^{29}Si, ^{17}O, ^{13}C, AND ^{1}H-NMR SPECTRA
OF ACETOXYALKYLSUBSTITUTED SILANES
$(CH_3)_{3-n}X_nSi(CH_2)_mOC(O_3)CH_3$*

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^{29}Si, ^{13}C, and in some cases ^{1}H and ^{17}O-NMR spectra of the compounds of the type $(CH_3)_{3-n}X_nSi(CH_2)_mOC(O)CH_3$ are presented for some combinations of substituents X = = OC_2H_5, Cl, and $OC(O)CH_3$ and alkyl chain length m. The silicon chemical shifts follow the trends established in other carbonfunctional compounds. The carbon chemical shifts of the acetoxyalkyl group show surprising variation as the silicon atom is substituted by acetoxy groups, the chemical shifts of which remain essentially constant.

In the previous paper of this series[1] we have investigated NMR spectra of the compounds of the type

$$(CH_3)_3Si(CH_2)_mY$$
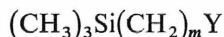
with Y = OR. In ^{29}Si-NMR spectra of these compounds upfield substituent chemical shifts (SCS) due to the OR substituents were observed for all the investigated substituents at almost all values of m except if R = $C(O)CH_3$. For this last substituent SCS of both signs occured depending on the length of the alkyl chain m. Since such upfield SCS were not observed in other compounds[2-6] of the above type with other substituents Y, and since the calculated charge distributions indicated polarization of the trimethylsilyl group under the influence of the strong electronegativity of the OR groups, it was suggested that the upfield SCS of the OR substituents are, at least partly, due to this polarization. With such interpretation, it is, however, difficult to explain downfield shifts which occur in the compounds of the above type if *e.g.* Y = Cl (ref.[7]) or $OC(O)CH_3$ (ref.[1]) though several factors (electric field effects, magnetic anisotropy *etc.*) may be invoked. In an attempt to clarify this problem

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we have investigated NMR spectra of the compounds of the type I

$$(CH_3)_{3-n}X_nSi(CH_2)_mY \qquad (I)$$

with substituents $X = OC_2H_5$, Cl, $OC(O)CH_3$ and $Y = Cl$ and $OC(O)CH_3$. In this communication the results related to the series of acetoxyalkylsubstituted silanes are presented in full extending thus an earlier preliminary communication[8].

TABLE I
^{29}Si and ^{13}C-NMR Chemical Shifts in the Compounds of the Type
$(CH_3)_{3-n}X_nSi(CH_2)_mOC(O)CH_3$

m	X^a	n	$^{29}Si^b$		$^{13}C^b$							
			δ	Δ^c	CH_3Si	CH_2-α	CH_2-β	CH_2-γ	$C(O)$	$CH_3{}^d$	OC^e	$CH_3{}^e$
1	OEt	0	0·3	0·3	−2·5	58·1			169·9	20·8	—	—
		1	9·0	− 4·5	−3·4	56·2			170·1	19·8	58·3	18·2
		2	−16·1	−10·0	−5·5	53·6			169·9	19·8	58·2	18·1
		3	−58·2	−13·7	—	50·7			169·8	19·5	58·2	17·7
	OAc	1	13·8	− 8·0	−3·0	56·5			171·0	19·5^f	171·0	21·8^f
		2	−18·1	−22·7	−2·2	55·5			173·6	19·1	170·2	21·9
		3	−82·5	−38·8	—	56·8			181·0	18·6	170·4	22·7
2	OEt	0	− 1·0	− 2·6	−2·6	16·6	60·8		168·4	19·6	—	—
		1	12·7	− 3·1	−2·4	17·1	60·2		168·4	20·0	57·1	18·0
		2^g	10·3^h	− 3·6	−5·1	14·8^h	59·8^h		168·7	19·7	57·0	17·6
		3	−50·7	− 4·8	—	11·4	59·3		168·2	19·4	57·0	17·2
	Cl	1	28·2	− 3·7	1·1	18·8	59·7		168·7	19·8	—	—
		2	29·9	− 4·1	5·5	21·7	59·1		169·3	20·4	—	—
		3	10·4	− 4·2	—	25·0	58·9		169·7	21·0	—	—
3	OEt	0	0·9	0·2	−2·3	12·1	23·0	66·1	168·6	20·0	—	—
		2	− 6·8^i	0·8	−5·0	10·3	22·7	66·3	169·6	20·5	58·0	18·5
	Cl	2	33·0	^{j}	5·2	18·1	22·3	65·4	169·8	20·8	—	—

