Reaction of 1-hydrohexafluoroisobutenyloxytrimethylsilane with fluoride ion sources. 2,2,2′,2′-Tetrakis(trifluoromethyl)divinyl ether

A. Yu. Volkonskii, E. M. Kagramanova, E. I. Mysov,† and N. E. Mysova*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5085. E-mail: volkonskii@ineos.ac.ru

The reaction of 1-hydrohexafluoroisobutenyloxytrimethylsilane (**2a**) with cesium fluoride in diglyme leads to elimination of trimethylfluorosilane to form the 1-hydrohexafluoroisobutenolate anion (**3**), which is silylated with trialkylchlorosilanes at the oxygen atom. In the presence of bis(trifluoromethyl)ketene *N*,*N*,*O*-trimethylaminoacetal or *N*-(α,α-difluoroalkyl)dialkylamines, silane **2a** is transformed into 2,2,2′,2′-tetrakis(trifluoromethyl)divinyl ether. The reaction of trifluoroacetic anhydride with *N*-(1,1,2,2-tetrafluoroethyl)diethylamine affords trifluoroacetyl fluoride in quantitative yield.

Key words: 1-hydrohexafluoroisobutenyloxytrimethylsilane, cesium fluoride, bis(trifluoromethyl)ketene *N*,*N*,*O*-trimethylaminoacetal, *N*-(α,α-difluoroalkyl)dialkylamines, 2,2,2′,2′-tetrakis(trifluoromethyl)divinyl ether, trifluoroacetic anhydride, trifluoroacetyl fluoride.

Perfluoroalkyl carbanions, as important reactive intermediates, have attracted considerable attention of researchers engaged in organofluorine chemistry.[1,2] The introduction of functional groups, which can be involved in conjugation with the carbanionic center, (for example, of the C=O group) into these anions leads to a substantial increase in stability of such mesomeric anions.[3] For example, α-hydrohexafluoroisobutyroyl fluoride is readily deprotonated with triethylamine to form a stable salt containing the heptafluoroisobutenolate anion.[3—5] To the contrary, the replacement of F atoms with H decreases substantially stability of the corresponding fluorocarbanions. For example, α-hydrohexafluoroisobutyric aldehyde (**1**), which is a close analog of α-hydrohexafluoroisobutyroyl fluoride, is readily enolized in dipolar aprotic solvents but does not give a conjugated anion in both pyridine and triethylamine.[5,6]

There are numerous examples (see the monograph[7]), where *C*-, *O*-, or *N*-silyl derivatives serve as convenient sources of the corresponding, including mesomeric, C-, O-, and N-anions in the presence of fluoride ions. In the present study, we attempted to extend this approach to 1-hydrohexafluoroisobutenyloxytrimethylsilane (**2a**) with the aim of generating the 1-hydrohexafluoroisobutenolate anion (**3**) and studied the reactivity of the latter.

† Deceased.

Results and Discussion

Initially, we studied the reaction of silyl ether **2a** with CsF in diglyme. The addition of silane **2a** to a suspension of CsF at room temperature is accompanied by a moderately exothermic reaction with partial dissolution of CsF to give a complex mixture consisting (^{19}F NMR spectroscopic data) of Me_3SiF (**4a**), cesium 1-hydrohexafluoroisobutenolate (**5**), 2,2,2′,2′-tetrakis(trifluoromethyl)divinyl ether (**6**),* and products of further transformations of the latter compound, the percentage of salt **5** in the reaction mixture being no higher than 20—25 mol.% (Scheme 1).

A decrease in the reaction temperature to 0——10 °C leads to a substantial decrease in the rates of all processes, except for fluorodesilylation, due to which the fraction of salt **5** can be increased to 80—85 mol.%. Unfortunately, the signals of all compounds in the NMR spectra of the resulting mixture are substantially broadened due, apparently, to exchange processes, which hinders the unambiguous identification of hexafluoroisobutenolate anion **3**. Therefore, we treated the reaction mixture with trimethylchlorosilane (**7a**), which led to regeneration of silyl ether **2a**. An attempt to use this reaction (see Scheme 1) for the synthesis of other silanes **2** (for example, of

* The addition/cycloaddition of Et_2O to divinyl ether **6** has been described in the literature.[8]

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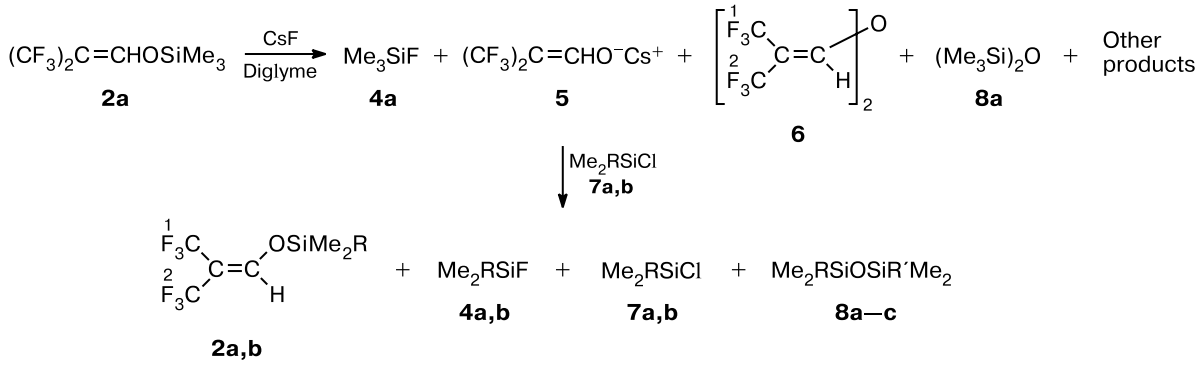
Scheme 1



