BONDED AND NONBONDED INTERACTIONS DISPLAYED IN SPECTRA OF ACYLOXYTRIMETHYLSILANES*

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The NMR and IR spectra of the acyloxysilanes $RC(O)OSi(CH_3)_3$ with various electron donating and electron withdrawing groups R are discussed in terms of polar and steric effect of group R and conformation heterogenity. $(CH_3)_3Si$-group was found to have constant polar effect in all the compounds studied. The conformation changes due to the rotation around $C(R)—C(O)$ bond were demonstrated by means of the IR spectra recorded at different temperatures. The difference in $\nu(C{=}O)$ frequency values of individual conformers is controlled also by steric effect of group R.

The character of the IR spectra of esters $RC(O)OR'$ in solution was explained by the electronic effect of R and R' groups[1-4], mass effect and coupling of the characteristic vibrations[5,6] and conformational phenomena[7-10]. The studies of the IR spectra of organosilicon esters $RC(O)$. $.OSiR'_3$ or $(RC(O)O)_nSiR'_{4-n}$ had revealed some regularities in values of the frequency of stretching vibration $\nu(C{=}O)$ and $\nu(C—O—Si)$, which were discussed mainly in terms of the polarity of Si—O bond[11-14]. While conformation phenomena of esters $RC(O)OR'$ have been becoming very well known (see *e.g.* refs[15-18]), conformation of silyl esters has not yet been studied at all**, despite that silicon may make conformation of some silyl esters different from that of $RC(O)OR'$ because of its possible interaction with electronegative molecular centers.

The NMR spectra of some methyl- and trimethylsilyl esters were examined earlier[20,21], and the chemical shifts $\delta(H)$, $\delta(C)$, $\delta(Si)$ were found to correlate linearly with the pK_a values of the corresponding acids.

Study of the IR and NMR spectra of the compounds $RC(O)OSi(CH_3)_3$ presented in this work was carried out to find out the role of the silicon atom in bonding and to clarify the possibility of a change of the conformation of esters due to the introduction of the silicon atom.

EXPERIMENTAL

Acyloxytrimethylsilanes $RC(O)OSi(CH_3)_3$ were prepared by the reaction of the corresponding acids with chlorotrimethylsilane as described earlier[22]. Chlorotrimethylsilane was allways

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added to a solution of acid RC(O)OH in diethylether, except of the compounds with R =
= $(CH_3)_3SiOCH_2$ and $(CH_3)_3SiSCH_2$, in which case the solution of chlorotrimethylsilane
in diethyl ether was slowly added to the mixture of the stoichiometric amounts of a carboxylic
acid and pyridine. The yields and physical properties of the compounds prepared in this work
are given in Table 1. Ethyl iodoacetate (b.p. 70—71°C/9 Torr, n_D^{20} 1·5057) was obtained by the
esterification of iodoacetic acid (supplied by Fluka, A.G., Buchs). Methyl ethylthioacetate
(b.p. 106°C/80 Torr, n_D^{20} 1·4626) was prepared by the reaction of methyl thioacetate with sodium
and ethyl bromide. Purity of both compounds was checked with NMR spectroscopy.

Infrared spectra of acyloxysilanes were recorded with a double-beam Zeiss, Model UR-20,
spectrophotometer. Concentration of acyloxysilanes was $7—9 . 10^{-2}$M in CCl$_4$. The frequency
scale of the instrument was calibrated in the usual way. The IR spectra of the solutions of the
compounds prepared in CS$_2$ were measured at $+35°C$ and $-50°C$ in temperature controlled
cell with AgCl windows produced by RIIC. Thickness of the cells was 0·01 cm.

^{1}H-NMR spectra were recorded for neat liquids on a modified Tesla BS-477 spectrometer
(60 MHz), using cyclohexane as internal reference compound; chemical shifts of the methyl
group attached to the silicon atom and coupling constants $J_{^{13}C-^1H}$ of the same group were
determined with an accuracy of $\pm0·01$ ppm and 0·2 Hz respectively.

