

<sup>29</sup>Si AND <sup>13</sup>C NMR SPECTRA OF SOME  
 ALKYLDIPHENYLCHLOROSILANES, ALKYLDIPHENYLSILANOLES  
 AND BIS(ALKYLDIPHENYLSILYL)CHROMATES

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<sup>29</sup>Si and <sup>13</sup>C NMR spectra of alkyldiphenylchlorosilanes, alkyldiphenylsilanoles, and bis(alkyldiphenylsilyl)chromates (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(R)X have been studied. The chemical shifts δ(<sup>29</sup>Si) are most affected by nature of the electronegative substituent X, *i.e.* Cl, OH or CrO<sub>3</sub>OSi(R).(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>. The δ(<sup>29</sup>Si) shifts due to effects of the substituents R can be correlated successfully with values of the Taft constants σ\*. Slopes of the correlation dependences have negative signs for all the groups of the studied compounds (increasing electron-acceptor ability of substituent R causes upfield shifts of δ(<sup>29</sup>Si)), and their values decrease with increasing electronegativity of the substituent X (sensitivity of the δ(<sup>29</sup>Si) shifts due to substituent R increases with increasing electronegativity of the substituent X). Methyl groups at γ-position of the chain of substituent R cause a diamagnetic shift of δ(<sup>29</sup>Si) by 0.6 to 3.3 ppm. The δ(<sup>13</sup>C) shifts depend little on nature of the substituent X. Chemical shifts δ(<sup>13</sup>C) of carbon atoms at α-, β-, and γ-positions of the substituent R with respect to silicon show a good linear correlation with the δ(<sup>13</sup>C) shifts of the corresponding carbon atoms in aliphatic hydrocarbons CH<sub>3</sub>R. Slopes of the correlation dependences of all the groups of studied compounds are close to 1, the intercepts for α- and β-positions are negative because of induction effect. Positive value of the intercepts for γ-positions reflects the influence of sterical γ-effect.

Our previous paper<sup>1</sup> summarizes results of studies of <sup>13</sup>C, <sup>29</sup>Si, <sup>117</sup>Sn, and <sup>119</sup>Sn NMR spectra of the compound type (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>YX, where Y are elements of the IVb group of periodic system (C, Si, Ge, Sn), and X are halogen atoms, hydroxyl group or CrO<sub>3</sub>OY(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> group. Out of these compounds the most important industrially are esters of chromic acid ((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>YO)<sub>2</sub>CrO<sub>2</sub> which are used as precursors of catalytic systems for low-pressure polymerization of α-olefins<sup>2,3</sup>.

Besides perphenylsilyl chromates analogous ester with one alkyl instead of phenyl group (*i.e.* type ((C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(R)O)<sub>2</sub>CrO<sub>2</sub>) have gained technical importance recently. The present paper deals with a study of <sup>29</sup>Si and <sup>13</sup>C NMR spectra of bis(alkyldiphenylsilyl) chromates and compounds of general formulae (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(R)Cl and (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(R)OH, where R = methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, isobutyl, octyl, benzyl, and cyclohexyl. Alkyldiphenylchlorosilanes and alkyldiphenyl-

silanoles are intermediates in preparation of the esters of chromium acid. The aim of the study is to confirm the presumed structure of the compounds, as the compounds  $(C_6H_5)_2Si(R)Cl$  were prepared by means of organolithium compounds, and isomerization of the alkyl substituent during the reaction course cannot be excluded<sup>4</sup>. The results should also enable a purity check of the above-mentioned catalytic precursors<sup>1</sup>.

## EXPERIMENTAL

Alkyldiphenylchlorosilanes (*Ia–Ik*), alkyldiphenylsilanoles (*Ila–Ilk*), bis(alkyldiphenylsilyl)-chromates (*IIla–IIlk*) and methyldiphenylsilyl acetate (*IV*) and benzoate (*VI*) were prepared according to refs<sup>5–7</sup>. Ethyldiphenylsilyl 4-nitrobenzoate (*V*) was prepared by reaction of ethyldiphenylchlorosilane and 4-nitrobenzoic acid in benzene in the presence of pyridine<sup>8</sup>. M.p. 84–85°C (chloroform–hexane 1 : 1 v/v). For  $C_{21}H_{19}NO_4Si$  (374.4) calculated: 67.54% C, 4.05% H, 3.75% N, 7.52% Si; found: 66.51% C, 4.56% H, 3.78% N, 7.31% Si.

