

ORGANOSILICON COMPOUNDS. CIII.*

THE PREPARATION AND VIBRATIONAL SPECTRA
OF SOME CHLOROMETHYL- AND ACETOXYMETHYL-SUBSTITUTED
SILANES

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Series of the compounds $\text{ClCH}_2(\text{CH}_3)_{3-n}\text{Si}(\text{OC}_2\text{H}_5)_n$, $\text{ClCH}_2(\text{CH}_3)_{3-n}\text{Si}(\text{OOCCH}_3)_n$, $\text{CH}_3\cdot\text{COOCH}_2(\text{CH}_3)_{3-n}\text{Si}(\text{OC}_2\text{H}_5)_n$, and $\text{CH}_3\text{COOCH}_2(\text{CH}_3)_{3-n}\text{Si}(\text{OOCCH}_3)_n$ ($n = 1-3$) were prepared and their IR spectra were measured. The Raman spectra of seven compounds are also reported. The assignment of typical bands to characteristic frequencies was proposed.

Within the framework of broader study of the effect of structure on the physico-chemical properties and reactivity of carbofunctional organosilicon compounds¹⁻³, in this work we synthesised series of chloromethyl- and acetoxyethyl-substituted methylethoxysilanes and methylacetoxysilanes and measured their vibrational spectra. Of chloromethyl-substituted silicon derivatives, only some methyl derivatives and hydrides^{4,5} have been studied. Because of the size and generally low symmetry of molecules of studied compounds, the complete vibrational analysis of their spectra cannot be made. It is to be expected, however, that given the assignment of characteristic vibrations, changes in wavenumber, or in intensity of absorption bands due to systematic structural changes in individual series may be followed. This comparative spectral analysis could thus contribute to the knowledge of bonding in these compounds.

EXPERIMENTAL

(Chloromethyl)trimethylsilane was prepared by vapour-phase chlorination of dimethyldichlorosilane⁶ and subsequent methylation of the formed (chloromethyl)methyldichlorosilane (69%) with methylmagnesium chloride in 85.4% yield (b.p. 97–97.5°C, ref.⁷ 97.1°C/743 Torr; n_D^{20} 1.4146, ref.⁸ 1.4180).

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(*Chloromethyl*)dimethylethoxysilane (1). Chlorination of trimethylchlorosilane in vapour phase afforded (chloromethyl)dimethylchlorosilane, b.p. 114.5—115°C (ref.⁹ 113.9°C/757 Torr) in 85.7% yield. Its reaction with ethanol in the presence of diethylaniline gave (chloromethyl)dimethylethoxysilane, b.p. 132—133°C (ref.¹⁰ 132°C); n_D^{20} 1.4177 (ref.¹⁰ 1.4187); d_{25}^{25} 0.9500 (ref.¹¹ 0.9438) 75.6% yield.

(*Chloromethyl*)methyldiethoxysilane (2). Reaction of (chloromethyl)methyldichlorosilane, prepared by vapour-phase chlorination of dimethyldichlorosilane⁶, with ethanol under simultaneous removal of the formed hydrogen chloride by flushing with dry nitrogen afforded (chloromethyl)methyldiethoxysilane in 72% yield. B.p. 69—70°C/20 Torr (ref.¹² 57—58°C/10 Torr); n_D^{20} 1.4144 (ref.¹² 1.4150); d_{25}^{25} 0.9937 (ref.¹² d_{40}^{20} 1.0052). Raman spectrum (cm^{-1}): 227,250 (4), 615 (10), 675 (2), 696 (1), 745 (4), 807 (2)b, 946 (1)vb, 1083 (2), 1102 (2), 1291 (1), 1398 (1), 1446 (2), 1479 (1), 2891 (5), 2916 (6), 2932 (10), 2975 (7).