^{a} Abreviations OEt $= OC_2H_5$ and OAc $= OC(O)CH_3$. ^{b} Chemical shifts in δ-scale (ppm units relative to external TMS line, diamagnetic shifts negative), error $\pm$ 0·3 ppm. ^{c} Substituent chemical shift (SCS) of the acetoxy group Δ defined as $\Delta = \delta$ (in $(CH_3)_{3-n}X_nSi(CH_2)_mOC(O)CH_3$) − δ (in $(CH_3)_{3-n}X_n(CH_2)_mH$). The chemical shilfts in $(CH_3)_{3-n}X_nSi(CH_2)_mH$ compounds taken from ref.[9]. ^{d} Methyl carbon of the acetoxy groups. ^{e} Carbons of the substituents X. ^{f} The assignment of the two lines can be intercharged. ^{g} Because of sample size possible error of all the chemical shifts ± 1 ppm. ^{h} Impurity lines at $\delta(Si) = -9\cdot4$ $\delta(C) = 13\cdot3$ and $58\cdot7$. ^{i} Values reported in ref.[10] was in error. ^{j} Data on the parent propane derivative not available.

RESULTS AND DISCUSSION

^{29}Si *Chemical Shifts*

In some respects the trends in the silicon chemical shifts (Table I) in the acetoxyalkyl substituted silanes confirm to the trends established in other series of compounds of the type *I* (for a review see ref.[9,10]). Though the SCS values of the acetoxy group are in some cases quite large, the presence of the acetoxy group does not change the overall general "sagging" pattern of the dependence of the chemical shift on the number *n* of substituents X. The SCS values of the acetoxy group are not constant and, in accord with the general trends[10], the shielding of the silicon nucleus is increased by the acetoxy substituent the more, the higher is the value of *n*, the shorter is the alkyl chain length *m*, and the more electronegative is the substituent X (supposing all other factors being equal).

In the series of acetoxymethylsubstituted silanes $(m = 1)$ the trends in chemical shifts and SCS are similar to those in compounds *I* with $Y = NH_2$(ref.[3]), CH_3 (ref.[9]), and Cl (ref.[7]) including the small positive SCS value for $n = 0$ which makes the acetoxy derivatives different from other compounds *I* with strongly electronegative substituents Y $(e.g.\, OR$ (ref.[1]) or F (ref.[4]) with similar σ_I constants[11]). Though there are several possible reasons for the positive SCS value[1], the effect is too small to be discussed in detail.

In ethoxysubstituted silanes (with $m = 1$) the SCS varies linearly with the number *n* of ethoxy substituents similarly as in other compounds *I* (for the plots see ref.[3]) and also the shifts correlate linearly with the shifts in $(CH_3)_{3-n}X_nSiCH_3$ compounds (Fig. 1) which correlation is a consequence of the dominating influence of the substituents directly bonded to the silicon atom. In acetoxysubstituted silanes, however, the SCS values are so large (in harmony with large electronegativity of this group) that the linear correlation is not applicable (Fig. 1).
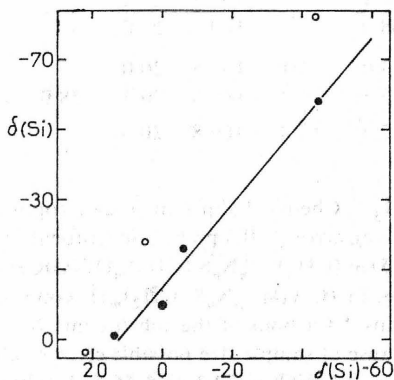

