42 Hz [26] and $N(CH_2CH_2O)_3SiC\alpha H{=}CH_2$($^2J(^{29}\text{Si},\text{C}_\alpha,\text{H})$ 5.74 Hz [24]). This can possibly be attributed not only to the influence of electronic charge on chlorine, but also to changes in the Si–C–H valency angle. The role of the latter factor can be deduced from NMR data obtained for organotin compounds [27]. As pointed out above, SiOR and SiCl substituents exert a completely different effect on chemical shifts. The same difference clearly comes out in the case of coupling constants. Thus, comparing two sets of $^1J(^{29}\text{Si},\text{C}_\alpha)$ and $^1J(^{29}\text{Si},\text{CH}_3)$ values measured for the same molecule, one can find a linear correlation between these quantities with a slope coefficient close to 1 (Fig. 2). However, compounds bearing SiOR substituents form another straight line, showing additional electronic and/or steric effects. The same

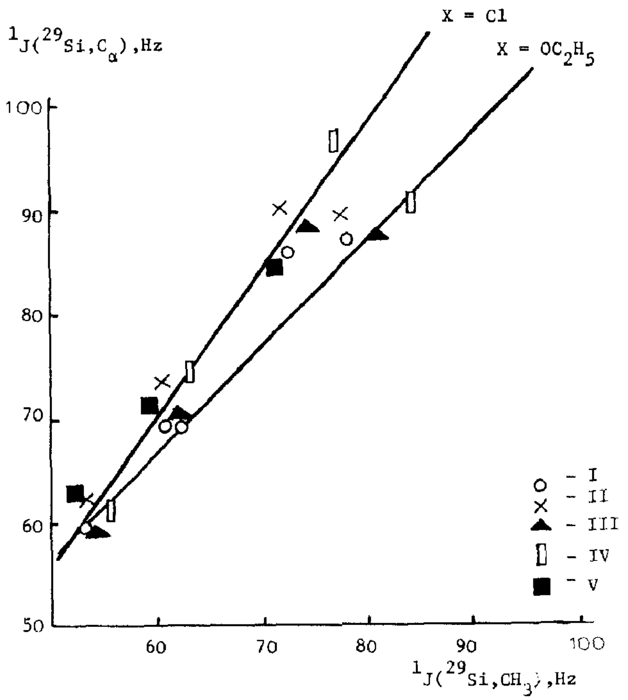


Fig. 2. $^1J(^{29}Si,C_\alpha)$ as a function of the $^1J(^{29}Si,CH_3)$ coupling constants in silylethylenes; X = Cl, $^1J(^{29}Si,C_\alpha) = -13.7 + 1.39\ ^1J(^{29}Si,CH_3)$($r = 0.980$); X = OC$_2H_5$, ^1J ($r = 0.979$).