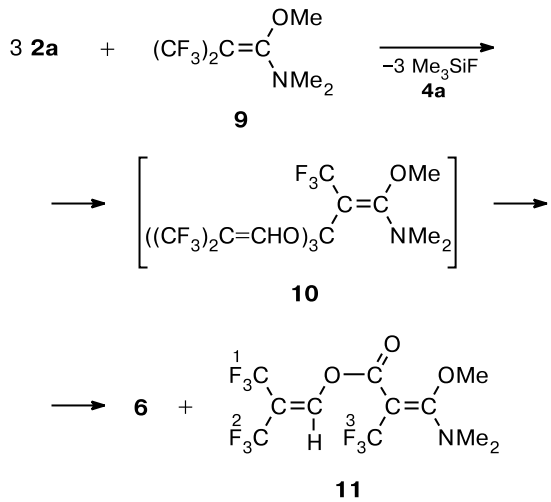
2a **4a** **5** **6** **8a** **2a,b** **4a,b** **7a,b** **8a—c**

2, 4, 7: R = Me (**a**), $CH=CH_2$ (**b**); **8:** R = R′ = Me (**a**), $CH=CH_2$ (**b**); R = Me, R′ = $CH=CH_2$ (**c**)

dimethylvinylsilane **2b**) failed, because the addition of chlorosilane **7b** to the reaction mixture led to rapid exchange of the substituents at different silicon atoms. As a result, the reaction afforded two silyl ethers **2a** and **2b**, two fluorosilanes **4a** and **4b**, two chlorosilanes **7a** and **7b**, and three disiloxanes, *viz.*, symmetrical **8a** and **8b** and mixed **8c** (NMR, GLC, GLC/MS).

This reaction (see Scheme 1) is also unsuitable for the synthesis of divinyl ether **6**, because the latter rather rapidly undergoes further transformations upon an increase in the temperature of the reaction mixture. Nevertheless, we succeeded in synthesizing ether **6** in high yield by treating silyl ether **2a** with an unusual fluoride ion source, *viz.*, bis(trifluoromethyl)ketene *N,N,O*-trimethylaminoacetal (**9**) (lability of the F atoms in aminoacetal **9** was documented[9]) (Scheme 2).

Scheme 2

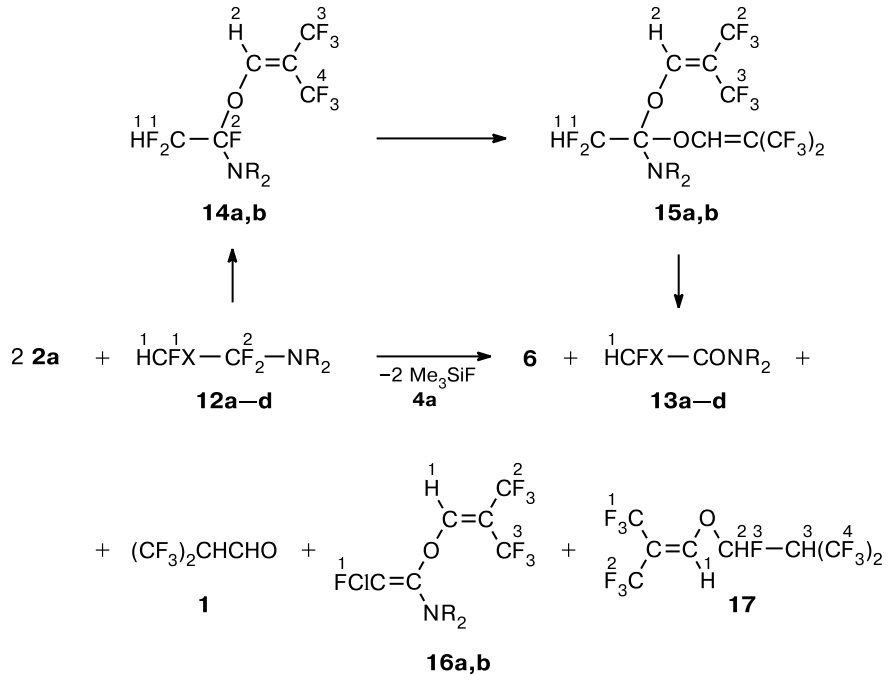


The reaction proceeds apparently through the corresponding ortho ester **10** (*cf.* Ref. 10), which is cleaved as described earlier[11a] to form ether and ester. So, mixing of silane **2a** with aminoacetal **9** in a molar ratio of 3 : 1 affords fluorosilane **4a**, divinyl ether **6**, and trifluoromethacrylic ester **11** in virtually quantitative yields.

The reaction presented in Scheme 2 can be used for the synthesis of divinyl ether **6**. However, one-third of the starting silyl ether **2a** is consumed for the formation of ester **11** as a by-product. In addition, the starting aminoacetal **9** is rather difficult to prepare. It is known that α,α-difluoroalkylamines **12** (Yarovenko's reagents) are readily accessible, contain two labile F atoms, which are easily replaced by the O atom, and theoretically could be convenient reagents for the transformation of silane **2a** into divinyl ether **6** (the formation of ethers as by-products in the reactions of alcohols with amines **12** has been described earlier[12]). Actually, mixing of silyl ether **2a** with amines **12a—d** in a molar ratio of 2 : 1 led to quantitative elimination of Me_3SiF (**4a**) to yield divinyl ether **6** and amides **13a—d** (Scheme 3).

