Hydrosilylation of Unsaturated Fluorinated Esters and Ethers with Hydrochlorosilanes

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Abstract—Hydrosilylation of allyl esters of fluoro acids and ethers of fluoro alcohols with hydrochlorosilanes in the presence of the Speier's catalyst was studied. Yields of adducts with ethers reach 62–68%, and with esters, 27–45%. By etherification of the adduts with ethers the respective ethoxysilanes were obtained in 41–43% yield. The latter reaction even in very mild conditions is complicated by the formation of a large amount of siloxanes. Yield of siloxanes is 22–32%.

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In order to obtain new monomeric silicon of unsaturated fluorine-containing esters and ethers compounds, we continued to study the hydrosilylation [1].

$$R_{f}COOCH_{2}CH = CH_{2} + HSiMe_{n}Cl_{3-n} \longrightarrow R_{f}COO(CH_{2})_{3}SiMe_{n}Cl_{3-n}, \quad (1)$$

$$I \qquad II \qquad III$$

$$Ha: R_{f} = C_{2}F_{5}, n = 1; HIb: R_{f} = CF_{3}OCF_{2}CF_{2}, n = 1; HIc: R_{f} = CF_{3}(CF_{2})_{5}; HId: R_{f} = F COO, n = 1;$$

$$He: R_{f} = F COO, n = 2; HIf: R_{f} = \sqrt{F} CF_{2}COO, n = 1; HIg: R_{f} = \sqrt{F} CF_{2}COO, n = 2.$$

$$H(CF_{2})_{n}CH_{2}OCH_{2}CH = CH_{2} + MeSiHCl_{2} \longrightarrow H(CF_{2})_{n}CH_{2}O(CH_{2})_{3}SiMeCl_{2}, \quad (2)$$

$$IV$$

$$IVa: n = 2, IVb: n = 4.$$

Yields of products at the hydrosilylation of ethers in the presence of the Speier's catalyst reached 62-68%, and of esters, 27-45% (see Tables 1 and 2). Lower yields in the case of esters are explained, as was shown earlier [2], by the side processes of splitting of ester bond and the formation of acyloxysilanes that earlier have not been isolated from the reaction mixture but were obtained in an independent synthesis. At the hydrosilylation of allyl perfluorofurancarboxylate with dimethylchlorosilane we isolated and characterized the corresponding acyloxysilane Va.

We studied also transformations of acyloxypropylalkoxysilanes at heating. We previously showed that γ trifluoroacetoxypropyltriethoxysilane when heated to 110–115°C in the presence of Et₃N, HCl, FeCl₃, and

$$\begin{array}{c} \left\langle F \right\rangle \\ O \end{array} CF_2 COOO(CH_2)_3 SiMe_2(OCOCF_2 \left\langle F \right\rangle) \end{array}$$

Va

EtOH split off ethyl trifluoroacetate [3]. In this study we found that upon further heating of the remainder after the removal of the ester at 270°C quantitative liberation occurred of a mixture of propylene and cyclopropane with the formation of brittle resin (see the figure). The acethoxypropyltriethoxysilane behaved similarly.

RCOO(CH₂)₃Si(OEt)₃

$$\xrightarrow{110-120^{\circ}C} \text{ RCOOEt} + [-(CH2)_3Si(OEt)_2-O-]_n$$

$$\xrightarrow{270^{\circ}C} C_4H_6 + [-Si(OEt)_2-O-]_n. \quad (3)$$

Comp.	Conditions	s of synthesis	X. 11.0/	1 00/ 11	120	$n_{\rm D}^{20}$	
no.	duration of boiling, h	final temperature, ° C	Yield, %	bp, °C/mm Hg	d_4		
IIIa	5	120	45	63-69/2	1.3717	1.3822	
IIIb	5	120	41	73/3	1.4106	1.3705	
IIIc	6	115	60	110-115/2	1.5373	1.3635	
IIId	2	140	42	82/2	1.5424	1.3835	
IIIe	4	160	33.5	113/4	1.4501	1.3790	
IIIf	3	140	27	103-104/4	1.5038	1.3808	
IIIg	6	140	31 ^a	100-105/4	1.4080	1.3720	
IVa	5	170	62	83/1-2		1.4038	
IVb	5	170	68	103-105/4	1.4185	1.3458	
V	6	140	31	134–135	1.5510	1.3525	
VIa	1.5	45-50	41	115-119/9	1.1170	1.3890	
VIb	1.5	45-50	43	132-135/3	1.2350	1.3764	
VIIa	1.5	45-50	32.4	190-200/6		1.3940	
VIIb	1.5	45–50	22.3	205-212/3	1.3274	1.3780	

Table 1. Conditions of synthesis, yields, and properties of compounds

^a Isolated $(F_{O}CF_{2}COOO(CH_{2})_{3}SiMe_{2}(OCOCF_{2}, F_{O})$ with bp 134–135°C/1 mm Hg, d_{4}^{20} 1.5510; n_{D}^{20} 1.3525. Found: C 29.42, H 1.80, F

30.4, 51 4.0.	$C_{17}\Pi_{12}O_6\Gamma_{18}SI.$	Calculated, %.	С 29.3, П	1./0, г	30.2, 5

