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Abstract

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FLUOROSILICON-ORGANIC COMPOUNDS. SIMPLE FLUOROSILICON-ORGANIC ETHERS

In previous papers ([1–3]) we reported the preparation of a series of fluorosilicon-organic compounds by the addition reaction of hydrosilanes to fluoroolefins in the presence of platinized carbon, and on certain features of the reaction itself. In the present work, the study of the addition reaction of hydrosilanes to unsaturated compounds was extended to simple ethers of allyl alcohol and 1,1,2-trifluoro-2-chloroethanol, as well as 1,1,2,2-tetrafluoroethanol

$$CH_2{=}CHCH_2OCF_2CFClH \text{ (I)} \quad \text{and} \quad CH_2{=}CHCH_2OCF_2CF_2H \qquad \text{(II)}$$

The aim of the work was not only the preparation and study of the properties of fluorinated silicon-organic ethers that had not previously been described—we were also interested in the influence of the structure of the hydrosilanes and of the experimental conditions on the course of the addition reaction, for example, of such substances as

Cl_3SiH, $C_2H_5SiCl_2H$, CH_3SiCl_2H, $C_3H_7SiCl_2H$, $(C_2H_5)(CH_3)SiClH$ and $(C_2H_5)_2(CH_3)SiH$,

i.e., compounds containing, along with the Si—H bond, a gradually decreasing number of chlorine atoms at Si. The experiments were carried out under comparable conditions (heating for 3 hr at 170–180° in the presence of 0.3 g of 1% Pt on carbon in a stainless-steel autoclave of 200 ml capacity). The results of the experiments and the reaction conditions are presented in Tables 1 and 2.

Table 1

$$\equiv Si{-}H + CH_2{=}CHCH_2OCF_2CFClH arrow \equiv SiCH_2CH_2CH_2OCF_2CFClH$$

Starting hydrosilane	Starting hydrosilane, g (mol)	I, g (mol)	1% Pt/C, g	Max. temp., °C	Heating time, hr	Max. pressure, atm	Reaction product	Yield, g	Yield, %
Cl_3SiH	35.0 (0.26)	45.4 (0.26)	0.3	164	3	14	$Cl_3SiCH_2CH_2CH_2OCF_2CFClH$	38	36
$(CH_3)(Cl_2)SiH$	68 (0.52)	92.1 (0.53)	0.3	170	3	10	$(CH_3)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$	115	76
$(C_2H_5)(Cl_2)SiH$	67.1 (0.52)	92.1 (0.53)	0.3	198	3	12	$(C_2H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$	121	76
$(C_3H_7)(Cl_2)SiH$	44.6 (0.3)	52.5 (0.3)	0.3	174	3	5	$(C_3H_7)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$	67	59
$(CH_3)(C_2H_5)(Cl)SiH$	38.0 (0.3)	52.5* (0.3)	0.3	182	3	15	$(CH_3)(C_2H_5)(Cl)SiCH_2CH_2CH_2OCF_2\times\times CFClH$	50	30
$(CH_3)(C_2H_5)_2SiH$	18.5 (0.18)	33.0** (0.19)	0.3	180	3	25	$(CH_3)(C_2H_5)_2SiCH_2CH_2CH_2OCF_2CFClH$	14	17
$(C_2H_5)(Cl_2)SiH$	38.7 (0.3)	47.5*** (0.3)	0.3	183	3	11	$(C_2H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CF_2H$	57	57

* $(C_2H_5)_2(Br)SiH$ also gives, in 18% yield, the product of addition to (I) (b.p. 124–125°/12 mm).
** $(C_2H_5)_3SiH$ adds to (I) poorly under these conditions.
*** With ether (II).