RESULTS AND DISCUSSION

The electron density on the oxygen atom in Si—O bond is generally known not
to be in harmony with an electronegativity of both atoms, but to be diminished
by the through space electron transfer to the silicon. Regardless of the exact mecha-
nism of such transfer[29,30], it was recently revealed, that the extent of the through
space interaction between $(CH_3)_3$Si-group and n_0 orbital (back bonding) in $(CH_3)_3$Si—
—O—C—X compounds is not the same in all these compounds, but depends on the
nature of the substituent X (ref.[31]). This makes for the variance of polar effect

TABLE I
The Yields and the Properties of the Compounds RC(O)OSi(CH$_3$)$_3$

R	n_D^{20}	B.p., °C/Torr	Yield, %
BrCH$_2$[a]	1·4407	83/28	42
$(CH_3)_3$SiOCH$_2$	1·4105	78/10	73
ICH$_2$	1·4719	80/11	31
CH$_3$OCH$_2$	1·4055	93/88	62
C$_6$H$_5$OCH$_2$	1·4843	100/2	50
$(CH_3)_3$SiSCH$_2$	1·4474	45/1	58
C$_6$H$_5$CH$_2$	1·4759	85/2	70
CH$_3$C(O)	1·4185	78/25	69

[a] Reported in work[23]: n_D^{20} 1·4362; b.p. 64—65°C/15 Torr.

of $(CH_3)_3Si$-group, and makes $(CH_3)_3Si$-group the greatest electron donor when X is the substituent with Taft σ^* constant higher than 0·5. There is enforced lack of back bonding in such compounds that would facilitate an interaction of the silicon atom with electron donors. (The ability of the silicon atom to make use of its sp^3d or sp^3d^2 orbitals to form more than four bonds is very well known[32].) From the almost comparable values of polar effect transmission over $C(sp^3)$ and $C(sp^2,$ carbonyl) centers[33] it follows that the substitution by the electron withdrawing groups X both in $(CH_3)_3Si$—O—C—X and $(CH_3)_3Si$—O—C(=O)—X compounds would lead to about the same electron accepting character of $(CH_3)_3Si$-group in both series of compounds. Similarly to the alkoxysilanes $(CH_3)_3Si$—O—C——X one would thus expect variable polar effect of $(CH_3)_3Si$-group also in $(CH_3)_3Si$——O—C(=O)—X compounds.

NMR Spectra

From the studies of ^{29}Si chemical shift in series of compounds $(CH_3)_3SiX$ (refs[20,34]) it can be deduced, that the magnitude of $\delta(Si)$ correlates with the electronic density on the silicon atom. This is also the case of $\delta(Si)$ for $(CH_3)_3SiOC(O)X$ compounds[20]. Our results[35] on some other of these compounds (X, $\delta(Si)$ in δ scale, relative to TMS signal in ppm units: CH_3, 21·8; $BrCH_2$, 21·1; CH_3OCH_2, 23·0; ICH_2, 24·9) revealed, despite that they were obtained under different conditions (neat liquids, technique described elsewhere[36]), that points of $\delta(Si)$ for X equal
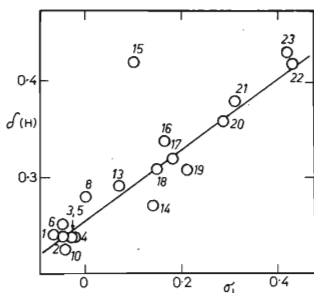

FIG. 1

Dependence of the Chemical Shift $\delta(H)$ of CH_3—Si Group of the $(CH_3)_3SiOC(O)R$ Compounds (Table II) on σ_I of Group R
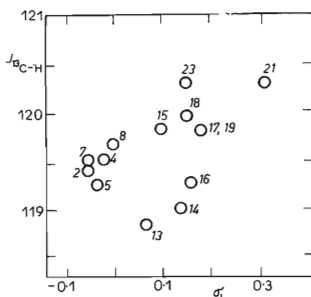
FIG. 2

Dependence of the Coupling Constant $J_{^{13}C^{-1}H}$ of CH_3—Si Group of the $(CH_3)_3$.SiOC(O)R Compounds (Table II) on σ_I of Group R

to ICH_2 and CH_3OCH_2 do not deviate from the correlation line of the dependance $\delta(Si)$ vs σ_X^* (appropriate correction was made on grounds of comparison of the values of $\delta(Si)$ of $CH_3CO_2Si(CH_3)_3$ acquired from both measurements).