The NMR spectra were obtained with a JNM-FX 100 (JEOL) apparatus equipped with a multi-nuclear probe and working at 25.047 MHz (<sup>13</sup>C) and 19.788 MHz (<sup>29</sup>Si) in pulse mode with Fourier transformation. The liquid substances were measured as about 50% (v/v) solutions in deuteriochloroform, the solid substances were measured as about 25% (w/v) solutions in the same solvent at room temperature. The solutions were measured in 10 mm (o.d.) NMR test tubes, and deuteriochloroform was used as an internal lock substance. The chemical shifts were related to internal (<sup>13</sup>C) or external (<sup>29</sup>Si) tetramethylsilane, the positive values denoting downfield shift. The <sup>29</sup>Si and <sup>13</sup>C chemical shifts were measured at digital resolution 1.22 Hz/point ( $\pm 0.06$  and 0.05 ppm, respectively), and inverse gated decoupling (<sup>29</sup>Si; irradiation during the acquisition time) or proton noise decoupling (<sup>13</sup>C).

## RESULTS AND DISCUSSION

Each of the proton-decoupled carbon spectra of *I–V* exhibited four signals of phenyl groups. Numbering of carbon atoms of phenyl group ( $C_{(1)}–C_{(4)}$ ) starts from  $C–Si$  atom; the signals of  $C_{(1)}–C_{(4)}$  were assigned in the same way as in ref.<sup>1</sup>.

Signals of carbon atoms of the aliphatic chains were assigned on the basis of multiplicity in the proton-coupled spectra, mutual comparison, and comparison with the published<sup>9</sup> values in the compounds  $(CH_3)_{3-n}X_nSi(CH_2)_mH$ . In the compounds  $(C_6H_5)_2Si(CH_2CH_2CH_3)X$  (where  $X = Cl$  or  $OH$ ) the  $–CH_2–$  groups were differentiated on the basis of results of selective decoupling. The irradiation frequency in this decoupling corresponded to the absorption frequency of  $–CH_2–CH_2–CH_3$  group (the <sup>1</sup>H NMR signal of propyl group at the lowest field). In the compound  $(C_6H_5)_2Si(CH_2CH_2CH_3)OH$  the <sup>13</sup>C NMR signal of  $SiCH_2$  is shifted downfield as compared with the signal of  $SiCH_2CH_2CH_3$ , which agrees with the assignment of signals of the compounds  $(CH_3)_3SiCH_2CH_2CH_3$  and  $(CH_3)_2Si(OC_2H_5)CH_2CH_2CH_3$  (ref.<sup>9</sup>), whereas with the compound  $(C_6H_5)_2Si(CH_2CH_2CH_3)Cl$  the order of shifts is reversed.

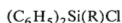
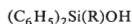
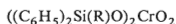
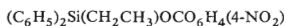
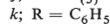
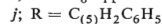
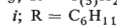
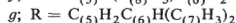
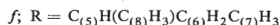
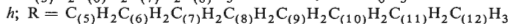
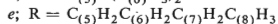
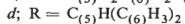
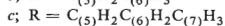
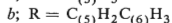
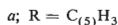
TABLE I

 $^{29}\text{Si}$  and  $^{13}\text{C}$  chemical shifts ( $\pm 0.1$ ; related to internal ( $^{13}\text{C}$ ) or external ( $^{29}\text{Si}$ ) tetramethylsilane) for the compounds I–V in deuteriochloroform