FIG. 1

A Plot of ^{29}Si Chemical Shifts in $(CH_3)_{3-n}$.$X_nSiCH_2OC(O)CH_3$ Against that in $(CH_3)_{4-n}X_nSi$ Compounds (open circles $X = OC(O)CH_3$, ful circles $X = OC_2H_5$, the solid line is the least-squares fit of the ful circles with correlation coefficient $r = 0.991$)

In the series of acetoxyethylsubstituted and acetoxypropylsubstituted silanes the shifts and the SCS follow the tendencies apparent among the corresponding values in other compounds of the type I (both with $Y = OR$ and others) though these trends were not correctly described[10] for the case of $m = 2$ and $n = 0$ (in this case, the generalizations of ref.[10] predict downfield SCS while in all the studied cases of substituents X and Y negative SCS values based on $\delta(^{29}Si) = 1\cdot6$ in $(CH_3)_3$. SiC_2H_5, ref.[9], were reported).

^{13}C and ^1H Chemical Shifts

The acetoxy group. In ethoxy- and chloro-substituted silanes the chemical shift of the carboxylic carbon varies only little (*i.e.* within $\delta = 168 - 170$) which is in accord with the reported observation that this carbon shielding in alkyl acetates is not affected by the alkyl group ($\delta = 170 \pm 1$) (ref.[12,13]). In the series of acetoxysubstituted (acetoxymethyl) silanes $(X = OC(O)CH_3)$ the changes in the shielding of the acetio xymethyl carboxylic carbon are, however, large though, surprisingly, the shfts of the other carboxylic carbons (*i.e.* those of the acetoxy groups bonded to the silicon atom) are almost constant and differ from those in the parent $(CH_3)_{4-n}$. $.Si(OC(O)CH_3)_n$ compounds by 0·8, 0·2 and 1·8 ppm if $n = 1$, 2, and 3, resp.[9]. (The assignment of the two lines to the two types of acetoxy groups based on intensity ratio is unambiguous for the compounds with $n = 2$ and 3). The trend in the shielding in the acetoxysubstituted silanes is such as one would expect for increasing ionisation of the acetoxy group with increasing n, so that with $n = 3$ the shift is practically the same as in $CH_3COO^-NH_4^+$ $\delta = 181\cdot7$) (ref.[14]). (We could not see any traces of hydrolysis or of impurities in either ^{13}C- or ^1H-NMR spectra of these compounds though such were observed in the IR spectra of some of the samples[15].) The low-field ionization shifts (with increased electron density) were noted[14] as difficult to explain. Application of Letcher and Van Wazer[16] theory to tetrahedral carbons has yielded[17] a U-shaped dependence of the shift on the net charge on the carbon atom. As a similar dependence can be expected to hold for planar carbonyl carbons the above ionization shift indicates that the point corresponding to the carboxylic carbon is on the branch in which increased electron density (or smaller positive net charge) leads to deshielding. If so, the trend in the carboxylic carbon shielding can be interpreted as corresponding to increasing electron density on this carbon atom with increasing n. Such interpretation would be in harmony with the accompanying small increase in the shielding of the methyl carbon of the same acetoxy group since certainly this carbon is on the oposite branch of the U-shaped dependence. On the other hand the chemical shift of the methyl carbon of the acetoxy group bonded directly to the silicon atom moves to a lower field as n is increased which change is in the opposite direction not only to the change of the shielding of the methyl carbon in the other acetoxy group but also oposite to the trend in the parent compounds[9] $(CH_3)_{4-n}$.

