Syntheses and Reactions of Metal Organics. XVI. Synthesis and Hydrolysis of Dimethoxysilanediyl Bis(polyfluoroalkanoate)

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Four new silicon compounds, dimethoxysilanediyl bis(5*H*-octafluoropentanoate), $(CH_3O)_2Si[OCO(CF_2)_4H]_2$, dimethoxysilanediyl bis(7*H*-dodecafluoroheptanoate), $(CH_3O)_2Si[OCO(CF_2)_6H]_2$, dimethoxysilanediyl bis(9*H*-hexadecafluorononanoate), $(CH_3O)_2Si[OCO(CF_2)_8H]_2$, and dimethoxysilanediyl bis(pentadecafluorooctanoate), $(CH_3O)_2Si[OCO(CF_2)_6CF_3]_2$, were prepared by the reaction of dichlorodimethoxysilane with sodium salts of fluoro-substituted carboxylic acid. The ^1H NMR, ^{13}C NMR, and ^{19}F NMR and IR spectral data of these silicon compounds were obtained. In the course of a study of the stability of the silicon compounds against hydrolysis by using ^1H NMR spectral measurements, it was found that the ease of hydrolysis of the SiOCOR and the $SiOCH_3$ moieties was exactly same.

Metal alkoxides have been the subject of extensive research owing to their potential as precursor materials for several applications, such as new ceramics, adhesives, and coupling agents, which are molecular bridges between the interface of an inorganic filler and an organic polymer. Many alkyl or aryl orthosilicates and their halogenated derivatives have been prepared[1] and the reactivities of these orthosilicates towards various types of electron donors such as amides and amines have been reported.[2]

In recent years, dramatic developments have been made in the utilization of organofluoro compounds, resulting in new high-performance materials. However, only a few research reports concerning fluoro-substituted alkoxides of metals have appeared in the literature.[3-7] In previous papers we reported on the syntheses of fluoroalkyl and fluoroaryl titanates[8] as well as the syntheses of fluoroalkyl silicates.[9] Although these alkoxides were expected to be stable against moisture, since many of the compounds having the fluorinated carbon structure possess water repellency, all of the products were very sensitive to water and were easy to decompose.

In our last paper, we reported the results of the syntheses and characterizations of new titanium compounds having three fluoro-substituted alkanoyloxyl groups and one butoxyl group.[10] An application for the surface modification against calcium carbonate was also reported. These compounds were found to be an effective substance for a new-type coupling agent, which increases the affinity between organofluoro polymers and some inorganic substances.

In this paper, the results of the syntheses and characterizations of new silicon compounds having two fluoro-substituted alkanoyloxyl groups and two methoxyl groups per molecule are reported.

The stability of these products against hydrolysis is also discussed.

Experimental

Special precautions were adopted to avoid any hydrolysis of the starting materials and products, and all experiments were carried out under an atmosphere of purified nitrogen to preclude oxygen and moisture.

Materials. Silicon tetrachloride (bp 57.5—58.0 °C) was obtained from Kanto Chemical Co., Inc. and purified by distillation. Dichlorodimethoxysilane (bp 100—102 °C) was prepared by the reaction of silicon tetrachloride with methanol; Found: Si, 17.3; Cl, 44.1; OCH_3, 38.3%, Calcd for $C_2H_6Cl_2O_2Si$: Si, 17.4; Cl, 44.0; OCH_3, 38.5%. 5*H*-Octafluoropentanoic acid (bp 40—42 °C/120 Pa), 7*H*-dodecafluoroheptanoic acid (bp 60—61 °C/106 Pa), 9*H*-hexadecafluorononanoic acid (bp 92—93 °C/53 Pa) and perfluorooctanoic acid (bp 89—90 °C/4000 Pa) were received as gifts[11] from Daikin Industries, Ltd. and purified by distillation. The purity of these acids was checked by the use of ^{19}F NMR spectra and gas chromatography (GLC), and no impurities were detected. Sodium salts of these acids were synthesized by the reaction of fluoro-substituted carboxylic acid with excess sodium hydrogencarbonate in tetrahydrofuran (THF). The solvents used were purified by the usual method.