Table 2. Analytical data of compounds

Comp.		Found, %				Formula	Calculated, %				
no.	С	Н	Cl	F	Si	Formula	С	Н	Cl	F	Si
IIIa	26.37	2.63				C7H9Cl2F5O2Si	26.30	2.84	22.2	29.07	8.8
IIIb	24.95	2.46	18.7	35.00	7.48	C ₈ H ₉ Cl ₂ F ₇ O ₃ Si	25.0	2.36	18.4	34.5	7.52
IIIc	25.34	1.94	13.9	48.65	5.3	$C_{11}H_9Cl_2F_{13}O_2Si$	25.4	1.7	13.7	47.6	5.4
IIId	27.68	1.82	14.5	47.8	5.7	$C_{11}H_9Cl_2F_{11}O_2Si$	27.45	1.88	14.7	47.38	5.8
IIIe	31.32	2.71		45.6	7.2	$C_{12}H_{12}ClF_{11}O_2Si$	31.2	2.6	7.7	45.4	6.1
IIIf	26.87	1.92	16.3	41.2	6.2	$C_{10}H_9Cl_2F_9O_3Si$	26.35	2.02	15.9	38.22	6.3
IIIg	30.13	2.92	7.6	40.7	7.6	C11H12ClF9O3Si	30.9	2.80		40.05	6.6
IVa	27.89	3.35	23.6	25.72	9.09	$C_7H_{12}Cl_2F_4OSi$	29.27	4.18			
IVb	27.66	3.17				$C_7H_{12}Cl_2F_8OSi$	27.91	3.10			
VIa	42.87	7.12		23.9	9.2	$C_{11}H_{22}F_9O_3Si$	43.1	7.12		24.8	9.1
VIb	38.36	5.31		37.2	7.0	$C_{13}H_{22}F_8O_3Si$	38.4	5.42		37.4	6.9
VIIa	39.01	5.47			10.1	$C_{18}H_{34}F_8O_5Si_2\\$	37.8	6.35			10.5
VIIb	34.56	4.41		41.9	8.9	$C_{28}H_{34}F_{16}O_5Si_2$	35.8	4.6		41.2	7.6

The etherification with ethanol of chlorosilanes **IV** containing a fluorinated organic group and an ether bond is not complicated by side processes of C–O

bond splitting. Yield of products of etherification is about 40%, even in very mild conditions formed up to 20–30% siloxanes and ethyl chloride.

$$\begin{split} H(CF_2)_n CH_2 O(CH_2)_3 SiMeCl_2 + C_2 H_5 OH &\rightarrow H(CF_2)_n CH_2 O(CH_2)_3 SiMe(OC_2 H_5)_2 + HCl \\ & VI \\ &+ [H(CF_2)_n CH_2 O(CH_2)_3 SiMe]_2 O + C_2 H_5 Cl, \\ & VII \\ VIa: n = 2, VIb: n = 4; VIIa: n = 2, VIIb: n = 4. \end{split}$$

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Evolution of propylene and cyclopropane upon heating of RCOO(CH₃)Si(OEt)₃ in the presence of FeCl₃: (*1*) $R = CH_3$ and (*2*) $R = CF_3$.

EXPERIMENTAL

Thr reaction products were analyzed on a LHM-72 chromatograph with a detector katharometer, column 4×2000 mm, stationary phase Chromaton N-AW + 15% PMS 20000, flow rate of carrier gas (helium) 60 ml min⁻¹. The temperature of the evaporator 550°C, of oven from 50 to 250°C, the programmed rate of heating 20 deg min⁻¹.

Reaction of hydrosilanes with allyl esters of fluorinated acids. To a mixture of 0.1 mol of unsaturated ester and 0.1 ml of 0.1 M solution of platinumhydrochloric acid in isopropyl alcohol (Speier's catalyst) was added 0.1 mol of hydrosilane at a rate that ensures the continuous increase in the boiling temperature of the mixture. The mixture was kept for a few hours until the boiling temperature remained unchanged, and then it was distilled. **Reaction of methyldichlorosilanes with allyl** ethers of fluorinated alcohols. To a mixture of 0.1 mol of allyl ether and 0.15 ml of Speier's catalyst heated to 100°C was added dropwise within one hour 0.11 mol of methyldichlorosilane. Then the mixture was maintained at boiling point for 0.5 hours and distilled.

Transformations of γ -(acyloxypropyl)triethoxysilane under the action of iron chloride. 0.31 mol of γ -acyloxypropyltriethoxysilane and 0.5 g of anhydrous iron chloride was placed into a Claisen flask connected through a condenser and a receiver with a gas meter, and then the device was maintained in an oil bath at 110–120°C. After 10 min boiling started in the flask. Ethyl ester of acid was distilled off (yield 95–97%).

The residue consisted of a viscous resin. The gas evolution was not observed. On heating the residue to 270–300°C vigorous evolution of gas started (a mixture of propylene with cyclopropane, totally 670 ml, 96%). In the flask remained a brittle resin (4.3 g).

Etherification of ethers. Into a flask with stirrer, thermometer, dropping funnel and rflux condenser cooled at the top with dry ice in acetone and connect through the column filled with calcium chloride with a water-jet pump was placed 0.1 mol of chlorosilane, and at the reaction mixture temperature 45–50°C was added in 1 hour 0.2 mol of anhydrous ethanol. The mixture was maintained then at the same temperature for another half an hour, and distilled.

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