(*Chloromethyl*)triethoxysilane (3). Reaction of (chloromethyl)trichlorosilane, prepared by radical chlorination of methyltrichlorosilane in vapour phase⁹, with ethanol under simultaneous removal of the formed hydrogen chloride by flushing with dry nitrogen gave (chloromethyl)triethoxysilane in 46.9% yield. B.p. 91—93°C/27 Torr (ref.¹³ 173—176°C); n_D^{20} 1.4069 (ref.¹⁴ 1.4145). Raman spectrum (cm^{-1}): 234 (7), 401 (3)vb, 627 (10)p, 697 (3), 786 (6), 810 (4)p?, 948 (3), 969 (3), 1097 (4)p?, 1296 (3), 1393 (1), 1457 (6), 1486 (3), 2723 (1), 2772 (1), 2896 (5)p, 2934 (10)p, 2978 (5).

(*Chloromethyl*)dimethylacetoxysilane (4) was obtained in 31.3% yield by reaction of (chloromethyl)dimethylchlorosilane with acethanhydride under simultaneous removal of the formed acetyl chloride. B.p. 79—80°C/22 Torr (ref.¹⁵ 42—45°C/7 Torr); n_D^{20} 1.4328 (ref.¹⁵ 1.4345). Raman spectrum (cm^{-1}): 216 (4), 331 (1), 381 (1)p, 390 (1)p, 481 (1)p, 589 (10)p, 624 (4)p, 663 (1)p, 686 (1), 702 (0.5), 754 (2), 807 (0.5), 825 (0.5), 845 (0.5), 934 (1)p, 1010 (0.5), 1099 (0.5), 1172 (0.5), 1252 (0.5), 1396 (1), 1425 (0.5), 1715 (1)p, 2915 (10), 2947 (8), 2980 (4).

(*Chloromethyl*)methyldiacetoxysilane (5). A mixture of 129 g (0.47 mol) of (chloromethyl)methyldichlorosilane and 105.6 g (1.03 mol) of acethanhydride was heated while simultaneously removing the acetyl chloride formed. After the formation of the chloride had ceased, the heating of the reaction mixture was stopped at the temperature of 105°C. Rectification afforded 26.3 g of fraction boiling 71—73°C/3 Torr (26.6% yield). For $\text{C}_6\text{H}_{11}\text{ClO}_4\text{Si}$ (210.7) calculated: 34.20% C, 5.26% H, 13.33% Si, 16.8% Cl; found: 33.73% C, 5.27% H, 13.54% Si, 16.79% Cl; n_D^{20} 1.4260, d_{25}^{25} 1.1856.

(*Chloromethyl*)triacetoxysilane (6). A mixture of 183.9 g (1 mol) of (chloromethyl)trichlorosilane and 337 g (3.3 mol) of acethanhydride was heated while simultaneously distilling off the formed acetyl chloride. The temperature of the reaction mixture was gradually raised to 95°C at which temperature the evolution of the acetyl chloride ceased. Fractional distillation yielded 42.5 g (16.7%) of (chloromethyl)triacetoxysilane boiling 95—98°C/3 Torr. For $\text{C}_7\text{H}_{11}\text{ClO}_6\text{Si}$ (254.7) calculated: 33.00% C, 4.35% H, 11.02% Si, 13.92% Cl; found: 33.16% C, 4.38% H, 11.00% Si, 14.18% Cl; n_D^{20} 1.4239, d_{25}^{25} 1.2779.

(*Acetoxymethyl*)trimethylsilane^{16,17} (13) was isolated from the reaction of potassium acetate with (chloromethyl)trimethylsilane in glacial acetic acid (18 h at 190°C) in 76.4% yield as fraction boiling 135—135.5°C (ref.¹⁶ 136°C/748 Torr); n_D^{20} 1.4047 (n_D^{25} 1.4060).

(*Acetoxymethyl*)dimethylethoxysilane (7). Reaction of (chloromethyl)dimethylethoxysilane with anhydrous potassium acetate in the presence of a catalytic amount of (acetoxymethyl)dimethylacetoxysilane produced (acetoxymethyl)dimethylethoxysilane in 36.9% yield. B.p. 169 to 170°C (ref.¹⁸ 53—57°C/8 Torr); n_D^{20} 1.4177 (ref.¹⁸ 1.4150). Raman spectrum (cm^{-1}): 186,

217 (8), 309 (0.5), 349 (1), 389 (0.5), 460 (1), 603 (10)p, 620, 645 (4)p, 696 (4), 734 (3), 754 (2), 805 (1.5), 846 (2), 886 (4), 940 (1), 981 (2)p, 1032 (2), 1084 (2), 1105 (2), 1220 (2), 1257 (1.5), 1293 (2), 1373 (1), 1415, 1434, 1447 (4), 1483 (2), 1741 (1.5), 2912 (10), 2935 (8), 2949 (9), 2969 (8).