Measurements and Instruments. The FT-IR spectra were measured in a liquid film or by a KBr method with a JEOL JIR-5300 spectrophotometer. Each spectrum was recorded at a resolution of 4 cm^{-1} with a total of 30 scans. Pulsed Fourier Transform 100-MHz ^1H NMR and 25-MHz ^{13}C NMR spectra were run in THF-d_8 with TMS as an internal standard using a JEOL JNR-PX-100 spectrometer at room temperature: ^1H NMR spectra (pulse repetition time, 5 s; number of accumulations, 20) and ^{13}C NMR spectra (pulse repetition time, 2.0 s; number of accumulations, 40000). The FT mode 90-MHz ^{19}F NMR spectra were recorded at 27 °C on a JEOL JNM-FX-90Q in THF with fluorobenzene (−113.6 ppm[12] from $CFCl_3$ in $CDCl_3$) as an external standard: pulse repetition time, 0.5 s; number of accumulation, 20. The assignments of the ^{19}F NMR spectra were referred to in the data book.[12] Gas chromatography was performed with a Hitachi 063 (PEG-6000 supported Chromosorb A NAW 30/60 mesh 5 m packed column, TCD) or Hitachi G-3000 gas chromatograph (OV-1 25 m Fused capillary column, FID) and these intensities were measured with a Hitachi 834 chromato processor or a Hitachi D-2500 chromato integrator.

Analytical Methods. Silicon was determined gravimetrically as silicon dioxide after the hydrolysis of silicon compounds by adding aqueous ammonia and burned in a quartz crucible. Chlorine was quantified by the Mohr method. Methoxyl groups were measured quantitatively as methanol by GLC after the hydrolysis of the products by adding a sodium hydroxide solution. The contents of the fluorinated alkanoyloxyl group having hydrogen at the end of the chain were estimated indirectly from the intensities against methoxyl protons by ^{1}H NMR spectra.

Syntheses of Dimethoxysilanediyl Bis(polyfluoroalkanoate). Synthesis of Dimethoxysilanediyl Bis(5*H*-octafluoropentanoate), $Si(OCH_3)_2[OCO(CF_2)_4H]_2$: Sodium 5*H*-octafluoropentanoate (6.18 g (23.1 mmol)) was added to a stirred solution of dichlorodimethoxysilane (1.69 g (10.5 mmol)) in 80 ml 1,1,2-trichloro-1,2,2-trifluoroethane at room temperature in a two-necked 200-ml flask connected with a reflux condenser and a three-way stop cock. The heterogeneous mixture was refluxed with stirring for 15 h. Completion of the reaction was checked by adding a silver nitrate solution to a portion of the clear upper solution. Sodium chloride produced and excess sodium 5*H*-octafluoropentanoate were removed by filtration. A transparent, slightly yellow, liquid was obtained after removing the solvent under reduced pressure (yield 5.08 g, 83.5%): IR 2965, 2855, 1782, 1462, 1402, 1340, 1270, 1198, 1162, 1080, 1049, 955, 928, 905, 855, 805, 775, 742, and 708 cm^{-1}; ^{1}H NMR δ=3.64(CH_3, s(singlet), 4.31H), 3.68(CH_3, s, 0.46H), 3.78(CH_3, s, 0.98H), 3.95(CH_3, s, 0.25H), and 5.98(CF_2H, t(t)(triplet(triplet)), *J*=51.6 (5.0) Hz, 2.0H); ^{13}C NMR δ=52.3(f, s), 52.5(f, s), 53.6(f, s), 55.1(f, s), 109.2(a, t(t), *J*=253.5(30.8) Hz), 109.3(b, t(m(multiplet)), *J*=265.6 Hz), 110.3(c, t(m), *J*=266.7 Hz), 111.6(d, t(t), *J*=266.7(31.5) Hz), 157.3(e, t, *J*=30.0 Hz), and 159.5(e, t, *J*=29.3 Hz) for $(HC^aF_2C^bF_2C^cF_2\text{-}C^dF_2C^eOO)_2Si(OC^fH_3)_2$; ^{19}F NMR δ=−25.4 (a, d(doublet), *J*=51.3 Hz, 4F), −17.3(b, s, 4F), −12.3(c, s, 4F), and −6.6(d, s, 4F) for $(HCF_2^aCF_2^bCF_2^cCF_2^dCOO)_2Si(OCH_3)_2$. Found: Si, 5.00; CH_3O, 10.8; $H(CF_2)_4COO$, 49.9 %. Calcd for $C_{12}H_8F_{16}O_6Si$: Si, 4.84; CH_3O, 10.7; $H(CF_2)_4COO$, 50.0 %.