As is seen from Table 1, the highest yields of addition products are given by the following hydrosilanes:

$$CH_3SiCl_2H,\ C_2H_5SiCl_2H,\ (C_2H_5)(CH_3)SiClH \text{ and } Cl_3SiH.$$

The increase in activity in this series of hydrosilanes is in agreement with our earlier observations ([2]), as well as with the conclusion of Speier et al. ([4]) concerning the difference in the rates of addition of Cl_3SiH and CH_3SiCl_2H when chloroplatinic acid is used as catalyst. The addition of CH_3SiCl_2H, $C_2H_5SiCl_2H$ to (I), as well as to other unsaturated compounds, unlike the other hydrosilanes, is accompanied by a sharp rise in temperature. In experiments on the simultaneous addition of selected pairs of hydrosilanes to (I), as evidenced by the data of Table 2, the picture changes. Comparison of the data in Tables 1 and 2 makes it possible to note the following:

Table 2

Starting hydrosilanes	Max. temp., °C	Max. pressure, atm	Distillation products	Amount of product, g	Yield of addition products, % of theory
$C_2H_5SiCl_2OCl_3SiH$*	179	16	$C_2H_5SiCl_2H$	13,0	–
$C_2H_5SiCl_2OCl_3SiH$*	179	16	ClSiH	13.4	–
$C_2H_5SiCl_2OCl_3SiH$*	179	16	$(C_2H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$	38,6	42
$C_2H_5SiCl_2OCl_3SiH$*	179	16	$Cl_3SiCH_2CH_2CH_2OCF_2CFClH$	38,7	42
$C_2H_5SiCl_2H(C_2H_5)(CH_3)SiClH$*	174	15	$(C_2H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$	24,5	27
$C_2H_5SiCl_2H(C_2H_5)(CH_3)SiClH$*	174	15	$(C_2H_5)(CH_3)(Cl)SiCH_2CH_2CH_2OCF_2CFClH$	28,7	33
$C_2H_5SiCl_2H(C_2H_5)_2(CH_3)SiH$**	189	15	$C_2H_5SiCl_2H$	{22, 0	–
$C_2H_5SiCl_2H(C_2H_5)_2(CH_3)SiH$**	189	15	$(C_2H_5)_2(CH_3)SiH$	{22, 0	–
$C_2H_5SiCl_2H(C_2H_5)_2(CH_3)SiH$**	189	15	$(C_2H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$	14,5	25
$C_2H_5SiCl_2H(C_2H_5)_2(CH_3)SiH$**	189	15	$(C_2H_5)_2(CH_3)SiCH_2CH_2CH_2OCF_2CFClH$	24,0	47
$Cl_3SiH(C_2H_5)_2(CH_3)SiH$*	159	9,5	Cl_3SiH	20,0	–
$Cl_3SiH(C_2H_5)_2(CH_3)SiH$*	159	9,5	$(C_2H_5)_2(CH_3)SiH$	9.3	–
$Cl_3SiH(C_2H_5)_2(CH_3)SiH$*	159	9,5	$Cl_3SiCH_2CH_2CH_2OCF_2CFClH$	18,2	20
$Cl_3SiH(C_2H_5)_2(CH_3)SiH$*	159	9,5	$(C_2H_5)_2(CH_3)SiCH_2CH_2CH_2OCF_2CFClH$	27,5	33

* Into the reaction were introduced 0.3 mole of each hydrosilane and 0.3 mole of (I). Amount of catalyst (1% Pt/C), 0.3 g. Reaction time 3 h.

** Into the reaction were introduced 0.25 mole of each hydrosilane and 0.25 mole of (I). The amount of catalyst and the reaction time were the same.

1. The conclusion made earlier regarding the high activity of hydrosilanes of the type $RSiCl_2H$ and R_2SiClH is confirmed.
2. Trichlorosilane adds to (I) somewhat less readily than $C_2H_5SiCl_2H$ and $(C_2H_5)(CH_3)SiClH$. However, in the presence of $C_2H_5SiCl_2H$, the addition of Cl_3SiH to (I) proceeds more actively.
3. The addition of $(C_2H_5)_2(CH_3)SiH$ to (I) jointly with $C_2H_5SiCl_2H$ and Cl_3SiH proceeds in higher yields than without these chlorosilanes.
4. The data of Table 2 indicate that, in terms of activity in the addition reaction, the alkylchlorosilicon hydrides studied can evidently be arranged in the following series: $R_3SiH > R_2SiClH > RSiCl_2H > Cl_3SiH$. However, it is not excluded that the increase in the yield of the addition product of $(C_2H_5)_2(CH_3)SiH$ to (I) in the presence of Cl_3SiH and $C_2H_5SiCl_2H$, as in the case of trichlorosilane, is associated with "activation" of the reaction through the readily occurring additions of $C_2H_5SiCl_2H$, Cl_3SiH to (I).