(*Acetoxymethyl*)methyl-diethoxysilane (8). Reaction of (chloromethyl)methyl-diethoxysilane with anhydrous potassium acetate in the presence of a catalytic amount of (acetoxymethyl)dimethylacetoxysilane afforded (acetoxymethyl)methyl-diethoxysilane in 62% yield. B.p. 85 to 86°C/16 Torr (ref.¹⁸ 84–87°C/13 Torr); n_D^{20} 1.4114 (ref.¹⁸ 1.4121). Raman spectrum (cm^{-1}): 185 (2), 226 (7), 336 (0.5), 377 (0.5), 457 (1.5), 469 (1), 615 (10)p, 632 sh p, 657 (6)p, 714 (3), 736 (5), 777 (1), 799 (3), 812 (3), 838 (3), 888 (6), 948 (3), 986 (3)p, 1038 (3), 1090 (5)p, 1104 (5)p, 1165 (0.5), 1223 (3), 1266 (1), 1297 (5), 1374 (1), 1414 (4), 1446 (8), 1457 (9), 1485 (4), 1744 (3), 2718 (0.5), 2752 (0.5), 2887 (6)p?, 2911 (8)p, 2927 (10)p, 2972 (7).

(*Acetoxymethyl*)triethoxysilane (9). Reaction of (chloromethyl)triethoxysilane with anhydrous potassium acetate in the presence of a catalytic amount of (acetoxymethyl)dimethylacetoxysilane afforded (acetoxymethyl)triethoxysilane, b.p. 103–105°C/16 Torr (ref.¹⁸ 96–99°C/10 Torr); n_D^{20} 1.4092 (ref.¹⁸ 1.4062). Raman spectrum (cm^{-1}): 225 (3), 295, 313 (0.5), 439 (0.5)vb, 476 (0.5)vb, 618 (7)p, 661 (3)p, 729 (1), 768 (2), 806, 816 (3), 885 (4)p, 946 (2), 966 (2), 985 (2), 1037 (1), 1090 (7), 1169 (0.5), 1222 (1), 1295 (6), 1372 (0.5), 1393 (1), 1452 (10), 1481 (4), 1743 (1)p?, 2721 (1), 2772 (1), 2877 sh, 2897 (6)p, 2936 (10)p, 2949 sh, 2979 (6).

(*Acetoxymethyl*)dimethylacetoxysilane (10). Reaction of (chloromethyl)dimethylchlorosilane with anhydrous potassium acetate in toluene yielded 84.3% of fraction boiling 84.5–86.5°C: 8 Torr (ref.¹⁵ 66–69°C/7 Torr); n_D^{20} 1.4388 (ref.¹⁹ 1.4220). Raman spectrum (cm^{-1}): 191 (1), 222 (2), 255 (1), 289 (0.5), 302 (1), 338 (2), 384 (1), 442 (0.5), 460 (1), 591 (10)p, 623 (2)p, 656 (2)p, 700 (2), 717 (2), 756 (0.5), 811 (0.5), 838 (1), 881 (3)p, 931 (3)p, 976 (1)p?, 1014 (1), 1030 (1), 1215 (1), 1255 (2), 1370 (0.5), 1412 (4), 1427 (4), 1715 (3)p?, 1736 (1)p?, 2914 (10)p, 2942 (9)p, 2973 (3). The yield of (acetoxymethyl)dimethylacetoxysilane was further increased by cleaving the by-product of this reaction, bis-1,3-(acetoxymethyl)-1,1,3,3-tetramethyldisiloxane (*A*) with acetanhydride: 1 mol of *A*, 1 mol of acetanhydride, and 0.2 mol of zinc chloride were mixed in a three-necked flask. As the reaction did not proceed on shaking the reaction mixture and cooling it to 0°C, the mixture was refluxed for 3 h and then it was briefly distilled *in vacuo*. Fractional distillation afforded 0.82 mol of (acetoxymethyl)dimethylacetoxysilane (41.0%).