Synthesis of Dimethoxysilanediyl Bis(7*H*-dodecafluoroheptanoate), $Si(OCH_3)_2[OCO(CF_2)_6H]_2$, Dimethoxysilanediyl Bis(9*H*-hexadecafluorononanoate), $Si(OCH_3)_2[OCO(CF_2)_8H]_2$, and Dimethoxysilanediyl Bis(pentadecafluorooctanoate), $Si(OCH_3)_2[OCO(CF_2)_6CF_3]_2$: The procedures and purification techniques were almost the same as those for the preparation of dimethoxysilanediyl bis(5*H*-octafluoropentanoate).

Dimethoxysilanediyl bis(7*H*-dodecafluoroheptanoate) was a slightly brown liquid (yield 81.9%): IR 2970, 2870, 1786, 1465, 1408, 1348, 1300, 1195, 1135, 1080, 1060, 940, 865, 835, 800, 775, 728, and 673 cm^{-1}; ^{1}H NMR δ=3.64(CH_3, s, 4.93H), 3.67(CH_3, s, 0.31H), 3.78(CH_3, s, 0.65H), 3.95(CH_3, s, 0.11H), and 6.0(CF_2H, t(t), *J*=51.6(5.0) Hz, 2.0H); ^{13}C NMR=52.3(h, s), 52.5(h, s), 53.6(h, s), 55.1(h, s), 109.3(a, t(t), *J*=253.5(31.5) Hz), 110.8—113.1 (b—f), 156.8(g, t, *J*=30.0 Hz), 156.1(g, t, *J*=31.5 Hz), 156.8(g, t, *J*=30.0 Hz), and 159.3(g, t, *J*=29.3 Hz) for $(HC^aF_2C^bF_2C^cF_2C^dF_2C^eF_2C^fF_2C^gOO)_2Si\text{-}(OC^hH_3)_2$; ^{19}F NMR δ=−25.4 (a, d, *J*=51.3 Hz, 4F), −17.3(b, s, 4F), −11.1(c, s, 4F), −10.4(d, s, 4F), −9.2(e, s, 4F), and −6.2(f, s, 4F) for $(HCF_2^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCOO)_2Si(OCH_3)_2$. Found: Si, 3.52; CH_3O, 7.78; $H(CF_2)_6COO$, 62.6 %. Calcd for $C_{16}H_8F_{24}O_6Si$: Si, 3.60; CH_3O, 7.95; $H(CF_2)_6COO$, 62.8 %.