Most of the simple organofluorosilicon ethers obtained, especially those containing chlorosilyl groups, are compounds sufficiently stable to heating. The fluoroether group of these compounds is not affected during Grignard reactions and hydrolysis.

Experimental Part

1,1,2-Trifluoro-2-chloroethyl ether of allyl alcohol CH_2=$CHCH_2OCF_2CFClH$ (I). It was obtained by a somewhat modified procedure described in work ([5]). In contrast to work ([5]), we

a somewhat larger amount of KOH and stirring were used. CF_2=CFCl was passed through a porous-glass plate sealed into the bottom of a flask equipped with a thermometer, a stirrer, and a reflux condenser. In this way we succeeded in increasing the yield of (I) from 45 to 89%. From 400 g (6.89 mole) of allyl alcohol in the presence of 70 g of KOH over 6 hr at a temperature not above 25°, after washing with water, drying with Na_2SO_4, and distillation on a column with glass packing, 1072 g (89%) of pure (I) was obtained—b.p. 110°/755 mm. Literature data ([5]): 109.2°/750 mm.

1,1,2,2-Tetrafluoroethyl ether of allyl alcohol CH_2=$CHCH_2OCF_2CF_2H$ (II). Obtained from allyl alcohol and tetrafluoroethylene under pressure—b.p. 74°/739 mm, d_4^{20} 1.2043; n_D^{20} 1.3273. Found MR 26.58; calculated MR 26.70. Yield based on allyl alcohol 80%.

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropylmethyldichlorosilane $(CH_3)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$ (III). 60 g (0.52 mole) of methyldichlorosilane and 92 g (0.53 mole) of (I) were heated at 170° in the presence of 0.3 g of 1% Pt on carbon for 3 hr. Maximum pressure 10 atm. Weight of reaction products 147 g. After distillation on a column with glass packing, 115 g (76%) of pure (III) was obtained—b.p. 215°/753 mm, d_4^{20} 1.3395, n_D^{20} 1.4160. Found MR 54.26; calculated MR 54.76.

Found %:	C 25.33; 25.37;	H 3.62; 3.61; Cl 36.49; F 19.68, 19.70;
$C_6H_{10}SiCl_3F_3O$, Calculated %:	C 24.89;	H 3.48; Cl 36.72; F 19.68;

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropylethyldichlorosilane $(C_2H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CF_2ClH$ (IV). The experimental conditions are presented in Table 1. Weight of the crude mixture of reaction products 152 g. (IV) had the following constants—b.p. 231.5°/751 mm, d_4^{20} 1.3155; n_D^{20} 1.4249. Found MR 59.01; calculated MR 59.25.

Found %:	C 27.93; 27.92	H 4.10; 4.04; Cl 33.50; F 18.01; 18.27,
$C_7H_{12}SiCl_3F_3O$, Calculated %:	C 27.69;	H 3.99; Cl 35.00; F 18.77;

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropyltrichlorosilane $Cl_3SiCH_2CH_2CH_2OCF_2CFClH$ (V). For the experimental conditions see Table 1. Weight of the crude mixture of reaction products 71 g. By distillation on a column with glass packing, (V) was obtained with the following properties: b.p. 213°/753 mm, d_4^{20} 1.4563, n_D^{20} 1.4230. Found MR 54.21; calculated MR 54.39.

Found %:		C 19.92; 20.12; H 2.39; 2.48; Cl 46.91 46.97; F 17.42; 17.13;
$C_5H_7SiCl_4F_3O$.	Calculated %:	C 19.36; H 2.28; Cl 45.78; F 18.36.