Compound	$\delta(^{29}\text{Si})$	$\delta(^{13}\text{C})$							
		$\text{C}_{(1)}$	$\text{C}_{(2)}$	$\text{C}_{(3)}$	$\text{C}_{(4)}$	$\text{C}_{(5)}$	$\text{C}_{(6)}$	$\text{C}_{(7)}$	$\text{C}_{(8)}$
<i>Ia</i>	10.7	134.4	134.0	128.0	130.5	0.9	—	—	—
<i>Ib</i>	12.6	133.5	134.3	128.0	130.4	8.6	6.7	—	—
<i>Ic</i>	11.0	133.8	134.2	128.0	130.4	16.7	19.0	17.7	—
<i>Id</i>	13.6	132.8	134.6	128.0	130.3	14.9	17.0	—	—
<i>Ie</i>	11.2	133.8	134.2	128.0	130.4	16.3	26.0 <sup>a</sup>	25.2 <sup>a</sup>	13.7
<i>If</i>	12.9	133.0	134.6	128.0	130.3	22.2	23.8	13.2 <sup>a</sup>	13.0 <sup>a</sup>
<i>Ig</i>	10.3	134.3	134.2	128.0	130.3	26.5	24.4	26.0	—
<i>Ih</i>	11.3	133.8	134.3	128.0	130.4	16.5	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>
<i>Ii</i>	10.9	132.7	134.6	127.9	130.2	26.5	27.6 <sup>a</sup>	26.6 <sup>a</sup>	26.5
<i>Ij</i>	7.0	132.6	134.5	127.9	130.6	26.5	135.7	129.1	128.1 <sup>c</sup>
<i>Ik</i>	1.9	132.8	135.1	128.0	130.7	—	—	—	—
<i>IIa</i>	— 1.8	137.0	133.9	127.9	129.9	—1.3	—	—	—
<i>IIb</i>	— 2.8	136.0	134.2	127.7	129.6	6.8	6.6	—	—
<i>IIc</i>	— 3.6	136.3	134.1	127.7	129.5	17.6	16.6	18.1	—
<i>IId</i>	— 2.7	135.1	134.5	127.6	129.6	13.4	17.0	—	—
<i>IIe</i>	— 3.4	136.3	134.2	127.7	129.5	14.8	26.4 <sup>a</sup>	25.1 <sup>a</sup>	13.7
<i>IIf</i>	— 3.3	135.4	134.5	127.6	129.5	20.9	23.8	13.3 <sup>a</sup>	13.0 <sup>a</sup>
<i>IIg</i>	— 3.8	136.7	134.1	127.7	129.5	25.4	24.1	26.2	—
<i>IIh</i>	— 3.5	136.3	134.2	127.7	129.5	15.1	<sup>d</sup>	<sup>d</sup>	<sup>d</sup>
<i>IIi</i>	— 5.1	135.2	134.5	127.6	129.5	25.4	27.8 <sup>a</sup>	26.7	26.7
<i>IIj</i>	— 8.1	135.1	134.3	127.6	129.7	25.1	137.4	128.8	128.0 <sup>e</sup>
<i>IIk</i>	—11.9	134.9	134.9	127.9	130.0	—	—	—	—
<i>IIIa</i>	11.3	134.8	134.2	128.0	130.4	—1.8	—	—	—
<i>IIIb</i>	11.4	134.3	134.5	128.0	130.4	6.9	6.6	—	—
<i>IIIc</i>	10.4	134.5	134.3	128.0	130.3	16.6 <sup>a</sup>	17.5 <sup>a</sup>	18.0	—
<i>IIId</i>	10.9	133.1	134.8	127.9	130.3	14.3	17.1	—	—
<i>IIIe</i>	10.7	134.4	134.4	128.0	130.3	14.8	26.3 <sup>a</sup>	25.0 <sup>a</sup>	13.7
<i>IIIf</i>	10.3	133.3	134.7	127.9	130.2	21.8	24.0	13.3 <sup>a</sup>	13.2 <sup>a</sup>
<i>IIIg</i>	10.3	134.9	134.5	128.0	130.3	25.5	24.2	26.2	—
<i>IIIh</i>	10.5	134.3	134.4	128.0	130.3	15.1	<sup>f</sup>	<sup>f</sup>	<sup>f</sup>
<i>IIIi</i>	8.4	133.3	134.8	127.9	130.2	26.4	27.8 <sup>a</sup>	26.9 <sup>a</sup>	26.6
<i>IIIj</i>	4.5	133.0	134.6	127.8	130.4	24.8	135.9	129.0	128.1 <sup>g</sup>
<i>IIIk</i>	0.2	133.2	135.2	128.0	130.6	—	—	—	—
<i>IV</i>	0.6	133.6	134.2	127.6	130.0	—2.8	170.8	22.3	—
<i>V</i>	4.4	132.0	134.8	127.7	130.6	5.3	6.5	164.2	136.2 <sup>h</sup>