Dimethoxysilanediyl bis(9*H*-hexadecafluorononanoate) was a slightly brown liquid (yield 70.5%): IR 2966, 2863, 1790, 1464, 1402, 1354, 1323, 1211, 1147, 1063, 997, 953, 854, 806, 769, 730, and 665 cm^{-1}; ^{1}H NMR δ=3.68(CH_3, s, 3.88H), 3.78(CH_3, s, 1.90H), 3.97(CH_3, s, 0.22H), and 5.9(CF_2H, t(t), *J*=51.1(5.0) Hz, 2.0H); ^{13}C NMR δ=52.4(j, s), 53.3(j, s), 54.8(j, s), 108.0(a, t(t), *J*=255.0(32.2) Hz), 108.3—112.5 (b—h), 155.5(i, t, *J*=30.8 Hz), and 156.4(i, t, *J*=30.8 Hz) for $(HC^aF_2C^bF_2C^cF_2C^dF_2C^eF_2C^fF_2C^gF_2C^hF_2C^iOO)_2Si(OC^jH_3)_2$; ^{19}F NMR δ=−24.2(a, d, *J*=51.3 Hz, 4F), −16.4(b, s, 4F), −10.3(c, s, 4F), −8.7(d—g, br(broad), 16F), and −5.4(h, s, 4F) for $(HCF_2^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCF_2^gCF_2^hCOO)_2Si(OCH_3)_2$. Found: Si, 3.15; CH_3O, 6.30; $H(CF_2)_8COO$, 70.2%. Calcd for $C_{20}H_8F_{32}O_6Si$: Si, 3.07; CH_3O, 6.33; $H(CF_2)_8COO$, 70.4%.

Dimethoxysilanediyl bis(pentadecafluorooctanoate) was a slightly brown liquid (yield 82.8%): IR 2952, 2849, 1780, 1480, 1440, 1402, 1330, 1240, 1202, 1148, 1100, 1080, 1018, 883, 838, 820, 812, 803, 778, 745, 735, 720, 698, and 660 cm^{-1}; ^{1}H NMR δ=3.64(CH_3, s, 1.65H), 3.67(CH_3, s, 3.05H), 3.79(CH_3, s, 0.14H), and 3.96(CH_3, s, 1.16H); ^{13}C NMR δ=52.4(i, s), 52.5(i, s), 52.7(i, s), 53.0(i, s), 111.6—118.7(a—g), and 156.8(h, t, *J*=30.8 Hz) for $(C^aF_3C^bF_2C^cF_2C^dF_2C^eF_2C^fF_2C^gF_2C^hOO)_2\text{-}Si(OC^iH_3)_2$; ^{19}F NMR δ=−13.9(b, s, 4F), −11.3 (c, s, 4F), −10.4(d, s, 4F), −9.2(e and f, br, 8F), −2.0(g, s, 4F), and 31.0 (a, t, *J*=12.2 Hz, 6F) for $(CF_3^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCF_2^gCOO)_2\text{-}Si(OCH_3)_2$. Found: Si, 2.95; CH_3O, 6.85%. Calcd for $C_{18}H_6F_{30}O_6Si$: Si, 2.87; CH_3O, 6.77 %.

Results and Discussion

The reaction of the synthesis of dimethoxysilanediyl bis(polyfluoroalkanoate) was heterogeneous in every cases, the same as the preparation of titanium butoxide tris(polyfluoroalkanoate).[10] However, the time to complete the reaction was comparably shorter than that of the titanium butoxide tris(polyfluoroalkanoate) synthesis, even in the reaction with the sodium fluoro-substituted alkanoate having a longer chain.

The NMR spectra of dimethoxysilanediyl bis(5*H*-ctafluoropentanoate), $Si(OCH_3)_2[OCO(CF_2)_4H]_2$, are shown in Figs. 1—3. In the ^{1}H NMR spectrum, three small signal peaks (δ=3.68(0.46H), 3.78(0.98H), and 3.95(0.25H)) were detected along with the main signal peak which originated from methyl protons at δ=3.64(4.31H). This fact shows that a part of the silicon compound was disproportionated to methoxysilanetriyl tris(5*H*-octafluoropentanoate), trimethoxysilyl 5*H*-octafluoropentanoate and tetramethoxysilane. The same observations were detected two kinds of carbons ($\underline{C}H_3$– and –$\underline{C}OO$–) in the ^{13}C NMR spectrum. On the other hand, the effect of the disproportionation on the chemical shift against the $\underline{H}CF_2$– proton signal was very slight and only a broadening was observed in the ^{1}H NMR spectrum. The effect of the disproportionation on the chemical shift of the ^{19}F NMR spectrum was not observed. The ^{13}C NMR spectrum was relatively complicated especially for the –$\underline{C}F_2$– signals (see Fig. 2). The resonance peaks of a carbon atom were coupled magnetically with the geminal and vicinal fluorine atoms.