(*Acetoxymethyl*)methyl-diacetoxysilane (12) was prepared by reaction of (chloromethyl)methyl-dichlorosilane with anhydrous potassium acetate in toluene; b.p. 110–112°C/4.5 Torr (ref.²⁰ 90–95°C/20 Torr); n_D^{20} 1.4351 (ref.²⁰ 1.4321).

(*Acetoxymethyl*)triacetoxysilane (13) was isolated from the reaction of (chloromethyl)trichlorosilane with anhydrous potassium acetate in toluene; b.p. 99–103°C/3 Torr (ref.²⁰ 79–82°C: 10 Torr); m.p. 81.5°C (ref.²⁰ 79.5°C).

IR spectra were recorded with Model UR-20, double-beam spectrophotometer (Zeiss, Jena) in the 4000–400 cm^{-1} region. Studied compounds were measured both as such (in subst.) in capillary layer using a composed KBr cell, and as 5% solutions in CCl_4 or in CS_2 . The frequency scale of the instrument was checked by polystyrene. The intensities of the bands listed in the table of wavenumbers are denoted as follows: very weak – vw, weak – w, medium – m, strong – s, very strong – vs, shoulder – sh, broad – b, very broad – vb.

Raman spectra were taken with RGS-2 grating spectrometer (Akademiewerkstätten für Forschungsbedarf der Akademie der Wissenschaften der DDR, Berlin). OIP-He-Ne laser was used as a source of irradiation. The intensities of Raman lines were estimated within 0–10,

TABLE I
Wavenumbers of IR Bands of Some Characteristic Vibrations of Chloromethyl- and Acetoxy-

| No | Compound | $\nu(\text{C}=\text{O})$ | $\gamma(\text{CH}_2)$ | $\nu(\text{C}_{\text{Ac}}-\text{O}-(\text{C}))^a$, $\nu(\text{C}_{\text{Ac}}-\text{O}-(\text{Si}))$ |
|----|--|---|-----------------------|---|
| 1 | $\text{ClCH}_2(\text{CH}_3)_2\text{SiOC}_2\text{H}_5$ | — | 1 297 w | — |
| 2 | $\text{ClCH}_2(\text{CH}_3)\text{Si}(\text{OC}_2\text{H}_5)_2$ | — | 1 298 w | — |
| 3 | $\text{ClCH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$ | — | 1 292 w | — |
| 4 | $\text{ClCH}_2(\text{CH}_3)_2\text{SiOOCCH}_3$ | 1 725 vs | 1 292 sh | 1 258 vs ^e |
| 5 | $\text{ClCH}_2(\text{CH}_3)\text{Si}(\text{OOCCH}_3)_2$ | 1 715 sh ^f 1 730 vs ^f 1 742 vs ^f | 1 290 sh | 1 235 vs 1 270 vs ^e |
| 6 | $\text{ClCH}_2\text{Si}(\text{OOCCH}_3)_3$ | 1 715 sh ^f 1 761 vs ^f | 1 290 sh | 1 220 vs 1 262 sh |
| 7 | $\text{CH}_3\text{COOCH}_2(\text{CH}_3)_2\text{SiOC}_2\text{H}_5$ | 1 745 s | 1 290 s | 1 229 s 1 257 s ^e |
| 8 | $\text{CH}_3\text{COOCH}_2(\text{CH}_3)\text{Si}(\text{OC}_2\text{H}_5)_2$ | 1 745 s | 1 292 s | 1 236 s 1 263 s ^e |
| 9 | $\text{CH}_3\text{COOCH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$ | 1 744 s | 1 299 m | 1 239 m 1 260 sh |
| 10 | $\text{CH}_3\text{COOCH}_2(\text{CH}_3)_2\text{SiOOCCH}_3$ | 1 725 vs 1 742 s | 1 288 s | 1 225 sh 1 253 vs ^e |
| 11 | $\text{CH}_3\text{COOCH}_2(\text{CH}_3)\text{Si}(\text{OOCCH}_3)_2$ | 1 713 sh ^f 1 739 s ^{f,g} | 1 289 s | 1 229 sh 1 243 vs |
| 12 | $\text{CH}_3\text{COOCH}_2\text{Si}(\text{OOCCH}_3)_3$ | 1 714 sh ^f 1 739 vs ^f | 1 291 m | 1 226 sh 1 242 vs |
| 13 | $\text{CH}_3\text{COOCH}_2(\text{CH}_3)_3\text{Si}$ | 1 741 vs | 1 290 sh | 1 226 vs 1 252 vs |
| 14 | $\text{CH}_3\text{COOCH}_2(\text{CH}_3)_3\text{C}$ | 1 740 vs | 1 290 sh | 1 220 sh 1 242 vs 1 269 s |
| 15 | $\text{CH}_3\text{COOCH}_2(\text{CH}_3)_2\text{COOCCH}_3$ | 1 742 vs | 1 290 sh | 1 210 sh 1 240 vs 1 265 sh |
| 16 | $\text{CH}_3\text{COOCH}_2(\text{CH}_3)\text{C}(\text{OC}_2\text{H}_5)_2$ | 1 749 vs | 1 290 sh | 1 237 vs 1 265 s |