The dependance of the proton chemical shift $\delta(H)$ of $(CH_3)_3Si$-group upon the diamagnetic term was demonstrated in the case of $(CH_3)_3SiOC(O)R$ compounds already earlier[20]. These results show, that the magnitude of $\delta(H)$ can be also used to estimate the electron density on the silicon atom. Our results on the ^1H-NMR of a greater number of the $(CH_3)_3SiOC(O)R$ compounds performed with the aim to make use of the relationship between $\delta(H)$ and polar effect of group R for the examination of the electron density on silicon in unreported acyloxysilanes $11-14$, 16 and 19 are summarised in Table II. The linear correlation between $\delta(H)$ of CH_3—
—Si-group and σ_I constant of group R is depicted in Fig 1. From the $\delta(H)$ values of the compounds $11-13$ it turns out that polar effect of $(CH_3)_3SiSCH_2$-, CH_3OCH_2- and $(CH_3)_3SiOCH_2$-groups is comparable. The deviation observed for benzoate (point No 15) has been ascribed to the diamagnetic anisotropy of the benzene ring. It was suggested[21] in ^{13}C-NMR studies of methyl benzoate that the methyl group will tend to be in close proximity to the aromatic ring and so will experience the observed deshielding. Such conformation is with regard to generally accepted view on the conformation of alkyl esters startling and will be touched later.

Empirical correlation between coupling constants $J_{^{13}C-^1H}$ of CH_3—X compounds and electronegativity of group X is not yet quite well understood, but found to have linear character[37]. From Fig. 2 it follows that no such linear relationship between $J_{^{13}C-^1H}$ of CH_3Si-group and $\sigma_I(R)$ exists for acyloxysilanes $(CH_3)_3SiOC(O)R$.

Infrared Spectra

The data on the compounds X—C(O)—OY fit in an approximate linear correlation between the two carbonyl–oxygen stretching frequencies $\nu(C=O)$ and $\nu(C-O-C)$ (refs[38,39]). From the data given in Table II it appears that no such correlation exists in narrower region, that is for compounds $(CH_3)_3SiOC(O)R$. The reason of it cannot be caused by the silicon atom, because no such linear correlation can be established with the literature data[7,25-28] on ethyl esters either. The linear dependance $\nu(C=O)$ vs $\nu(C-O-C)$ does not exist even for separate conformers of $(CH_3)_3SiOC(O)R$ or $C_2H_5OC(O)R$ compounds. The value of $\nu(C=O)$ frequency was used to examine the degree of M—O bond ionicity in R—C(O)OMR₃ compounds with M = Si, Ge, Sn, Pb[14], and the IR spectra of $R_3SiOC(O)CH_3$ compounds with R = alkyl were rationalized in terms of greater polarity of Si—O bond compared to that of C—O bond in alkyl esters. However it was pointed out that polarity of Si—O bond is not so large, as it would correspond to pure electronegativity of $(CH_3)_3Si$-group, because of some degree of back bonding in Si—O