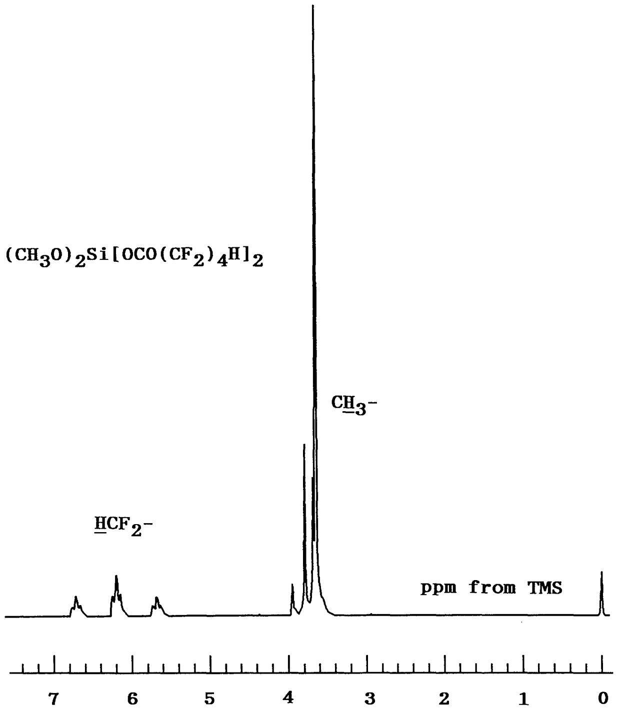

Fig. 1. Pulsed fourier transform 100 MHz ^{1}H NMR spectrum of **$(CH_3O)_2Si[OCO(CF_2)_4H]_2$** in THF-$d_8$.

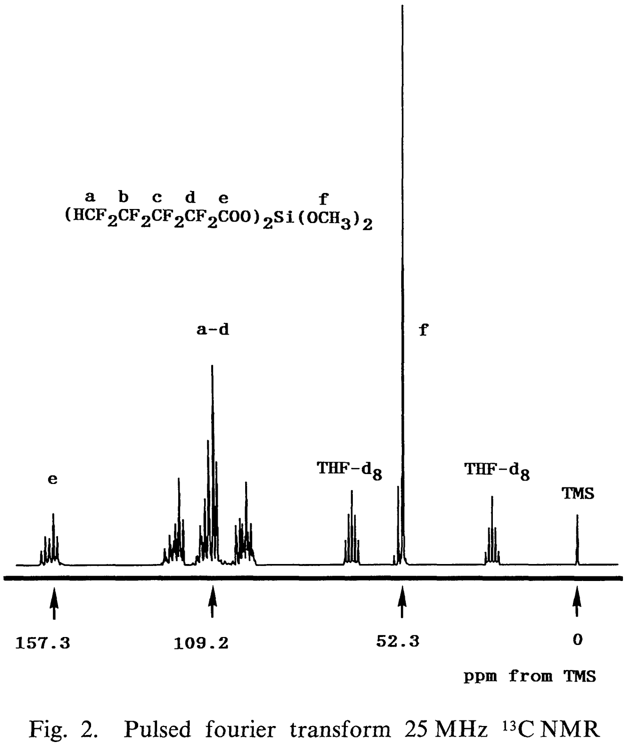

Fig. 2. Pulsed fourier transform 25 MHz ^{13}C NMR spectrum of **$(CH_3O)_2Si[OCO(CF_2)_4H]_2$** in THF-$d_8$.