^a C_{Ac} denotes the carbon of acetoxy group; ^b C_{Et} denotes the carbon of ethoxy group; ^c all the bands observed in the $900-1000\text{ cm}^{-1}$ region are recorded for carbon analogues, irrespective of possible occurrence of deformation vibrations (see text); ^d the assignment is uncertain⁵ due to low characteristic of this vibration (the carbon of different types); ^e overlap with the deforma-

methyl-Substituted Compounds, cm^{-1}

| $\nu(\text{C}_{\text{Et}}-\text{O})^b$ | $\rho(\text{CH}_3)$ | $\nu(\text{C}-\text{C})^c$ | $\nu(\text{C}-\text{Cl})$ | $\nu(\text{Si}-\text{C})^d$ |
|--|-------------------------|----------------------------|---------------------------|-----------------------------|
| 1 083 vs | 1 170 m | 952 m | 730 m | 671 m |
| 1 109 vs | | | 753 m | |
| 1 083 vs | 1 170 s | 960 m | 743 m | 694 m |
| 1 107 vs | | | | |
| 1 083 vs | 1 171 s | 969 m | 788 sh | 692 m |
| 1 106 vs | | | | |
| — | 1 020 s | 940 s | 730 m | 690 m |
| | 1 049 m | | | |
| — | 1 020 s | 946 s | 720 m | 650 w |
| | 1 050 m | | | |
| — | 1 020 s | 953 s | 720 w | 668 w |
| | 1 048 m | | | |
| 1 084 s | 1 035 m | 952 m | — | 646 w |
| 1 108 s | 1 170 m | 980 w | | |
| 1 084 vs | 1 036 m | 962 m | — | 656 w |
| 1 108 vs | 1 170 m | 980 sh | | |
| 1 084 vs | 1 038 m | 950 sh | — | 665 w |
| 1 106 vs | 1 172 m | 968 m | | |
| | | 983 sh | | |
| — | 1 020 s | 935 s | — | 729 m |
| | 1 034 m | | | |
| | 1 050 sh | | | |
| — | 1 019 s | 945 s | — | 734 m |
| | 1 050 m | | | |
| — | 1 021 m | 932 m | — | 699 m |
| | 1 050 m | 960 m | | |
| — | 1 034 m | 980 w | — | 706 m |
| | | | | |
| — | 1 030 s | 920 w | — | — |
| | 1 047 s | 940 w | | |
| | | 990 m | | |
| — | 1 027 m | 920 w | — | — |
| | 1 053 s | 933 w | | |
| | 1 164 s | 951 m | | |
| — | 1 070 vs ^{h,i} | 910 w | — | — |
| | 1 100 s ^{h,i} | 940 m | | |
| | 1 140 s | 952 sh | | |
| | 1 162 m | 969 m | | |
| | 1 185 s | 978 sh | | |

tion vibration of the methyl on silicon, $\delta(\text{SiCH}_3)$; ^f the intensity of the band is dependent on the concentration of the compound; ^g the band is split; ^h in this region there are also deformation vibrations $\rho(\text{CH}_3)$; ⁱ probable overlap with intense $\nu(\text{C}-\text{O})$ bands of ethoxy group.

regardless of spectral sensitivity of the instrument; the symbol p is used to denote polarised lines. Polarisation measurements were made with the aid of polarisation rotor and scrambler.