.$Si(OC(O)CH_3)_n$. It is also possible that steric effects contribute to the observed variations in the chemical shifts, but the changes are too small to allow a serious discussion, which applies also to the shifts of the methyl carbon of the acetoxy group in compounds with $m = 2$ and 3.

In the proton NMR spectra, negligible changes in the proton shifts were observed (Table II) both for the acetoxy groups bonded directly to the silicon atom and for the acetoxy group in acetoxyalkylsubstituted ethoxysilanes; the methyl proton of the acetoxymethyl group in compounds with $X = OC(O)CH_3$ is gradually deshielded as n is increased (*i.e.* an opposite trend to that observed on the carbon of the same group) but again the changes are too small, 0·3 ppm in total.

TABLE II

^{1}H-NMR Data on the Compounds of the Type $(CH_3)_{3-n}X_nSiCH_2OC(O)CH_3$[a]

X	n	$\delta^{b,c}$					$J(^{29}Si-C-^1H)^d$	$J(^{13}C-^1H)$	$J_{(H-H)}^{b,f}$
		CH_3-Si	CH_3-	$-CH_2-O$	$CH_3C(O)$	CH_2Si		CH_3Si	C_2H_5
C_2H_5O	0	0·027	—	—	1·992	3·708	6·6	119·5	
		0·068	—	—	1·972	3·685	6·7	120·1	
	1	0·131	1·138	3·668	1·998	3·730	6·8	119·5^g	6·9
		0·140	1·162	3·667	1·989	3·694	(6·8)	119·4^g	6·9
	2	0·149	1·163	3·760	2·002	3·707	7·1	120·1^g	6·9
		0·136	1·195	3·759	1·934	3·659		119·0^g	7·0
	3	—	1·182	3·823	2·012	3·746			7·2
		—	1·211	3·815	1·997	3·676			7·0
$CH_3C(O)O$	1	0·282	1·990^h		1·990	3·804	7·0	120·6	
		0·308	2·003^d		2·015	3·760	7·2	120·3	
	2	0·498	2·017^h		2·032	3·843	(8·2)	122·9^g	
		0·496	2·036^h		2·073	3·805		122·3^g	
	3	—	2·058^h		2·224	3·972	—	—	

[a] Chemical shifts in δ scale (*i.e.* in ppm units, positive values for shifts to lower field from TMS line). Coupling constants J in Hz. [b] Measured in 1 : 9 $CHCl_3$ solutions, where two values are given that on the first line was obtained in $CHCl_3$ solution and that on the second line in CCl_4. [c] Standard deviation $\pm0·003$ ppm. [d] The same as [b], values in parenthesis obtained in 2 : 1 solutions maximum standard deviation $\pm0·2$ Hz. [e] The same as [b] except that 2 : 1 solutions were measured Maximum standard deviation $\pm0·2$ Hz. [f] Standard deviation $\pm0·2$ Hz. [g] Only one satelite could be measured, estimated error $\pm0·5$ Hz. [h] Acetoxy group of the substituent X.

Though, in general, and in contrast to ^{1}H-NMR spectra, the ^{13}C-NMR spectra are knwon to depend only little on the solvent and concentration, the chemical shifts of carbonyl carbons were shown to depend significantly on these conditions of measurement (see e.g.[18-20]). Since it was impractical to measure ^{13}C-NMR spectra of diluted solutions of the studied compounds, ^{1}H-NMR spectra were recorded in two solutions in order to asses these effects. As it is apparent from Table II the solvent change from CHCl$_3$ to CCl$_4$ has a small effect on the shifts but the trends are not changed. Therefore it seems resonable to expect that the trends in ^{13}C chemical shifts are also not affected but, nevertheless, one should bear in mind that the ^{13}C as well as the ^{29}Si-NMR spectra were recorded in neat liquids.