A group of stronger intensity peaks from the terminal HCF_2– (triplet(triplet)) was observed at 109.2 ppm from TMS in THF-d_8, and the other –CF_2– peaks were weaker.

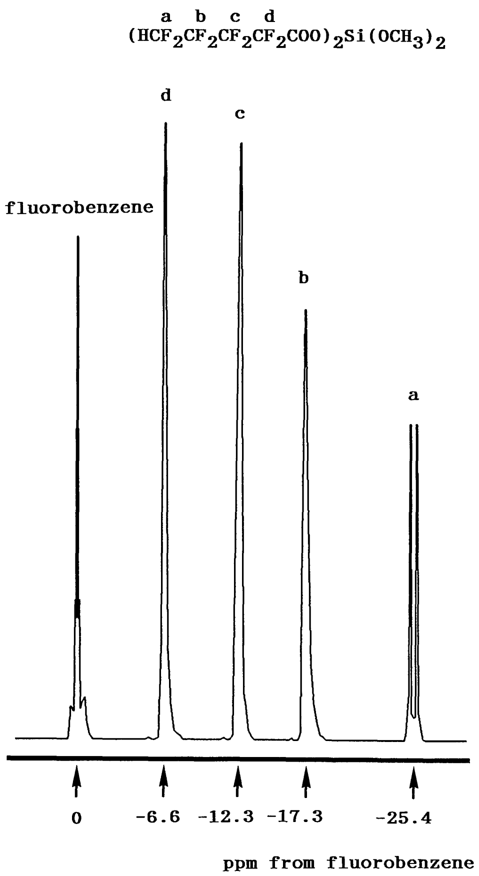

Fig. 3. Pulsed fourier transform 90 MHz ^{19}F NMR spectrum of **$(CH_3O)_2Si[OCO(CF_2)_4H]_2$** in THF.

In the case of the ^{13}C NMR spectra, it is well known that for fluorinated carbon atoms, the peak intensities of a carbon bonded to a hydrogen atom, such as HCF_2–, H_2CF–, or –HCF–, are stronger than those of a carbon bonded only to fluorine atoms, such as CF_3– or –CF_2–. In the ^{13}C NMR spectra, it was very difficult to make assignments against –CF_2– of almost all the silicon compounds prepared. Only for the simplest one, dimethoxysilanediyl bis(5*H*-octafluoropentanoate), were we able to make an assignment.

These silicon compounds possessed a structure essentially similar to that of the titanate-type coupling agents having fluorocarbon chains.[10] In the titanate-type coupling agents, the TiOCOR moiety was stable in water, although the TiOR' was only moderately stable against water. Therefore, the stability of the silicon compounds to hydrolysis was investigated. From the ^{1}H NMR spectrum of the reaction mixture of dimethoxysilanediyl bis(7*H*-dodecafluoroheptanoate) and water (molar ratio 10:1) in THF-d_8 (internal standard TMS), the intensity ratio of the produced acid COO$\underline{H}$ (13.9 ppm) and the produced methanol O$\underline{H}$ (4.0 ppm) was precisely 1:1. This means that the ease of hydrolysis of the SiOCOR and the $SiOCH_3$ moieties was exactly same. The same observation was obtained from the other prepared silicon compounds.

Moreover, the instabilities to hydrolysis of these silicon compounds were proved as follows. In a 100-ml beaker, 1 g of dimethoxysilanediyl bis(7*H*-dodecafluoroheptanoate) in 50 cm^3 methanol was stirred exposed to the atmosphere at room temperature for 24 h. A white precipitate formed. A white powder was obtained after filtration, washing with 1,1,2-trichloro-1,2,2-trifluoroethane and vacuum drying. The FT-IR spectrum of this powder was the same as that of silica gel. The same observation was obtained from the other silicon compounds.

In conclusion, these dimethoxysilanediyl bis(polyfluoroalkanoate)s were very sensitive to water and decomposed easily, although they had the fluorinated carbon structure which exhibits the property of water repellency.

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