<sup>a</sup> The assignment can be opposite; <sup>b</sup>  $\delta(\text{CH}_2) = 33.0; 31.9; 29.2; 29.1; 23.0; 22.7$ ;  $\delta(\text{CH}_3) = 14.1$ ;<sup>c</sup>  $\delta(\text{C}_{(9)}) = 125.0$ ; <sup>d</sup>  $\delta(\text{CH}_2) = 33.5; 31.9; 29.3; 29.2; 23.0; 22.7$ ;  $\delta(\text{CH}_3) = 14.1$ ; <sup>e</sup>  $\delta(\text{C}_{(9)}) = 124.3$ ; <sup>f</sup>  $\delta(\text{CH}_2) = 33.3; 31.9; 29.2; 29.1; 22.9; 22.7$ ;  $\delta(\text{CH}_3) = 14.1$ ; <sup>g</sup>  $\delta(\text{C}_{(9)}) = 124.7$ ;<sup>h</sup>  $\delta(\text{C}_{(9)}) = 131.2$ ;  $\delta(\text{C}_{(10)}) = 123.4$ ;  $\delta(\text{C}_{(11)}) = 154.5$ .

Numbering of carbon atoms in cyclohexyl substituent of *Ii-IIIi* ( $C_{(5)}-C_{(8)}$ ) starts from the carbon atom bound to silicon atom, numbering of carbon atoms of phenyl group in benzyl substituent starts from the carbon atom bound to methylene group. Numbering of phenyl group in 4-nitrobenzoic acid ( $C_{(8)}-C_{(12)}$ ) starts from the carbon atom bound to carboxyl group whose carbon atom is designed as  $C_{(7)}$ . Carbon atom of carboxyl group in *IV* is designed as  $C_{(6)}$ , whereas  $C_{(7)}$  belongs to  $CH_3COO$  in this compound.

*I**II**III**IV**V**VI*

In the  $^{29}Si$  NMR spectra of *I-VI* only one signal was found beside the standard. Values of the  $\delta(^{29}Si)$  and  $\delta(^{13}C)$  shifts of the individual compounds are given in Table I. The  $^{29}Si$  and  $^{13}C$  NMR spectra confirm unambiguously the structures of compounds given in the above formulae.

TABLE II

Dependence between  $\delta(^{29}Si)$  of the compounds  $(C_6H_5)_2Si(R)X$  and  $pK_a$  values of the corresponding acids  $HX$

X	OH	$CH_3COO$	$C_6H_5COO$	$4-O_2NC_6H_4COO$	$HCrO_4$	Cl
$pK_a$ (HX)	15.7	4.7 (ref. <sup>13</sup> )	4.2 (ref. <sup>14</sup> )	3.5 (ref. <sup>15</sup> )	-0.6	0.98-7.0 (ref. <sup>12</sup> )
$\delta(^{29}Si)$ ; R = $CH_3$	-2.8	0.6	2.5	-	11.4	12.6
$\delta(^{29}Si)$ ; R = $C_2H_5$	-1.8	-	-	4.4	11.3	10.8