RESULTS AND DISCUSSION

The values of the wavenumbers (inclusive intensities) and polarisation of Raman lines, obtained from the Raman spectra of seven compounds, are listed for individual compounds in Experimental. In harmony with the expectation, the measurements of the Raman spectra of several casually chosen samples showed that these spectra, due to the low symmetry of molecules, are very similar to the infrared spectra. The survey of characteristic wavenumbers found in the IR spectra of studied compounds is presented in Table I, along with the proposed assignment of the bands to individual vibrational types. In assigning the wavenumbers of absorption band maxima we made use of some earlier works^{4,5,21-26}. (Chloromethyl)trimethylsilane was used in the present work as basic compound for comparing the spectra of chloromethyl-substituted compounds. Goubeau assigned the absorption band²¹ at 757 cm^{-1} in the spectrum of $\text{ClCH}_2(\text{CH}_3)_2\text{SiCl}$ to the C—Cl stretching frequency; in the case of $(\text{ClCH}_2)_2\text{Si}(\text{CH}_3)_2$ the author observed four bands⁴ located within the $695\text{--}746\text{ cm}^{-1}$ region. In the case of $\text{ClCH}_2(\text{CH}_3)_3\text{Si}$ we propose to assign the band at 760 cm^{-1} (shoulder 745 cm^{-1}) to this vibration, while the bands at 703 cm^{-1} and 645 cm^{-1} may be ascribed to the $\nu(\text{Si—C})$ vibrations⁵. A similar approach was also used in assigning $\nu(\text{Si—C})$ and $\nu(\text{C—Cl})$ in the compounds denoted by numbers 1–6, in Table I, which presents also tentative assignment.

All the compounds measured contain methylene group inserted between silicon (carbon) atom and chlorine or acetoxy group. Unfortunately, the bands of this group are usually of low intensity and are, as a rule, overlapped with other bands. Thus, for example, much more intense bands corresponding to SiOC_2H_5 grouping interfere in the region of $\delta(\text{CH}_2)$ deformation vibrations. These absorption bands of the methylene group can be clearly observed with (chloromethyl)trimethylsilane, in which case they are located at 1109 cm^{-1} and 1181 cm^{-1} . In the region of the stretching and scissoring vibrations in most cases the bands corresponding to the methylene group coincide with the bands of the methyl groups attached either to silicon or to carbon. The exception is the $\gamma(\text{CH}_2)$ absorption band at $1290 \pm 2\text{ cm}^{-1}$ which will be discussed later.

In Table I are not listed characteristic wavenumbers of methyl groups on silicon, which generally occur at constant wavenumbers²⁵ SiCH_3 : ρ $760\text{--}860\text{ cm}^{-1}$, δ $1250\text{--}1260\text{ cm}^{-1}$ (see footnotes in Table I), δ sciss $1410\text{--}1420\text{ cm}^{-1}$, and ν_{as} 2960 cm^{-1} . Not included in Table I is also characteristic band of vibration of the methyl on carbon at 1380 cm^{-1} . The bands of comparatively low intensity are particularly those occurring the region of the C—H stretching vibrations, and that also in measuring the compounds *in subst.* in capillary layer.