Com-pound		$RC(O)OSi(CH_3)_3$		
	R	σ_I	$\nu(C{=}O)$	$\nu(C{-}O{-}Si)$
1	$(CH_3)_3C$	−0·07	1 712	1 173
2	$(CH_3)_3SiCH_2$	−0·05	1 692, 1 703	1 255, 1 266 sh
3	$(CH_3)_2CH$	−0·03	1 712, 1 718	1 207, 1 258
				1 268 sh, 1 278 sh
4	$(CH_3)_3CCH_2$	−0·02	—	—
5	$(CH_3)_2CHCH_2$	−0·03	1 717	1 258, 1 265 sh
6	C_2H_5	−0·05	1 713, 1 720	1 205, 1 269 sh
				1 283
7	CH_3	−0·05	1 722	1 268
8	H	0	1 713	1 207
9	$CH_3C(O)(CH_2)_2$		1 719	1 163, 1 211
10	$C_6H_5CH_2$	0·04	1 716, 1 720	1 173, 1 270
11	$(CH_3)_3SiSCH_2$		1 721	1 185, 1 288,
				1 312
12	$(CH_3)_3SiOCH_2$		1 717, 1 744	1 152, 1 222
13	CH_3OCH_2	0·07	1 719, 1 741	1 134, 1 202
14	$C_6H_5OCH_2$	0·14	1 720, 1 749	1 202, 1 214 sh
15	C_6H_5	0·10	1 703	1 119
16	ICH_2	0·16	1 717	1 286
17	$BrCH_2$	0·18	1 714, 1 730,	1 172, 1 295,
			1 721, 1 743 sh	1 312 sh
18	$ClCH_2$	0·15	1 721, 1 748	1 193, 1 307
				1 319
19	$CNCH_2$	0·21	1 764	1 287
20	$CH_3C(O)$	0·29	1 714, 1 722 sh	1 148, 1 324
			1 742, 1 788	
21	Cl_2CH	0·31	1 730, 1 750	1 260, 1 303
22	Cl_3C	0·43	1 752	1 273
23	F_3C	0·42	1 771	1 169

[a] Quantities ν are in cm^{-1}; [b] chemical shifts are in δ scale relative to TMS signal, in ppm units, coupling constants are in Hz units; [c] ref.[7]; [d] ref.[25]; [e] ref.[24]; [f] methyl ester; [h] ref.[27];

bond. As it was mentioned in the introduction, one would expect the extent of back bonding in acyloxytrimethylsilanes to be variable and alike to that in alkoxytrimethylsilanes. If so, the difference in $\nu(C{=}O)$ frequency values between the corresponding $(CH_3)_3SiOC(O)R$ and $C_2H_5OC(O)R$ compounds would diminish with increasing electron withdrawing ability of the substituent R. This is not the case.

TABLE II

(Continued)

RC(O)OSi(CH$_3$)$_3$			RC(O)OC$_2$H$_5$	
δ(H)$_{CH_2(CO)}$	δ(H)$_{CH_3-Si}$	J(^{13}C—H)CH$_3$Si	ν(C=O)	ν(C—O—C)
—	0.24	—	1 728^c	—
1.74	0.24	119.38	—	—
—	0.24	—	1 736^c	—
2.04	0.24	119.52	—	—
—	0.24	119.26	—	—
—	0.25	—	1 741^d	—
2.17	—	119.50	1 745^d	1 236, 1 245 sh^e
—	0.28	119.68	1 733^d	—
—	0.25	119.64	—	—
—	0.23	—	1 741^d	—
3.25	0.31	—	1 743^f	1 259^f
4.02	0.28	119.47	—	—
3.81	0.29	118.84	—	—
2.55	0.27	118.99	1 739, 1 767^h	—
—	0.42	119.83	1 725^e	—
3.93	0.34	119.28	1 743	1 259
3.95	0.32	119.81	1 742, 1 760^h	1 281^e
4.07	0.31	119.97	1 742, 1 767^h	1 288, 1 311^e
3.50	0.31	119.83	1 756^h	—
—	0.36	—	1 732, 1 758^i	—
—	0.38	120.32	1 750, 1 772^h	1 268, 1 302^e
—	0.42	120.56	1 769^h	1 266, 1 310^e
—	0.43	120.32	1 789^e	1 319^e

(CH$_3$)$_3$SiOC(O)R compounds possess the value of ν(C=O) frequency regularly by about 18—22 cm^{-1} lower than corresponding ethyl esters. This is also true of the corresponding conformers of all the compounds having group R of threefold symmetry. The magnitude of ν(C=O) frequency is thus controlled in acyloxytrimethylsilanes by the electronic factors in the same manner as described for alkyl esters[1–4,40].