$^{29}\text{Si}$  NMR Spectra

In all the compounds  $(\text{C}_6\text{H}_5)_2\text{Si}(\text{R})\text{X}$  the chemical shift  $\delta(^{29}\text{Si})$  is affected by the substituent X in dominant way, the nature of the substituent R being far less significant. With the compounds *II* ( $\text{X} = \text{OH}$ ) the values  $\delta(^{29}\text{Si})$  show generally an upfield shift as compared with the standard, whereas with the compounds *I* and *III* they are shifted downfield. This agrees well with available literature data<sup>1,10</sup> giving the values  $-11.9$  and  $1.9$  for  $(\text{C}_6\text{H}_5)_3\text{SiOH}$  and  $(\text{C}_6\text{H}_5)_3\text{SiCl}$ , respectively. McFarlane and Seaby<sup>11</sup> and Marsmann and Horn<sup>12</sup> found a relatively good linear dependence between values of the chemical shifts  $\delta(^{29}\text{Si})$  of  $(\text{CH}_3)_3\text{SiX}$  and strengths of the corresponding acids  $\text{HX}$ , the increasing acidity (decreasing  $\text{p}K_a$ ) being connected with downfield shift of  $\delta(^{29}\text{Si})$ . We have not enough experimental data for construction of a similar dependence. However, from examples of Table II it is clear that the mentioned trend is maintained with the compounds  $(\text{C}_6\text{H}_5)_2\text{Si}(\text{CH}_3)\text{X}$  and  $(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_2\text{H}_5)\text{X}$ , too.

Whereas increasing electron-acceptor ability of the group X causes the  $\delta(^{29}\text{Si})$  to shift downfield, the influence of substituent R is just opposite. Fig. 1 gives dependences of  $\delta(^{29}\text{Si})$  vs the Taft  $\sigma$  constants of the substituent R (ref.<sup>16,17</sup>). The dependences evaluated by the least squares method fit well the linear equation:

$$\delta(^{29}\text{Si}) = \rho\sigma^* + \rho_0 \quad (1)$$

Parameters of the linear correlation are summarized in Table III. All the dependences show negative value of the  $\rho$  constant; the intercepts of the dependences ( $\rho_0$  constants) have negative value for compounds *II* and positive value for compounds *I* and *III*.

The opposite influences of the substituents R and X can be explained qualitatively on the basis of the model of general dependence of the chemical shifts  $\delta(^{29}\text{Si})$  on electron density around the silicon atom, which was recently discussed in detail by Schraml and coworkers<sup>18</sup>. This dependence (expressed approximately in the coordinates  $\delta(^{29}\text{Si}) \sim \sum\sigma^*$ ) is known to have a U-shape, their parameters (especially those of its extreme) depending on nature of all the substituents.

TABLE III  
Parameters of linear correlation of Eq. (1)

Compounds	$\rho$ , ppm	$\rho_0$ , ppm	$r^a$	$N^b$
<i>I</i>	$-13.31$	$9.94$	$0.967$	$10$
<i>II</i>	$-11.16$	$-4.88$	$0.904$	$10$
<i>III</i>	$-13.57$	$8.56$	$0.925$	$10$

<sup>a</sup> Correlation coefficient; <sup>b</sup> number of experimental data.