The methyl group bonded to the silicon atom. The carbon chemical shifts parallel those in the parent $(CH_3)_{3-n}X_nSi(CH_2)_mH$ compounds only to some extent, the substituent effect of the remote acetoxy group is not constant for the compounds of the same m (e.g. in the compounds with $m = 3$ the substituent effect is $+0.5$ ppm in if $n = 0$ but it is $+1.2$ ppm if $n = 2$ and $X = OC_2H_5$). In compounds with alkyl chain length m larger than 1, the substituent effect has the sign expected on the electro-negativity grounds (introduction of the acetoxy group shifts the methyl carbon resonance to lower field) but in compounds with $m = 1$ the acetoxy group brings about a shift to a higher field. Similar high-field shifts are observed in other com-pounds (e.g. amines[3], alkoxy derivatives[1]) of the type I and also in the parent com-pounds $(CH_3)_{3-n}X_nSi(CH_2)_mH$ when going from $m = 1$ to $m = 2$. They are ap-parently due to steric effects since the terminal methyl groups are in the gamma posi-tion relative to the methyl group bonded to the silicon atom. One can speculate that the different SCS in compounds of the same m are due to different conformations prevailing in the compounds of different n. Proton chemical shifts vary only very little, a small increase in both $J(^{29}Si—^1H)$ and $J(^{13}C—^1H)$ coupling constants with increasing n is apparent from Table II.

The ethoxy group. Similarly as in other ethoxysilanes[9,21] both carbon and proton chemical shifts and vicinal proton-proton coupling constants remain the same as m or n is changed; a trend is apparent in ^{17}O chemical shifts which will be mentioned latter.

The methylene groups. When the available data for methyl and ethyl acetates[13,22] are compared with the chemical shifts in methane and ethane[23] the substituent effects of the acetoxy group on α and β carbons are found to be $+54$ and $+8.3$ ppm, resp. In the studied acetoxyalkylsubstituted silanes such SCS are observed only in the compounds with $m = 2$, where these effects are $+53.4 \pm 1.2$ and 8.4 ± 2.4 ppm, resp., as calculated from the data in Table I and in ref.[9]. The limited data for the compounds with $m = 3$ give smaller values 48.5 and 6.2 ppm (and -6.4 ppm for γ effect) while in the (acetoxymethyl)silanes larger α effects are observed (with the

exception of the compound with $X = OC(O)CH_3$ and $n = 3$, in which case the effect is $+61.6$ ppm, all the effects are within $+57.6 \pm 0.5$ ppm). Since the chemical shift of the methylene carbons in all (acetoxymethyl)silanes are essentially the same, the large value of the SCS in (acetoxymethyl)triacetoxysilane is obviously caused by the relatively large shielding ($\delta = -4.8$) in the parent methyltriacetoxysilane, which is probably due to steric compression with the carbonyl groups[13].

^{17}O *Chemical Shifts*

As it is apparent from Table III, the ^{17}O chemical shift provide only very little information. The shift of the oxygen in the ethoxy groups shows the trend similar to that found[21] in methylethoxysilanes, the oxygens of the acetoxy group have too wide lines so that the chemical shift of the C(O) oxygen chemical shift could not be measured and the shift of the C—O—C oxygen could be measured only in two Compounds in which the line width was larger than the change in the chemical shift.

EXPERIMENTAL

Preparation and other properties of the studied acetoxyalkylsubstituted silanes are described elsewhere[24]. Details of the spectrometer and measuring technique were given earlier[2,25] for ^{13}C and ^{29}Si spectra. ^{17}O-NMR spectra were measured at 8·12 MHz and the chemical shifts were determined relatively to the line of external H_2O. All the samples were measured in neat liquids and, with the exception of the compound with $X = OC_2H_5$, $m = 2$, and $n = 2$ were pure according to their NMR spectra. The impurity lines observed in the mentioned compound are given in Table I. The assignment of the ^{13}C lines to individual carbons in the molecules was streightforward on the basis of intensity considerations and comparison with analogous compounds.