In the case of tetrafluoroethyl-substituted amines **12a,b**, all intermediate products of the replacement of the F_α atoms, *viz.*, α-fluoroaminoacetals **14a,b** (*cf.* Ref. 13) and amidoacetals **15a,b** (*cf.* Refs 11b and 14), were detected by NMR spectroscopy. At the same time, the reactions with chlorine-containing amines **12c,d** produced divinyl ether **6** and chlorofluoroacetamides **13c,d** along with small amounts of α-hydrohexafluoroisobutyric aldehyde (**1**), chlorofluoroketene aminoacetals **16a,b**, and isobutenyl isobutyl ether **17**. The formation of the latter is associated with an insignificant excess of amine **12c** with respect to a stoichiometric amount and indicates that, in the absence of silyl ether **2a**, the excessive fluoride ions, which are present in the reaction mixture, are bound at the double bonds of divinyl ether **6**. The formation of aldehyde **1** and aminoacetals **16a,b** provides evidence that the 1-hydrohexafluoroisobutenolate anion (**3**), which is reversibly generated from amidoacetals **15a,b** and **18a,b*** (Scheme 4, path *a*), can both attack the conju-

Scheme 3



12, 13: X = F, R = Et (**a**), $CH_2CH_2CH_2CH_3$ (**b**); X = Cl, R = Et (**c**), $CH_2CH_2CH_2CH_3$ (**d**)

14, 15: R = CH_2CH_3 (**a**), $CH_2CH_2CH_2CH_2CH_3$ (**b**); **16:** R = CH_2CH_3 (**a**), $CH_2CH_2CH_2CH_2CH_3$ (**b**)

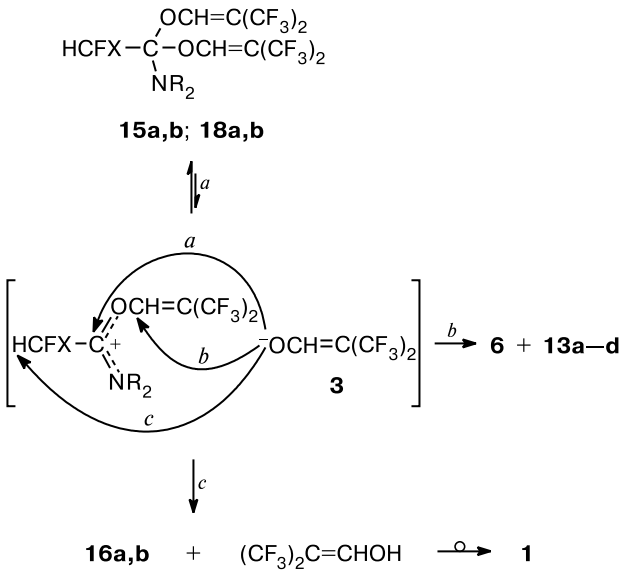
gated carbocation at the carbenium or vinyl C atoms (Scheme 4, path *b*) and eliminate the proton from the α position with respect to the cationic center (Scheme 4, path *c*) (*cf.* Refs 11c and 15).

The cleavage according to the path *c* (see Scheme 4) partially occurs with the involvement of the relatively more acidic CHFCl group, but it is completely suppressed in the case of the CHF_2 group, whose acidity is seven orders of magnitude lower.[16]

Divinyl ether **6**, diethylamides **13a,c**, and diethylaminoacetal **16a** have close boiling points, which complicates the purification of ether **6**. However, the change from diethylamines **12a,c** to dibutylamines **12b,d**, which form amides **13b,d** and aminoacetal **16b** having much higher boiling points, allowed us to isolate divinyl ether **6** in high yield by simple distillation.

The fact that two F atoms in α,α-difluoroalkylamines **12** can be efficiently replaced with the O atom under aprotic conditions was also exemplified by the reaction of tetrafluoroethylamine **12a** with trifluoroacetic anhydride, which proceeds already at room temperature to give

Scheme 4



18: X = Cl, R = Et (**a**), Bu^n (**b**)

trifluoroacetyl fluoride in virtually quantitative yield (Scheme 5).

* Presumably, ionization of amidoacetals **15a,b** and **18a,b** is favored by the presence of Me_3SiF acting as a kind of a Lewis acid.

Scheme 5

$$(CF_3CO)_2O + \mathbf{12a} \xrightarrow{20\ ^\circ C} 2\ CF_3COF + \mathbf{13a}$$
97.5%

This approach to the synthesis of acyl fluorides makes it possible to use both acyl residues of carboxylic acid anhydride (unlike the results of the earlier study[17]) as well as both active F atoms of α,α-difluoroalkylamine **12** (*cf.* Refs 18—20) for the preparation of the target acid fluoride. In addition, this procedure eliminates the problems inherent in conventional methods,[18—20] which are associated with elimination of HF as a by-product. This is of particular importance in experiments performed in glassware.

In conclusion, it should be noted that the generation of the 1-hydrohexafluoroisobutenolate anion (**3**) from silyl ether **2a** and various fluoride ion sources proved to be possible (unlike deprotonation of aldehyde **1**). The O atom of mesomeric anion **3** easily attacks various electrophiles with retention of the CF_3 groups, which indicates that this anion is similar to nonfluorinated enolate anions (*cf.*, for example, Ref. 21) and underlines its substantial difference from the perfluorinated analog, *viz.*, the heptafluoroisobutenolate anion.

Experimental

The ^1H and ^{19}F (CF_3COOH as the external standard) NMR spectra were recorded on Perkin—Elmer R-32 and Bruker WP-200SY spectrometers. The IR spectra were measured on a UR-20 spectrometer. The Raman spectra were recorded on a Ramanor HG-2S spectrometer. The mass spectra and GLC-mass spectra were obtained on a VG 7070E mass spectrometer (EI, 70 eV).

Silyl ether **2a**,[22] aminoacetal **9**,[23] fluoroalkylamines **12a**[24] and **12c** (see Ref. 18 with consideration for the comments[25]) were synthesized as described earlier. Other starting compounds and solvents were purified and dried according to standard procedures. The experiments were carried out under dry argon. For mixtures, the molar ratios of the main components are given. The melting points, IR spectra, Raman spectra, and the results of elemental analysis are given in Table 1. The NMR spectra and mass spectra are listed in Table 2.