In assigning the absorption bands characteristic for acetoxy group we started from the work by Rochow²² who performed the assignment of the absorption bands of the acetoxy groups directly bound to silicon for silanes of the type $(\text{CH}_3)_{4-n}\text{Si} \cdot (\text{OOCCH}_3)_n$, where $n = 1-4$. The author found that $\nu(\text{C}=\text{O})$ increases with increasing number of acetoxy groups from 1725 cm^{-1} to 1765 cm^{-1} , while $\nu(\text{C}_{\text{Ac}}-\text{O}-\text{Si})$ decreases from 1267 cm^{-1} to 1200 cm^{-1} . Trimethylacetoxysilane was also studied by Freeman²³ ($\nu(\text{C}=\text{O})$ 1715 cm^{-1}) and by Egoročkin²⁴ ($\nu(\text{C}=\text{O})$ 1725 cm^{-1}). Contrarily to the substances studied by Rochow²², spectra of all the members of the series $\text{CH}_3\text{COOCH}_2(\text{CH}_3)_{3-n}\text{Si}(\text{OOCCH}_3)_n$ ($n = 1-3$), i.e. the compounds containing the methylene group inserted between the silicon and the acetoxy group, exhibit two bands in the carbonyl region: the narrow band at $1713-1725 \text{ cm}^{-1}$ and the broad band at $1739-1742 \text{ cm}^{-1}$ (see Table I). On the basis of the analysis of the spectra in the carbonyl region we believe that the acetoxy group attached to silicon shows the maximum at the lower wavenumber side (compare 1725 cm^{-1} for $\text{ClCH}_2 \cdot (\text{CH}_3)_2\text{SiOOCCH}_3$ and $(\text{CH}_3)_3\text{SiOOCCH}_3$ (ref.²²)); the maximum at the higher wavenumber side may be assigned to the acetoxy group bonded to silicon *via* methylene group (compare 1741 cm^{-1} for $\text{CH}_3\text{COOCH}_2(\text{CH}_3)_3\text{Si}$, Table I). Similar values of the wavenumbers of carbonyl group were also observed with carbon analogues (compounds 14-16, Table I). All the members of the series $\text{CH}_3\text{COOCH}_2 \cdot (\text{CH}_3)_{3-n}\text{Si}(\text{OC}_2\text{H}_5)_n$ ($n = 1-3$) showed only one carbonyl absorption band with constant maximum at 1745 cm^{-1} . In the $950-1300 \text{ cm}^{-1}$ region there are several bands which correspond to the stretching and deformation vibrations of $\text{Si} \cdot \text{OOCCH}_3$, or COOCH_3 and SiOC_2H_5 grouping. By comparing different series of model compounds we attempted at dividing these bands to several groups according to vibrational modes (Table I). We excluded first absorption bands at 1250 to 1260 cm^{-1} , which undoubtedly belong to deformation vibration of the methyl on silicon²⁵. All the ethoxy derivatives (1-3, 7-9) had characteristic doublet at $1083 \text{ cm} \pm 2 \text{ cm}^{-1}$ and $1108 \pm 2 \text{ cm}^{-1}$, irrespective of the number of ethoxy groups in the molecule. These are the bands due to the C—O stretching vibration. In addition to this doublet the ethoxy group shows always the band at $950-969 \text{ cm}^{-1}$, corresponding to the C—C stretching vibration. Rocking vibrations of the methyl groups of the ethoxy compounds are characterised by the band at 1170 cm^{-1} (compare ref.²⁶, Table I).

In the spectra of organosilicon compounds containing acetoxy group it was observed²² that compounds 3-5 and 10-12 show two bands due to deformation vibrations $\rho(\text{CH}_3)$ at 1020 cm^{-1} and 1050 cm^{-1} , while compounds 7-9 and 13 show only one band at $1034-1038 \text{ cm}^{-1}$. The values of corresponding wavenumbers for carbon analogues are somewhat shifted, due to the coupling of vibrations. The band at $932-980 \text{ cm}^{-1}$ originates obviously from the C—C stretching vibration, of acetoxy derivatives (Table I). The spectra of all the compounds studied, except 1-3, show in the $1230-1250 \text{ cm}^{-1}$ region very intense band, as a rule, of large

half-width, which is sometimes split. The higher wavenumber side of this broad band frequently overlaps with the band of $\delta(\text{Si}-\text{CH}_3)$ vibrations. In the close vicinity there is an additional band at $1290 \pm 2 \text{ cm}^{-1}$, which, with regard to its relatively high intensity, cannot be assigned to eventual presence of acetic acid²². It is apparently associated with $\gamma(\text{CH}_2)$ vibrations of the methylene group in studied compounds.

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