Additional information on bonded and nonbonded interactions in acyloxytrimethylsilanes may emerge from the IR study of a conformation of these compounds.

It became known earlier, that the more stable form of simple saturated esters being rather I than II, except R is bulky, which causes destabilization of I relative to II (ref.[18]). From the results from this laboratory[41] it turned out that acyloxysilanes $(CH_3)_3SiOC(O)R$ with R = H, CH_3 possess conformation I. Similarly to these compounds also other compounds $(CH_3)_3SiOC(O)R$ with isotropic group R (No 1, 7, 8, 15, 22, 23) have only one and symmetrical absorption band in carbonyl region (Table II). It is therefore reasonable to ascribe the same conformation (I, R = = $(CH_3)_3Si$) to them. Having assumed a great volume of $(CH_3)_3Si$-group, this finding can be attributed to probable stabilization of this conformer by the $(p - d)_\sigma$ $C=O\rightarrow Si$ interaction. The splitting of carbonyl absorption into two bands for acyl-oxytrimethylsilanes 2, 3, 5, 10 and $12-14$, 17, 18, 21 can be ascribed to the equilibrium $III \rightleftarrows IV*$. The difference between both frequencies $\nu(C=O)$ is generally about $20-25$ cm^{-1} for electronegative group X (C_6H_5O, Cl, Br) and much less for X = alkyl, when only shoulder on the low-frequency side of $\nu(C=O)$ band is formed. The same situation is encountered with alkyl esters with an asymmetrical group located α to the carbonyl, where high-frequency peak of the carbonyl band is due to the more stable rotamer like IV, and the low-frequency peak is due to the less stable rotamer like III (refs[7,8,27,43]). General claim for the splitting of carbonyl band of esters with asymmetrical group located α to the carbonyl curiously fails for acyloxytrimethylsilanes with R = $BrCH_2$ (only shoulder on high-frequency side), $(CH_3)_3SiSCH_2$ and ICH_2. when only one peak belonging to $\nu(C=O)$ is observed. (The only absorption peak $\nu(C=O)$ of the compound 9 is apparently brought about by the cyclic "pseudo" ester form[43] (see ref.[44]). With the aim to ascertain whether this is a special feature of acyloxysilanes, the IR spectra of methyl trimethylsilyl-thioacetate and ethyl iodoacetate (Table II) were recorded and the lack of splitting was found also with these compounds. It was inferred for alkyl esters[45] that the size of a group attached to the carbonyl bond, rather than its I effect is of principle importance in determining both the distribution of rotamers and the carbonyl band intensity, but mainly I effect is responsible for the value of $\nu(C=O)$ frequency. Appearance of only one absorption band $\nu(C=O)$ can be thus result of either conformational homogenity or close resemblance of $\nu(C=O)$ frequency values of both types of conformers. The estimation of the concentration ratio of conformers III and IV is hard to do, but changes in the intensity of both peaks of carbonyl band along temperature enable us to make deeper insight into the above conformation equilibria. Temperature changes of the IR spectra in the region of $1100-1400$ cm^{-1} and $1700-1800$ cm^{-1} for several acyloxytrimethylsilanes are recorded in Fig. 3. The IR spectra of $(CH_3)_3SiOC(O)R$ compounds show following significant changes upon cooling the sample from $35°C$ to $-50°C$:

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*   The splitting of carbonyl absorption of some acyloxytrimethylsilanes was first described in the paper[42].

R = CH_2Cl. The band at 1319 cm^{-1} becomes more intensive than that at 1307 cm^{-1}. The intensity ratio of the bands at 1721 and 1748 cm^{-1} changes in favor of the latter.

R = CH_2Br. The band at 1319 cm^{-1} disappears, and the intensity of the band at 1307 cm^{-1} slightly increases. The intensity ratio of the bands at 1721 and 1743 cm^{-1} dramatically changes in favour of the latter.

R = CH_2I. The asymmetric band at 1717 cm^{-1} shifts to lower frequency.