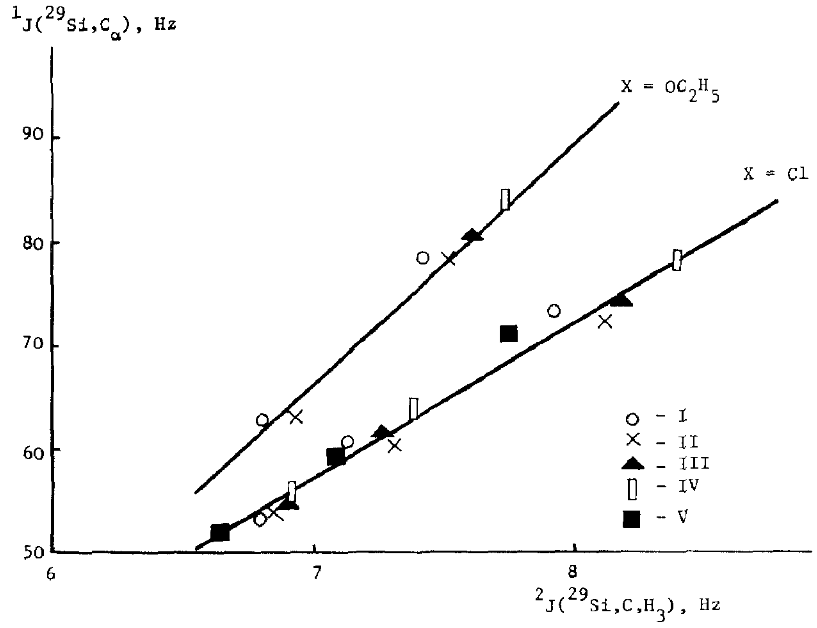


Fig. 3. Correlation between $^1J(^{29}Si,CH_3)$ and $^2J(^{29}Si,C,H)$ coupling constants in silylethylenes; X = Cl, $^1J(^{29}Si,CH_3) = -49.5 + 15.2\ \ ^2J(^{29}Si,C,H)$ ($r = 0.989$); X = OC$_2$H$_5$, $^1J(^{29}Si,CH_3) = -110.5 + 25.2\ ^2J(^{29}Si,C,H)$ ($r = 0.990$).

picture is found when comparing $^{1}J(^{29}\mathrm{Si,CH_3})$ and $^{2}J(^{29}\mathrm{Si,C,H})$ coupling constants. Here, too, SiOR-substituted compounds account for a separate correlation line (Fig. 3). These findings can possibly be explained by stronger $(p-d)_\pi$ conjugation in the Si–O bond in comparison with the Si–Cl bond. However, it is necessary to take into account the steric differences of the SiOR and SiCl substituents, too. The importance of the steric contribution can be inferred from the lack of correlation between the $^{1}J(^{29}\mathrm{Si,C_\alpha})$ and $^{1}J(^{29}\mathrm{Si,C_\alpha,H})$ couplings.

Vicinal $^{3}J(^{29}\mathrm{Si,H})$ CC in the molecules Ia–h and IIa–h show considerable stereospecificity: for *trans*-disposition of the silicon and hydrogen atoms this coupling is larger than that for a *cis*-orientation. The same relationship between the *cis,trans*-couplings $^{3}J(^{29}\mathrm{Si,H})$ has been found for vinyltriethoxysilane [24], vinyltrimethylsilane [19] and β-silylstyrene [8]. Replacement of the phenyl group in β-silylstyrene by chlorine atom leads to a decreased *cis*-$^{3}J(^{29}\mathrm{Si,H})$ in vinylsilanes I and II: $^{3}J(^{29}\mathrm{Si,H})$ coupling constants for the same Si substituents in Ia–d amount to 2.34–8.50 Hz, whereas in β-silylstyrene they are equal to 7.7–13.99 Hz [8]. As in the case of β-silylstyrenes, the compounds I and II studied here show increased $^{3}J(^{29}\mathrm{Si,H})$ coupling constants with increasing number of electronegative substituents attached to the silicon atom (Table 5). Consequently, an increase in the positive charge on the silicon atom plays a predominant role in determining the $^{3}J(^{29}\mathrm{Si,H})$ value.

Experimental

NMR spectra were recorded on a Bruker WM-360 spectrometer at 360.13 Hz (^{1}H), 90.5 MHz (^{13}C), 70.5 MHz (^{29}Si) and 48.82 MHz (^{17}O) using $\mathrm{CDCl_3}$ as solvent. The ^{1}H, ^{13}C and ^{29}Si spectra were referred to TMS as internal standard; the ^{17}O spectra to $\mathrm{H_2O}$ as external standard. All spectra were measured at 303 K. The chemical shift measurements were accurate to 0.01 ppm (^{13}C, ^{29}Si), 0.3 ppm (^{17}O); the coupling constants to 0.07 Hz. The ^{13}C, ^{29}Si and ^{17}O spectra were obtained using broad-band proton decoupling. The time between pulses was 5 μs for ^{1}H (60°), 15 μs for ^{13}C (45°), 15 μs for ^{29}Si (45°), and 30 μs for ^{17}O (90°). Long-range coupling constants were measured as described elsewhere [24].

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