Reaction of silane 2a with CsF in diglyme. Cesium 1-hydrohexafluoroisobutenolate (5). ***A.*** Freshly distilled silyl ether **2a** (4.75 g, 18.8 mmol) was added dropwise to a stirred suspension of freshly calcined CsF (3.85 g, 25.6 mmol) in anhydrous diglyme

Table 1. Boiling points, results of elemental analysis, and IR (Raman) spectra of the compounds synthesized

Compound	B.p./°C (*p*/Torr)	Found / Calculated (%)					Molecular formula	IR (Raman), ν/cm^{-1}
		C	H	F	Cl	N		
6	47—48 (8)	27.8 28.1	0.63 0.59	66.3 66.6	—	—	$C_8H_2F_{12}O$	1722 w, 1670 v.s (1722 v.s, 1666 v.s) (C=C)
11	109—113 (1)	34.5 35.2	2.69 2.69	45.6 45.6	—	4.06 3.73	$C_{11}H_{10}F_9NO_3$	1725 v.s, 1683 s, 1610 v.s (1721 m, 1681 s, 1598 m) (C=O, C=C)
12d	52—55 (1)	48.8 48.9	7.90 7.79	22.8 23.2	14.3 14.4	5.78 5.70	$C_{10}H_{19}ClF_3N$	—

Table 2. ^1H and ^{19}F NMR spectra and mass spectra of the compounds synthesized

Compound	NMR, δ (*J*/Hz)		MS, *m/z* (I_{rel} (%))
	^1H	^{19}F	
2b [a]	1.04 (s, 6 H, Me); 6.51—6.88 (m, 3 H, $CH=CH_2$); 8.07 (br.s, 1 H, CH)	16.7 (br.q, 3 F, F(2), $^4J_{F(2),F(1)}$ = 6.2); 18.8 (br.q, 3 F, F(1), $^4J_{F(1),F(2)}$ = 6.2)	264 $[M]^+$ (1.9), 249 $[M - Me]^+$ (21.1), 237 $[M - C_2H_3]^+$ (2.5), 168 $[M - C_2H_3 - CF_3]^+$ (1.6), 149 $[M - C_2H_3 - CF_4]^+$ (3.2), 141 $[C_4HF_4O]^+$ (100), 113 $[C_3HF_4]^+$ (26.1), 89 $[(C_2H_3)MeSiF]^+$ (62.9), 85 $[(C_2H_3)Me_2Si]^+$ (51.7), 77 $[Me_2SiF]^+$ (32.7), 63 $[MeSiHF]^+$ (26.2), 59 $[Me_2SiH]^+$ (25.7)[b]
6 [c]	7.38 (from 8.8 to 9.0 [a]) (br.s, CH)	14.5 (qd, 6 F, F(2), $^4J_{F(2),F(1)}$ = 6.4, $^4J_{F(2),H}$ = 1.5); 17.4 (q, 6 F, F(1), $^4J_{F(1),F(2)}$ = 6.4)	342 $[M]^+$ (38.5), 323 $[M - F]^+$ (26.5), 163 $[C_4HF_6]^+$ (99.5), 160 $[C_4HF_5O]^+$ (26.4), 159 $[C_4F_5O]^+$ (75.3), 113 $[C_3HF_4]^+$ (13.9), 112 $[C_3F_4]^+$ (15.8), 75 $[C_3HF_2]^+$ (50.4), 69 $[CF_3]^+$ (100), 51 $[CHF_2]^+$ (12.3)

(*to be continued*)

Table 2 (*continued*)