The substituent with dominant influence determines position of the extreme with respect to the both coordinates of the dependence. Its increasing electron-acceptor ability causes the position of the extreme to shift downfield<sup>9</sup>. A rough measure of this shift is the value of intercepts of the correlation dependences — the  $\varrho_0$  constants in the equations type (1). The compounds I–III studied by us have their extremes shifted (in accordance with  $pK_a$  values of the corresponding acids HX) downfield in the order  $\varrho_0(II) < \varrho_0(III) < \varrho_0(I)$ . Effect of the other substituents depends on values  $\sum\sigma^*$  of all the substituents and on their position with respect to the extreme of the dependence  $\delta(^{29}\text{Si})$  vs  $\sum\sigma^*$ . For the  $\sum\sigma^*$  values lower than the extreme coordinate all the substituents act in the same direction. Value of the slope  $\varrho$  of Eq. (1) has positive sign in such case. For the  $\sum\sigma^*$  values higher than the extreme coordinate the dominant substituent has opposite effect to the other substituents. In such case correlation  $\delta(^{29}\text{Si})$  vs  $\sum\sigma^*$  forms a part of descending section of the general dependence  $\delta(^{29}\text{Si})$  vs  $\sum\sigma^*$ , and the  $\varrho$  constant has negative sign. The compounds studied by us represent the latter alternative with respect to the presence of two phenyl groups and substituent X. High values of  $\sum\sigma^*$  of the rest  $(\text{C}_6\text{H}_5)_2\text{SiX}$  not only correspond to negative values of  $\varrho$  constants of Eq. (1) but also to order of their absolute values. The latter reflect steepness of the correlation dependences in a given section of the general dependence. It is natural that this steepness increases with increasing distance from the extreme, which, however, also means that sensitivity of chemical shifts  $\delta(^{29}\text{Si})$  to variation of the substituents R in the compounds  $(\text{C}_6\text{H}_5)_2\text{Si}(\text{R})\text{X}$  increases, too.

With all the studied classes of compounds we observed a characteristic diamagnetic shift of silicon resonances due to methyl groups at  $\gamma$ -position of the aliphatic chain

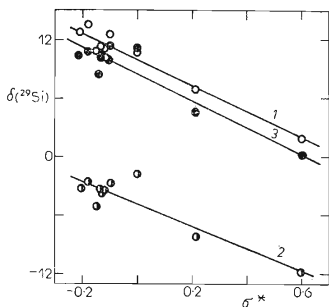


FIG. 1

Dependence of  $\delta(^{29}\text{Si})$  chemical shifts of the compounds  $(\text{C}_6\text{H}_5)_2\text{Si}(\text{R})\text{X}$  on values of the Taft  $\sigma^*$  constants of the substituents R. 1  $(\text{C}_6\text{H}_5)_2\text{Si}(\text{R})\text{Cl}$ , 2  $(\text{C}_6\text{H}_5)_2\text{Si}(\text{R})\text{OH}$ , 3  $[(\text{C}_6\text{H}_5)_2\text{Si}(\text{R})\text{O}]_2\text{CrO}_2$

with respect to silicon atom ( $\gamma$ -effect). This shift is defined as  $\Delta\delta(^{29}\text{Si}) = \delta(^{29}\text{Si})(\text{A}) - \delta(^{29}\text{Si})(\text{B})$  (where A means a compound with R substituent having one or two methyl groups at  $\gamma$ -position, B means the corresponding compound with R substituent having hydrogen atoms instead of methyl groups at the  $\gamma$ -position), and its value is  $-0.6$  to  $-3.3$  ppm according to nature of the substituents X and R and to number of methyl groups at  $\gamma$ -position (Table IV).

TABLE IV  
Sterical  $\gamma$ -effect of methyl groups on  $\delta(^{29}\text{Si})$  in compounds I–III

R		$\Delta\delta(^{29}\text{Si})$ , ppm		
A <sup>a</sup>	B <sup>a</sup>	I	II	III
<i>c</i>	<i>b</i>	-1.6	-0.8	-1.0
<i>f</i>	<i>d</i>	-0.7	-0.6	-0.6
<i>g</i>	<i>d</i>	-3.3	-1.1	-1.0
<i>g</i>	<i>b</i>	-2.3	-1.0	-1.1

<sup>a</sup> See the text.

TABLE V  
Parameters of linear correlation of Eq. (2)

Compound	<i>m</i> <sup>a</sup>	<i>k</i>	<i>q</i> , ppm	<i>r</i> <sup>b</sup>	<i>N</i> <sup>c</sup>
I	$\alpha$	0.93	-5.43	0.982	9
I	$\beta$	1.02	-8.22	0.984	8
I	$\gamma$	1.05	+2.42	0.979	4
II	$\alpha$	1.00	-8.03	0.984	9
II	$\beta$	1.06	-9.42	0.991	8
II	$\gamma$	1.03	+3.00	0.973	4
III	$\alpha$	1.04	-8.84	0.990	9
III	$\beta$	1.05	-9.00	0.991	8
III	$\gamma$	1.03	+2.97	0.973	4

<sup>a</sup> Position of the carbon atom in the substituent R with respect to silicon atom or to carbon atom of methyl group; <sup>b</sup> correlation coefficient; <sup>c</sup> number of experimental data.