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropylpropyldichlorosilane $(C_3H_7)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$ (VI). The experimental conditions are described in Table 1. The reaction products (91 g) were distilled on a column and then under vacuum. The ether (VI), obtained in an amount of 59 g, had the following constants: b.p. 115.5°/8 mm, d_4^{20} 1.2763, n_D^{20} 1.4270. Found MR 63.91; calculated MR 64.02.

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropylmethylethyldichlorosilane $(CH_3)(C_2H_5)(Cl)SiCH_2CH_2CH_2OCF_2CFClH$ (VII). Under conditions analogous to those described above (see Table 1), 79 g of reaction products was obtained, from which, by distillation on a column, (VII) was isolated with the following constants: b.p. 223°/746 mm, d_4^{20} 1.1918, n_D^{20} 1.4175. Found MR 59.82; calculated MR 59.76.

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropylmethyldiethylsilane $(CH_3)(C_2H_5)_2SiCH_2CH_2CH_2OCF_2CFClH$ (VIII). After distillation of 45.5 g of reaction products obtained under-

under conditions analogous to those described above (see Table 1), (VIII) was isolated with the following constants: b.p. 94°/7 mm, d_4^{20} 1.0776, n_D^{20} 1.4149. Found MR 64.31; calculated MR 64.52.

Found %:		C 43.37; 43.55; H 7.22; 7.49; Cl 13.70; 13.52 F 22.12; 21.81
$C_{10}H_{20}SiClF_3O$.	Calculated %:	C 43.38; H 7.29; Cl 12.81; F 20.59

The starting $(CH_3)(C_2H_5)_2SiH$ and (I) were isolated in amounts of 10 g and 14 g, respectively.

1,1,2,2-Tetrafluoroethyl ether of γ-hydroxypropyldichloroethylsilane $(C_2H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CF_2H$ **(IX).** The experimental conditions are presented in Table 1. From 80 g of reaction products, after two distillations under vacuum, (IX) was obtained—b.p. 207.2°/749 mm, d_4^{20} 1.2837, n_D^{20} 1.4033. Found MR 54.63; calculated MR 54.46.

Found %:		C 28.57; 28.51; H 4.22; 4.28; Cl 26.11; 25.95; F 26.99; 26.64.
$C_7H_{12}SiCl_2F_4O$.	Calculated %:	C 29.27; H 4.21; Cl 24.70; F 26.47.

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropyltrimethylsilane $(CH_3)_3SiCH_2CH_2CH_2OCF_2CFClH$ **(X).** Obtained from 30 g of (IV) and

CH_3MgBr, prepared from 6.1 g of Mg and CH_3Br in 200 ml of absolute ether. After decomposition with water, drying over Na_2CO_3, and distillation, 17 g (66% of theory) of (X) was isolated—b.p. 182°/742 mm, d_4^{20} 1.0866, n_D^{20} 1.3985. Found MR 55.32; calculated MR 55.50.

Found % :		C 39.25; 39.14; H 6.63; 6.58. Cl 14.90; 14.84; F 21.83; 21.99
$C_8H_{16}SiClF_3O$.	Calculated % :	C 38.63; H 6.48; Cl 14.25; F 22.92

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropyldimethylethylsilane $(CH_3)_2(C_2H_5)SiCH_2CH_2CH_2OCF_2CFClH$ **(XI).** Obtained in an amount of 23.1 g (64%) under the conditions of the preceding experiment from 42 g of (V) and CH_3MgBr, prepared from 12 g of Mg and CH_3Br in 300 ml of ether. (XI) had the following constants: b.p. 204°/740 mm; d_4^{20} 1.0771, n_D^{20} 1.4073. Found MR 60.09; calculated MR 60.01.

Found % :		C 41.40; 41.63; H 7.01; 7.07; Cl 14.09; 14.13; F 22.29; 22.09.
$C_9H_{18}SiClF_3O$.	Calculated % :	C 41.14; H 6.90; Cl 13.49; F 21.69

The results of the experiments on the joint addition of hydrosilanes to (I) are presented in Table 2.

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