R = $(CH_3)_3SiSCH_2$. The intensity ratio of the bands at 1288 and 1312 cm^{-1} changes. The shoulder of the asymmetric absorption band with maximum at 1721 cm^{-1} becomes more apparent while the intensity of the band at 1721 cm^{-1} diminishes. A number of evidence has been put together to support the interpretation of the carbonyl band splitting of heterosubstituted alkyl esters in terms of the rotational isomerism[46], but their accumulated weight is often considered not to be persuasive. The above described temperature changes of infrared spectra for acyloxysilanes with R = $ClCH_2$, $BrCH_2$ convincingly demonstrate the existence of the conformational equilibrium $III \rightleftarrows IV$, and are consistent with previously considered opinion,
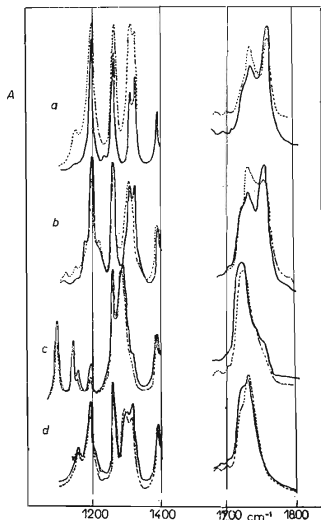

Fig. 3

The Infrared Spectra of the Acyloxysilanes $(CH_3)_3SiOC(O)R$ at $-50°C$ (full line) and $35°C$ (dashed line); R = $ClCH_2$ (a), $BrCH_2$ (b), ICH_2 (c), $(CH_3)_3SiSCH_2$ (d)

that rotamer with heteroatom close to the carbonyl group (high-frequency peak of the carbonyl band) is really more stable. Changes in the IR spectra of the acyloxy-trimethylsilanes with $R = ICH_2$ and $(CH_3)_2SiSCH_2$ let us to distinguish between two possible explanations of the only $v(C=O)$ absorption band in the spectra of these compounds considered earlier. It turns out that both types of conformers (III and IV) are present in solution and have similar value of $v(C=O)$ frequency. This closeness of the $v(C=O)$ frequences deteriorates the possibility of their ascription to the individual conformers III and IV. It was inferred that equilibrium $III \rightleftarrows IV$ is controlled mainly by the electronegativity of group R. The results presented here further show that the difference in the $v(C=O)$ frequency values of the above conformers can be significantly influenced also by the steric effect of group R.
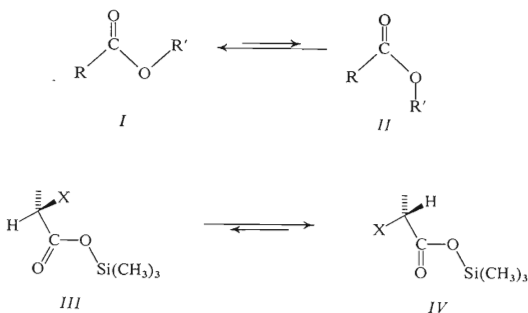
Temperature measurement of the IR spectra of benzoyltrimethylsilane revealed very slight change of the shape of $v(C=O)$ absorption band (shift of the absorption maximum from 1 703 to 1 696 cm^{-1} upon cooling of the sample from 35°C to $-50°$C). The intensity of other absorption bands did not change. The interpretation of the NMR spectra of this compound introduced earlier was consistent with the preference of the conformer with benzene ring close to $(CH_3)_3Si$-group (conformer II). But from the above discussion it follows that this conformer would be less stable than the conformer with $(CH_3)_3Si$-group in close proximity of the carbonyl group. The deshielding of $(CH_3)_3Si$-group protons and low value of $v(C=O)$ frequency might be caused also by the electron flow from the methyl groups to the carbonyl oxygen, presuming electron withdrawing effect of the phenyl group is reduced. The temperature changes in the IR spectra of benzoyltrimethylsilane resemble those of other acyloxysilanes with symmetrical group α to carbonyl, but they only show

dominant preference of one conformer "unwilling" to decrease its amount on temperature change without specification of which type it is.

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