Compound	NMR, δ (*J*/Hz)		MS, *m*/*z* (I_{rel} (%))
	^{1}H	^{19}F	
11 [c]	3.19 (s, 6 H, NMe_2); 4.08 (s, 3 H, OMe); 8.40 (br.s, 1 H, CH)	16.0 (qd, 3 F, F(2), $^4J_{F(2),F(1)}$ = 6.5, $^4J_{F(2),H}$ = 1.5); 18.3 (q, 3 F, F(1), $^4J_{F(1),F(2)}$ = 6.5); 24.7 (br.s, 3 F, F(3))	375 $[M]^+$ (5.2), 356 $[M - F]^+$ (5.2), 342 $[M - CH_2F]^+$ (5.0), 323 $[M - CH_2F_2]^+$ (5.0), 223 $[M - CH_2F_2 - C_2F_4]^+$ (6.3), 196 $[M - C_4HF_6O]^+$ (100), 163 $[C_4HF_6]^+$ (15.5), 159 $[C_4F_5O]^+$ (14.3), 113 $[C_3HF_4]^+$ (15.2), 94 $[Me_2NCF_2]^+$ (10.3), 94 $[C_3HF_3]^+$ (10.3), 75 [C_3HF_2 or Me_2NCF]$^+$ (11.1), 72 $[C_3HFO]^+$ (29.8), 69 $[CF_3]^+$ (51.2), 44 $[Me_2N]^+$ (38.1), 44 $[C_2HF]^+$ (17.3)
12d [d]	0.88 (t, 6 H, H(5), $^3J_{H(5),H(4)}$ = 7); 1.26 (m, 4 H, H(4)); 1.47 (m, 4 H, H(3)); 2.83 (m, 4 H, H(2)); 6.13 (ddd, 1 H, H(1), $^2J_{H(1),F(1)}$ = 48, $^3J_{H(1),F(2A)}$ = 6.5, $^3J_{H(1),F(2B)}$ = 4.5)	−72.0 (dt, 1 F, F(1), $^2J_{F(1),H(1)}$ = 48, $^3J_{F(1),F(2)}$ = 15); −12.6 (dm, 1 F, F(2A) or F(2B), $^2J_{F(2A),F(2B)}$ = 200); −10.0 (dm, 1 F, F(2B) or F(2A), $^2J_{F(2B),F(2A)}$ = 200)	245 $[M]^+$ (6.3), 225 $[M - HF]^+$ (3.5), 202 $[M - C_3H_7]^+$ (50.3), 160 $[M - C_3H_7 - C_3H_6]^+$ (64.6), 146 $[M - C_3H_7 - C_4H_8]^+$ (32.0), 57 $[C_4H_9]^+$ (100), 56 $[C_4H_8]^+$ (27.7), 55 $[C_4H_7]^+$ (11.2), 41 $[C_3H_5]^+$ (58.7), 29 $[C_2H_5]^+$ (63.5), 27 [C_2H_3 or CHN]$^+$ (15.0)[e]
13d [f]	1.6 (m, 6 H, H(5)); 2.0 (m, 4 H, H(4)); 2.3 (m, 4 H, H(3)); 4.0 (m, 4 H, H(2)); 7.6 (d, 1 H, H(1), $^2J_{H(1),F}$ = 50)	−64.8 (d, CF, $^2J_{F,H(1)}$ = 50)	223 $[M]^+$ (1.2), 188 $[M - Cl]^+$ (9.4), 180 $[M - C_3H_7]^+$ (21.9), 156 $[Bu_2NCO]^+$ (41.7), 138 $[M - C_3H_7 - C_3H_6]^+$ (100), 124 $[M - C_3H_7 - C_4H_8]^+$ (15.3), 100 $[BuNHCO]^+$ (11.8), 57 $[C_4H_9]^+$ (50.9), 55 $[C_4H_7]^+$ (11.0), 42 $[C_3H_6]^+$ (15.9), 41 $[C_3H_5]^+$ (38.8), 30 $[CH_4N]^+$ (15.3), 29 $[C_2H_5]^+$ (44.2), 27 [C_2H_3 or CHN]$^+$ (14.1)[e]
16a [g]	1.02 and 1.13 (both t, 6 H, H(3), $^3J_{H(3),H(2)}$ = 7.1); 3.43 (m, 4 H, H(2)); 7.31 (br.d, 1 H, H(1), $^5J_{H(1),F(1)}$ = 19.9)	−39.5 (br.dq, 1 F, F(1), $^5J_{F(1),H(1)} \approx$ $\approx {}^7J_{F(1),F(3)} \approx$ 25); 13.3 (q, 3 F, F(2), $^4J_{F(2),F(3)}$ = 7.8); 19.8 (dq, 3 F, F(3), $^7J_{F(3),F(1)}$ = 27.3, $^4J_{F(3),F(2)}$ = 7.8)	329 $[M]^+$ (8.2), 314 $[M - Me]^+$ (13.1), 310 $[M - F]^+$ (7.0), 294 $[M - Cl]^+$ (17.4), 229 $[M - CONEt_2]^+$ (11.5), 203 (10.2), 175 (10.2), 100 $[Et_2NCO]^+$ (100), 72 $[Et_2N]^+$ (62.8), 56 $[C_3H_6N]^+$ (17.8), 44 $[C_2H_6N]^+$ (22.0), 42 $[C_2H_4N]^+$ (23.2), 29 $[C_2H_5]^+$ (55.1), 27 [C_2H_3 or CHN]$^+$ (15.0)[e]
16b [f]	1.6 (m, 6 H, H(5)); 2.0 (m, 4 H, H(4)); 2.3 (m, 4 H, H(3)); 4.0 (m, 4 H, H(2)); 8.3 (br.d, 1 H, H(1), $^5J_{H(1),F(1)}$ = 19.1)	−37.2 (br.dq, 1 F, F(1), $^5J_{F(1),H(1)} \approx$ $\approx {}^7J_{F(1),F(3)} \approx$ 25); 13.7 (q, 3 F, F(2), $^4J_{F(2),F(3)}$ = 7.7); 20.0 (dq, 3 F, F(3), $^7J_{F(3),F(1)}$ = 27.2, $^4J_{F(3),F(2)}$ = 7.7)	385 $[M]^+$ (0.9), 366 $[M - F]^+$ (3.5), 350 $[M - Cl]^+$ (6.8), 342 $[M - C_3H_7]^+$ (12.4), 300 $[M - C_3H_7 - C_3H_6]^+$ (53.8), 156 $[Bu_2NCO]^+$ (36.9), 100 $[BuNHCO]^+$ (12.7), 57 $[C_4H_9]^+$ (100), 55 $[C_4H_7]^+$ (16.8), 42 $[C_3H_6]^+$ (20.1), 41 $[C_3H_5]^+$ (55.3), 29 $[C_2H_5]^+$ (55.8), 27 [C_2H_3 or CHN]$^+$ (13.1)[e]
17 [h]	3.55 (m, 1 H, H(3)); 6.00 (br.dd, 1 H, H(2), $^2J_{H(2),F(3)}$ = 57.5, $^3J_{H(2),H(3)}$ = 3.0); 7.26 (br.s, 1 H, H(1))	−52.2 (br.ddh, 1 F, F(3), $^2J_{F(3),H(2)}$ = = 57.5, $^3J_{F(3),H(3)} \approx$ $\approx {}^4J_{F(3),F(4)} \approx$ 10); 14.0 (br.dd, 6 F, F(4), $^3J_{F(4),H(3)} \approx$ $\approx {}^4J_{F(4),F(3)} \approx$ 8.5); 15.0 (br.q, 3 F, F(2), $^4J_{F(2),F(1)}$ = 6.5); 17.6 (q, 3 F, F(1), $^4J_{F(1),F(2)}$ = 6.5)	362 $[M]^+$ (18.6), 343 $[M - F]^+$ (14.7), 211 $[M - (CF_3)_2CH]^+$ (13.5), 183 $[M - (CF_3)_2CCHO]^+$ (15.1), 180 $[(CF_3)_2C{=}CHOH]^+$ (15.1), 161 $[C_4H_2F_5O]^+$ (41.0), 160 $[C_4HF_5O]^+$ (21.8), 159 $[C_4F_5O]^+$ (17.3), 141 $[C_4HF_4O]^+$ (30.2), 113 $[C_3HF_4]^+$ (97.8), 95 $[C_3H_2F_3]^+$ (16.7), 75 $[C_3HF_2]^+$ (13.8), 69 $[CF_3]^+$ (76.4), 51 $[CHF_2]^+$ (100), 29 $[CHO]^+$ (12.7)

[a] In diglyme.
[b] For Si-containing ions, data only for the ^{28}Si isotope are given.
[c] In CD_2Cl_2.
[d] Without a solvent.
[e] For Cl-containing ions, data only for the ^{35}Cl isotope are given.
[f] In acetone-d_6.
[g] In CCl_4.
[h] In $CDCl_3$.