<sup>13</sup>C NMR Spectra

The <sup>13</sup>C NMR spectra of phenyl substituents of the compounds *I–III* show characteristic shifts of  $\delta(^{13}\text{C})$  which are found with all phenylsubstituted silanes<sup>19</sup>. Generally it can be stated that the shifts  $\delta(^{13}\text{C})$  of carbon atoms at individual positions of phenyl substituent related to the shifts  $\delta(^{13}\text{C})$  of unsubstituted benzene (128.5 ppm against tetramethylsilane) defined as  $\Delta\delta(^{13}\text{C}_{(n)})$  values (*n* means denotation of carbon atoms) are little sensitive to composition of the rest of the molecules, *i.e.* composition of  $\text{C}_6\text{H}_5\text{Si}(\text{R})\text{X}$  fragment. The least differences in the values  $\Delta\delta(^{13}\text{C})$  ( $-0.5$  to  $-0.9$ ) are found for carbon atoms at *meta* positions of the phenyl substituent. A slight sensitivity to variation of the substituents R or X can be observed for the values  $\Delta\delta(^{13}\text{C}_{(4)})$  which vary within the limits 1.7 to 2.2 ppm (compounds *I* and *III*) and 1.0 to 1.5 ppm (compounds *II*). The signals due to carbon atoms at *ortho* position ( $\text{C}_{(2)}$ ) are shifted downfield by average 5.4 to 6.4 ppm as compared with those of benzene. In this case the  $\Delta\delta(^{13}\text{C}_{(2)})$  shifts seem to be more sensitive to variation of substituent R (differences in compound series having the same X are 0.6 to 1.0 ppm) than to that of X (for various X and constant R it is 0.1 to 0.3 ppm). Relatively highest changes with variation of substituent (both X and R) are found with the signals of the carbon atoms at *ipso* position. This can be seen from differences of  $\Delta\delta(^{13}\text{C}_{(1)})$  values of the compounds *II* (6.4 to 8.5 ppm) and those of *I* and *III* (4.1 to 5.9 and 4.5 to 6.4 ppm, respectively) and from broader limits inside each class of compounds with the same X and varying R (1.8 to 2.1 ppm for the *ipso* position; 0.3 to 1.0 for other positions). No simple dependence between the  $\delta(^{13}\text{C})$  shifts of phenyl substituents and nature of the other substituents could be found.

It is noteworthy that the differences between  $\delta(^{13}\text{C}_{(3)})$  and  $\delta(^{13}\text{C}_{(4)})$  are about 2 ppm. This fact indicates a relatively weak contribution of (*p–d*)  $\pi$  conjugation between the phenyl nucleus and silicon atom<sup>20,21</sup>.

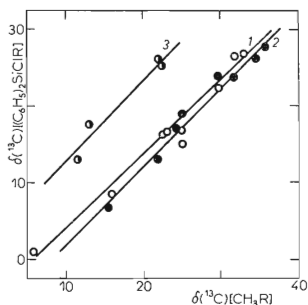


FIG. 2

Dependence of  $\delta(^{13}\text{C})$  of the substituents R in the compounds  $(\text{C}_6\text{H}_5)_2\text{Si}(\text{R})\text{Cl}$  on  $\delta(^{13}\text{C})$  of the corresponding carbon atoms in the alkanes  $\text{CH}_3\text{R}$ . 1  $\text{C}_{(a)}$ , 2  $\text{C}_{(\beta)}$ , 3  $\text{C}_{(\gamma)}$