TABLE III
^{17}O NMR-Data for $(C_2H_5O)_n(CH_3)_{3-n}SiCH_2OC(O)CH_3$ Compounds

n	$O(C_2H_5)$		$O(COCH_3)$	
	$\delta(^{17}O)^{a,b}$	w^c	$\delta(^{17}O)^{a,d}$	w^c
1	10	150	132	250
2	19	180	130	250
3	14	200	^{e}	

^{a} Chemical shifts in ppm units, relative to external H_2O line. Positive values indicate shift to low field of the reference line. ^{b} Standard deviation ±4 ppm. ^{c} Line widths. ^{d} Standard deviation ±7 ppm. ^{e} Too wide to be measured.

REFERENCES

1. Schraml J., Chvalovský V., Mägi M., Lippmaa E.: This Journal, in press.
2. Nguyen-Duc-Chuy, Chvalovský V., Schraml J., Mägi M., Lippmaa E.: This Journal *40*, 875 (1975).
3. Schraml J., Nguyen-Duc-Chuy, Chvalovský V., Mägi M., Lippmaa E.: Org. Magn. Resonance *7*, 379 (1975).
4. Schraml J., Včelák J., Engelhardt G., Chvalovský V.: This Journal *41*, 3758 (1976).
5. Schraml J., Chvalovský V., Mägi M., Lippmaa E.: This Journal *42*, 306 (1977).
6. Čapka M., Schraml J., Jancke H.: This Journal, in press.
7. Lippmaa E., Mägi M., Engelhardt G., Jancke H., Chvalovský V., Schraml J.: This Journal *39*, 1041 (1974).
8. Schraml J., Pola J., Chvalovský V., Mägi M., Lippmaa E.: J. Organometal. Chem. *49*, C 19 (1973).
9. Schraml J., Chvalovský V., Mägi M., Lippmaa E.: This Journal, in press.
10. Schraml J., Bellama J. M. in the book: *Determination of Organic Structures by Physical Methods* (F. C. Nachod, J. J. Zuckerman, E. W. Randall, Eds), Vol. 6, p. 203. Academic Press, New York 1976.
11. Ritchie C. D., Sager W. F.: Progr. Phys. Org. Chem. *2*, 323 (1964).
12. Stothers J. B.: *Carbon*-13 NMR *Spectroscopy*, p. 300. Academic Press, New York 1972.
13. Delletier S. W., Djarmati Z., Pape C.: Tetrahedron *32*, 995 (1976).
14. Ref.[12], p. 295.
15. Jakoubková M.: Private communication.
16. Letcher J. H., Van Wazer J. R. in the book: *Topics in Phosphorus Chemistry* (M. Grayson, E. J. Griffith, Eds), p. 76. Interscience, New York 1967.
17. Radeglia R.: Z. Phys. Chem. (Leipzig) *256*, 453 (1975).
18. Nakashima T. T., Maciel G. E.: Org. Magn. Resonance *4*, 321 (1972).
19. Nakashima T. T., Traficante D. D., Maciel G. E.: J. Phys. Chem. *78*, 124 (1974).
20. Fezney J., Partington P., Roberts G. C. K.: J. Magn. Resonance *13*, 268 (1974).
21. Harris R. K., Kimber B. J.: Org. Magn. Resonance *7*, 460 (1975).
22. Christl M., Reich H. J., Roberts J. D.: J. Amer. Chem. Soc. *93*, 3463 (1971).
23. Ref.[12], p. 56.
24. Jakoubková M., Reich P., Papoušková Z., Novák P., Pola J., Chvalovský V.: This Journal *38*, 3471 (1973).
25. Lippmaa E., Pehk T., Past J.: Eesti NSV Tead. Akad. Toim. Füüs-Matem. Tehn. Tead. Seeria *16*, 345 (1967).

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