(10 mL) at 20 °C. After completion of the weakly exothermic reaction and dissolution of a substantial amount of CsF, the reaction mixture was stirred for 10 min, during which the mixture was cooled to 20 °C. Then the mixture was allowed to stand for 1 h. The ^{19}F NMR spectroscopic data demonstrated that the starting silane **2a** was completely consumed and the solution contained cesium salt **5** (^{19}F NMR, δ: 24.1 (br.s)), Me_3SiF (**4a**), divinyl ether **6** (1.0 : 4.55 : 1.45), and a substantial amount of nonidentified impurities (numerous signals with different intensities and multiplicities at δ 25—15 with a total integral intensity of ~20%).

B. Analogously, the reaction of CsF (1.18 g, 7.77 mmol) and silyl ether **2a** (1.99 g, 7.89 mmol) in diglyme (5 mL) performed at 0 °C for 1.5 h afforded a suspension, whose liquid fraction did not contain silane **2a** and consisted of cesium salt **5**, Me_3SiF (**4a**), divinyl ether **6**, and, apparently, HMDS (**8a**) (^{1}H NMR, δ: 0.56 (s)) (1.0 : 1.30 : 0.17 : 0.04), as well as a noticeable amount (12—13%) of nonidentified impurities (GLC, NMR). Trimethylchlorosilane (**7a**) with 97% purity (0.89 g, 7.94 mmol; 3% of HMDS (**8a**) as an impurity) was rapidly added with stirring and cooling (0 °C) to the reaction mixture. Then the mixture was stirred for 0.5 h and allowed to stand for 1.5 h. The solution contained (NMR, GLC and GLC/MS, without considering diglyme) silyl ether **2a**, divinyl ether **6**, aldehyde **1** (keto : enol = 1 : 2), Me_3SiF (**4a**), Me_3SiCl (**7a**), HMDS (**8a**) (1.0 : 0.24 : 0.10 : 2.00 : 0.41 : 0.10), and ~10% of nonidentified impurities (signals with different intensities and multiplicities at δ 20—10 (^{19}F NMR)).

Cesium salt 5. ^{1}H NMR, δ: 8.99 (br.m). ^{19}F NMR, δ: 25.55 and 25.45 (both br.m, 3 F each, CF_3).

C. Analogously, an interaction of CsF (2.72 g, 17.9 mmol) and silyl ether **2a** (3.70 g, 14.7 mmol) in diglyme (10 mL) at −10 °C for 2 h afforded a suspension, whose liquid fraction did not contain silane **2a** and consisted of cesium salt **5** (^{1}H NMR, δ: 8.95 (br.s); ^{19}F NMR, δ: 25.3 (br.s)), Me_3SiF (**4a**), divinyl ether **6**, and, apparently, HMDS (**8a**) (^{1}H NMR, δ: 0.55 (s)) (1.0 : 1.18 : 0.05 : 0.02), as well as small amounts (5—7%) of nonidentified impurities (GLC, NMR). Chlorosilane **7b** with 94.5% purity (2.20 g, 17.2 mmol; 4.7% of Me_2SiCl_2 and 0.8% of disiloxane **8b** as impurities) was rapidly added with stirring and cooling (−10 °C) to the reaction mixture. Then the mixture was stirred for 0.5 h and allowed to stand for 1.5 h. The solution contained (NMR, GLC, and GLC/MS, without considering diglyme) silyl ethers **2b** and **2a**, divinyl ether **6**, aldehyde **1** (keto : enol = 1 : 3.7), fluorosilanes **4a** and **4b**, chlorosilanes **7a** and **7b**, disiloxanes **8a**, **8b**, and **8c**, Me_2SiF_2 (1.0 : 0.51 : 0.05 : : 0.12 : 1.04 : 0.77 : 0.21 : 0.44 : 0.03 : 0.05 : 0.01 : 0.04), and a small amount (~5%) of nonidentified impurities. The reaction mixture was filtered. The residue was washed with diglyme (3×1 mL) and Et_2O (3×2 mL) and dried *in vacuo* over P_2O_5. A white nonhygroscopic powder was obtained in a yield of 2.85 g. Volatile products (1.05 g) were distilled from the combined diglyme filtrates (15.40 g) into a trap (−78 °C) *in vacuo* (8 Torr) at 20 °C. These products consisted predominantly of fluoro- and chlorosilanes **4a**, **4b**, **7a**, and **7b** (1.00 : 1.02 : 0.23 : 0.19) with impurities of silyl ethers **2b** and **2a** (1 : 1), HMDS (**8a**), and Me_2SiF_2 and traces of disiloxanes **8b** and **8c**, aldehyde **1**, and diglyme (NMR, GLC). A ~40% solution (4.31 g) of a mixture of silanes **2b**—**2a** (1.5 : 1.0) in diglyme containing small amounts of fluoro- and chlorosilanes **4b**, **7a**, and **7b**, disiloxanes **8a**, **8b**, and **8c**, and aldehyde **1** (NMR, GLC) and then a virtually pure 10—15% solution of a mixture of silanes **2b**—**2a** (7 : 1) (8.13 g) in diglyme (NMR, GLC) were distilled from the residue into a trap (−78 °C) at 20 °C (1 Torr).

Reaction of silane 2a with aminoacetal 9. 2,2,2′2′-Tetrakis(trifluoromethyl)divinyl ether (6) and 1-hydrohexafluoroisobutenyl β-dimethylamino-β-methoxytrifluoromethacrylate (11). Freshly distilled aminoacetal **9** (2.2210 g, 9.3656 mmol) was added with cooling (−78 °C) to freshly distilled silyl ether **2a** (7.2230 g, 28.637 mmol) and the reaction mixture was allowed to stand at 20 °C. After one day, the reaction mixture contained divinyl ether **6**, hexafluoroisobutenyl ester **11**, and Me_3SiF (**4a**) (1 : 1 : 3) (NMR). Distillation afforded 2.40 g (92.7%) of Me_3SiF (**4a**) with ≥99% purity (GLC), 3.02 g (94.3%) of divinyl ether **6** with ≥98.5% purity (GLC), and 2.78 g (78.5%) of hexafluoroisobutenyl ester **11** with ≥98% purity (NMR).

