Synthesis of Fluorine-containing Organosilicon Oligomers

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New fluorine-containing organosilicon oligomers, $R_F(CH_2CHSiR_3)_xR_F$ {$x = 2$ or 3, $R_F = C_3F_7$ or $CF(CF_3)$-$[OCF_2CF(CF_3)]_yOC_3F_7$, $y = 0$ or 1; R = OMe or Me} were obtained by the reactions of fluoroalkanoyl peroxides with the corresponding vinylsilanes in excellent to moderate yields under very mild conditions.

Recently, the increasing importance of organosilicon compounds in applications for new functional materials has led to considerable interest in the introduction of fluoroalkyl groups into these compounds.[1] It has been shown that the hydrosilylation of fluorine-containing alkenes promoted by organotransition metal catalysts such as platinum,[2] ruthenium,[3] rhodium[3] and palladium[3] complexes is a convenient synthetic tool for the introduction of perfluoroalkyl groups. In the course of our study on the reactivity of fluoroalkanoyl peroxides, which are useful reagents for the introduction of fluoroalkyl groups into arenes[4] or alkenes,[5] we were interested in preparing fluorine-containing organosilicon compounds since preparative

Table 1 Reactions of vinylsilanes with peroxides

			$R_F(CH_2CHSiR_3)_xR_F$	
Run	R in $R_3SiCH{=}CH_2$	R_F in $(R_FCO_2)_2$	Isolated yield (%)[a]	Product ratio: $(x = 2)/(x = 3)$
1	OMe	C_3F_7–	34	74/26
2	OMe	$C_3F_7OCF(CF_3)$–	65	86/14
3	OMe	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$–	46	72/28
4	Me	$C_3F_7OCF(CF_3)$–	93[b,c]	—
5	Me	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$–	95[b,c]	—

[a] Based on the peroxide used. [b] Determined by GC. [c] A trace of the trimer was detected.

methods for these compounds had hitherto been limited. We have studied the synthesis of fluorine-containing organosilicon compounds by the reactions of fluoroalkanoyl peroxides with vinylsilanes, and now describe our results.

In a typical experiment, a solution containing perfluorobutyryl peroxide (117 mmol) and trimethoxyvinylsilane (234 mmol) in Freon 113 ($CF_2ClCFCl_2$; 500 ml) was stirred at 30 °C for 10 h under nitrogen. The mixture was then distilled under reduced pressure to give a colourless oligomer (26.5 g; b.p. 111–115 °C at 6 mmHg), $C_3F_7[CH_2CHSi(OMe)_3]_xC_3F_7$ **1** (x = 2 or 3): IR: ν/cm^{-1}: 1230 (CF_2) and 1355 (CF_3); ^1H NMR ($CDCl_3$) δ 0.6–2.8 ($-CH_2-$, $=CH-$) and 3.6 (OMe); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −4.8 (3F), −39.0 (2F) and −52.2 (2F); GC-MS **1a** (x = 2): m/z 634 (M^+), 603, 451, 419, 354, 242, 141, 121 and 91; **1b** (x = 3): m/z 750 (M^+ −32), 433, 215, 121 and 91. The reactions of several other fluoroalkanoyl peroxides with vinylsilanes were carried out under similar conditions (Scheme 1), and the results are summarized in Table 1.

$$R_FC(:O)OOC(:O)R_F + xCH_2{=}CHSiR_3 \xrightarrow{30\,^\circ C} \underset{\textbf{1}}{R_F(CH_2CHSiR_3)_xR_F}$$

x = 2 or 3
R_F = $-C_3F_7$ or $-CF(CF_3)[OCF_2CF(CF_3)]_yOC_3F_7$, y = 0 or 1
R = OMe or Me

Scheme 1

As Table 1 shows, both perfluoroalkylated and perfluorooxa-alkylated organosilicon oligomers were produced from the corresponding fluoroalkanoyl peroxides in excellent to moderate yields. In these reactions, hardly any fluoroalkylvinylsilanes ($R_FCH{=}CHSiR_3$) were formed. These results suggest that the reaction does not proceed by electron transfer from the substrate to the peroxide as proposed for styrene,[5] but rather by the usual free radical addition to vinylsilanes of fluoroalkyl radicals produced by the homolytic decomposition of peroxides. Products bearing reactive groups such as methoxy are useful not only as monomers for functional fluorine-containing organosilicon polymers but also as surface-active substances. In fact, **1** [R_F = $CF(CF_3)OC_3F_7$, R = OMe] was tested for surface activity as a new type of fluorine-containing silane coupling agent. Contact angles of a wettability standard solution (9.3% solution of ethylene glycol monoethyl ether in formamide) on glass treated with this agent (2 wt%) were found to increase significantly from 14.8 to 60.4°. Further extension to the synthesis and properties of other new fluorine-containing silicon oligomers with fluoroalkanoyl peroxides is now being studied.

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