The chemical shifts  $\delta(^{13}\text{C})$  of carbon atoms in aliphatic chain of the substituent R in the compounds *I–III* show a good linear correlation dependence on those of the corresponding carbon atoms of aliphatic hydrocarbon in which methyl group is substituted by  $(\text{C}_6\text{H}_5)_2\text{SiX}$  group (Fig. 2, X = Cl). Parameters of linear correlation of the equation

$$\delta(^{13}\text{C}_{(m)}) [(\text{C}_6\text{H}_5)_2\text{Si}(\text{R})\text{X}] = k \cdot \delta(^{13}\text{C}_{(m)}) [\text{CH}_3\text{R}] + q, \quad (2)$$

where *m* means position of carbon atom in substituent R with respect to silicon atom or to carbon atom of methyl group, respectively, are summarized in Table V.

TABLE VI

$^{13}\text{C}$ -Substituent chemical shifts for alkyl groups in compounds *I–III* with respect to parent alkanes

Compound	Effect			
	$\text{C}_{(\alpha)}$	$\text{C}_{(\beta)}$	$\text{C}_{(\gamma)}$	$\text{C}_{(\delta)}$
<i>Ia</i>	3.2	—	—	—
<i>Ib</i>	2.9	1.0	—	—
<i>Ic</i>	1.3	3.1	2.3	—
<i>Id</i>	-1.0	1.6	—	—
<i>Ie</i>	3.2	1.1	0.3	0.6
<i>If</i>	-2.7	0.9 (0.1)	0.1	—
<i>Ig</i>	-2.2	-0.6	1.7	—
<i>Ih</i>	2.6	—	—	—
<i>IIa</i>	1.0	—	—	—
<i>IIb</i>	1.1	0.9	—	—
<i>IIc</i>	2.2	0.7	2.7	—
<i>IId</i>	-2.5	1.6	—	—
<i>IIe</i>	1.7	1.5	0.2	0.6
<i>IIf</i>	-4.0	0.9 (0.2)	0.1	—
<i>IIg</i>	1.1	-0.9	1.9	—
<i>IIh</i>	1.2	—	—	—
<i>IIIa</i>	0.5	—	—	—
<i>IIIb</i>	1.2	0.9	—	—
<i>IIIc</i>	1.2	1.6	2.6	—
<i>IIId</i>	-1.6	1.7	—	—
<i>IIIe</i>	1.7	1.4	0.1	0.6
<i>IIIf</i>	-3.1	1.1 (0.2)	0.1	—
<i>IIIg</i>	1.2	-0.8	1.9	—
<i>IIIh</i>	1.2	—	—	—

All the dependences show a slope near 1, which indicates that chemical shifts in aliphatic substituents of the compounds *I–III* and those of the comparison hydrocarbons obey the same effects. The dependences for  $\alpha$ - and  $\beta$ -positions do not much differ. For the both positions negative values of the intercepts  $q$  were found in accordance with sign of inductive effect of the  $(C_6H_5)_2SiX$  group. The intercepts  $q$  are positive for  $\gamma$ -position. Schraml and coworkers<sup>9</sup> obtained qualitatively the same results in a study of the compounds type  $(CH_3)_{3-n}X_nSi(CH_2)_mH$ . The authors<sup>9</sup> ascribe positive value of the intercept for  $\gamma$ -position to complex character of this shift which is markedly influenced by paramagnetic  $\delta$ -effect of the other substituents at silicon atom. Similar to the above-cited paper we observed that increasing aliphatic chain and increasing electronegativity of the substituent X result in diamagnetic shift of the  $^{13}C$  SCS values (Substituent Chemical Shifts) defined as the difference  $\delta(^{13}C) [(C_6H_5)_2Si(R)X] - \delta(^{13}C) [HR]$  (Table VI). From the Table it can also be seen that the  $\gamma$ -effect of silyl group causes a downfield shift of  $\delta(^{13}C_{(\gamma)})$  in all the cases. This is especially striking with the compounds having methyl group at  $\gamma$ -position. Non-additive character of this effect becomes prominent when comparing the compounds with one (*Ic–IIIc*) and with two methyl groups (*Ig–IIIg*) at  $\gamma$ -position.

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