Synthesis of dibutylamines 12b,d. *A.* *N*-(1,1,2,2-Tetrafluoroethyl)dibutylamine (12b). A mixture of freshly distilled dibutylamine (41.6 g, 0.322 mol) and tetrafluoroethylene (46 g, 0.46 mol) was shaken in a steel autoclave at 30—40 °C for 12 h, at 50—60 °C for 60 h, and at 70 °C for 16 h. Volatile products were removed. Distillation of the residue afforded tetrafluoroethylamine **12b** in a yield of 32.5 g (44.0%), b.p. 34—36 °C (1 Torr), the purity was ~93% (~4% of HCF_2CONBu_2 as an impurity) (NMR, GLC). Amine **12b** was noticeably hydrolyzed during distillation in a glass vessel and can be stored in glassware for a short time without visible decomposition only at −78 °C. ^{1}H NMR (without a solvent), δ: 0.82 (t, 6 H, H(5), $^3J_{H(5),H(4)}$ = 7.0 Hz); 1.20 (m, 4 H, H(4)); 1.40 (m, 4 H, H(3)); 2.75 (m, 4 H, H(2)); 5.70 (tt, 1 H, H(1), $^2J_{H(1),F(1)}$ = 50.8 Hz, $^3J_{H(1),F(2)}$ = 3.1 Hz). ^{19}F NMR, δ: −56.5 (dt, 2 F, F(1), $^2J_{F(1),H(1)}$ = 50.8 Hz, $^3J_{F(1),F(2)}$ = 7.2 Hz); −14.5 (br.s, 2 F, F(2)).

B. ***N*-(2-Chloro-1,1,2-trifluoroethyl)dibutylamine (12d).*** A mixture of freshly distilled dibutylamine (38.7 g, 0.299 mol) and chlorotrifluoroethylene (49.3 g, 0.423 mol) was kept in a sealed glass tube at 20 °C for 14 days and periodically shaken. Then the tube was opened, and virtually pure chlorotrifluoroethylene (NMR, GLC) was collected into a trap (−78 °C) in a yield of 13.8 g (95.6%). The remaining liquid was filtered. Distillation of the filtrate afforded chlorotrifluoroethylamine **12d** with a purity of ≥98% (NMR, GLC) in a yield of 56.65 g (77.1%). Storage of amine **12d** in a glass vessel led to its gradual decomposition even at −10 °C, but **12d** is quite stable at −78 °C.

Reaction of silane 2a with *N*-(1,1,2,2-tetrafluoroethyl)diethylamine (12a). Freshly distilled silyl ether **2a** (0.5184 g, 2.055 mmol) was mixed with freshly distilled amine **12a** (0.1643 g, 0.939 mmol) with 99% purity (1% of diethylamide **13a**) at −78 °C and sealed in a glass tube.** After 0.5 h (at 20 °C), the reaction mixture (NMR spectroscopic data) contained Me_3SiF (**4a**), silane **2a**, amine **12a**, α-fluoroaminoacetal **14a**, amidoacetal **15a**, and amide **13a** (1.0 : 0.39 : 0.009 : 0.19 : : 0.46 : 0.09). After 4.5 h (at 20 °C), the starting amine **12a** and α-fluoroaminoacetal **14a** were absent, but divinyl ether **6** appeared (**4a** : **2a** : **6** : **15a** : **13a** = 1.0 : 0.16 : 0.04 : 0.52 : 0.12) (NMR). The complete conversion of amidoacetal **15a** was

* Dibutylamine **12d** was covered by patents,[14] but neither its synthesis nor its properties were documented.

** Contrary to the data published in the literature,[18,24] amine **12a** is partially hydrolyzed in a glass vessel in the course of distillation or during storage even at −10 °C.

achieved only after 3 days at 20 °C and one day at 30 °C (**4a** : **2a** : **6** : **13a** = 1.0 : 0.14 : 0.59 : 0.64) (NMR, GLC).

N-[1,2,2-Trifluoro-1-(1-hydrohexafluoroisobutenyloxy)ethyl]diethylamine (**14a**). ^{1}H NMR, δ: 1.2 (br.t, 6 H, H(4), $^3J_{H(4),H(3)} \approx 7$ Hz); 3.0 (br.q, 4 H, H(3), $^3J_{H(3),H(4)} \approx 7$ Hz); 6.0 (br.t, 1 H, H(1), $^2J_{H(1),F(1)} \approx 53$ Hz); 7.7 (br.s, 1 H, H(2)). ^{19}F NMR, δ: −56.7 and −55.0 (both br.dd, AB system, 2 F, F(1), $^2J_{F(1A),F(1B)} = 293.5$ Hz, $^2J_{F(1),H(1)} \approx 53$ Hz); −27.3 (br.s, 1 F, F(2)); 14.70 (q, 3 F, F(3), $^4J_{F(3),F(4)} \approx 6$ Hz); 17.57 (q, 3 F, F(4), $^4J_{F(4),F(3)} \approx 6$ Hz).

(*N*,*N*-Diethyl)difluoroacetamide di(1-hydrohexafluoroisobutenyl)acetal (**15a**). ^{1}H NMR, δ: 1.2 (br.t, 6 H, H(4), $^3J_{H(4),H(3)} \approx 7$ Hz); 3.0 (br.q, 4 H, H(3), $^3J_{H(3),H(4)} \approx 7$ Hz); 6.2 (t, 1 H, H(1), $^2J_{H(1),F(1)} = 52.8$ Hz); 7.7 (br.s, 2 H, H(2)). ^{19}F NMR, δ: −55.5 (d, 2 F, F(1), $^2J_{F(1),H(1)} = 52.8$ Hz); 14.74 (q, 6 F, F(2), $^4J_{F(2),F(3)} = 6.2$ Hz); 17.41 (q, 6 F, F(3), $^4J_{F(3),F(2)} = 6.2$ Hz).

Reaction of silane 2a with *N*-(1,1,2,2-tetrafluoroethyl)dibutylamine (12b). Freshly distilled silyl ether **2a** (0.22675 g, 0.8989 mmol) was mixed with freshly distilled amine **12b** (0.0958 g, 0.39 mmol) with ~93% purity (~4% of dibutylamide **13b**) at −78 °C and sealed in a glass tube. After 10 min (20 °C), the reaction mixture contained (NMR spectroscopic data) Me_3SiF (**4a**), silane **2a**, amine **12b**, α-fluoroaminoacetal **14b**, amidoacetal **15b**, and amide **13b** (1.0 : 2.35 : 0.61 : 0.97 : : 0.03 : 0.08). After 40 min (at 20 °C), the conversion of the starting silane **2a** was ~100%, and the **14b** : **15b** ratio was 4 : 3 (NMR). After 5 h (at 20 °C), α-fluoroaminoacetal **14b** was also absent in the reaction mixture, but divinyl ether **6** appeared (**4a** : **2a** : **6** : **15b** : **13b** = 1.0 : 0.11 : 0.04 : 0.54 : 0.08) (NMR). The complete conversion of amidoacetal **15b** was achieved only after 40 h at 20 °C and 5 h at 40 °C (**4a** : **2a** : **6** : **13b** = 1.0 : 0.1 : 0.59 : 0.66) (NMR, GLC).

Silyl ether **2a** (39.12 g, 155.1 mmol) was added dropwise with stirring and cooling (−78 °C) to amine **12b** (17.98 g, 73 mmol) with ~93% purity containing ~4% (~0.72 g) of dibutylamide **13b**. The reaction mixture was allowed to warm to room temperature with stirring. After completion of the weakly exothermic reaction, the mixture was heated at 40—45 °C for 9 h, the gaseous compounds being collected into a trap (−78 °C). At 20 °C, volatile compounds were distilled *in vacuo* (20 Torr) into the same trap (−78 °C). A mixture containing Me_3SiF (**4a**) (13.60 g, 101.2%) and aldehyde **1*** (0.28 g) (NMR, GLC) was obtained in a yield of 13.89 g. Distillation of the residue afforded 23.82 g (95.4%) of divinyl ether **6** with a purity of >98% (NMR, GLC), b.p. 35—37 °C (3 Torr), and 14.67 g of dibutylamide **13b** with 96.5% purity (3.5% of ether **6** as an impurity) (NMR, GLC) (the yield was ~90% taking into account the purity and content of amide **13b** in the starting amine **12b**), b.p. 56—58 °C (1 Torr) (*cf.* lit. data[26]: b.p. 95 °C (1.5 Torr)).

(*N*,*N*-Dibutyl)difluoroacetamide (**13b**). ^{1}H NMR (without a solvent), δ: 0.85 (m, 6 H, H(5)); 1.25 (m, 4 H, H(4)); 1.50 (m, 4 H, H(3)); 3.30 (m, 4 H, H(2)); 6.30** (t, 1 H, H(1), $^2J_{H(1),F} =$ 50 Hz). ^{19}F NMR, δ: −45.8 (d, CF_2, $^2J_{F,H(1)} = 50$ Hz).

N-[1,2,2-Trifluoro-1-(1-hydrohexafluoroisobutenyloxy)ethyl]dibutylamine (**14b**). ^{1}H NMR, δ: 0.98 (m, 6 H, H(6)); 1.35 (m, 4 H, H(5)); 1.60 (m, 4 H, H(4)); 2.90 (m, 4 H, H(3)); 5.94 (td, 1 H, H(1), $^2J_{H(1),F(1)} = 55$ Hz, $^3J_{H(1),F(2)} = 2.4$ Hz); 7.70 (br.s, 1 H, H(2)). ^{19}F NMR, δ: −56.0 and −54.74 (both ddd, AB system, 2 F, F(1), $^2J_{F(1A),F(1B)} = 300$ Hz, $^2J_{F(1),H(1)} = 55$ Hz, $^3J_{F(1),F(2)} = 8.8$ Hz); −28.3 (br.s, 1 F, F(2)); 14.96 (q, 3 F, F(3), $^4J_{F(3),F(4)} = 6.4$ Hz); 17.77 (q, 3 F, F(4), $^4J_{F(4),F(3)} = 6.4$ Hz).

(*N*,*N*-Dibutyl)difluoroacetamide di(1-hydrohexafluoroisobutenyl)acetal (**15b**). ^{1}H NMR, δ: 0.98 (m, 6 H, H(6)); 1.35 (m, 4 H, H(5)); 1.60 (m, 4 H, H(4)); 2.90 (m, 4 H, H(3)); 6.11 (t, 1 H, H(1), $^2J_{H(1),F(1)} = 50$ Hz); 7.70 (br.s, 2 H, H(2)). ^{19}F NMR, δ: −55.08 (d, 2 F, F(1), $^2J_{F(1),H(1)} = 50$ Hz); 14.87 (q, 6 F, F(2), $^4J_{F(2),F(3)} = 6.4$ Hz); 17.53 (q, 6 F, F(3), $^4J_{F(3),F(2)} = 6.4$ Hz).

Reaction of silane 2a with *N*-(2-chloro-1,1,2-trifluoroethyl)diethylamine (12c). Freshly distilled amine **12c** (0.3883 g, 2.048 mmol) was added with cooling (−78 °C) to freshly distilled silyl ether **2a** (1.0104 g, 4.006 mmol) and the mixture was allowed to stand at 20 °C. After one day, the starting compounds were completely consumed, and the reaction mixture contained Me_3SiF (**4a**), divinyl ether **6**, chlorodiethylfluoroacetamide (**13c**), aldehyde **1**, chlorofluoroketene aminoacetal **16a**, and isobutenyl isobutyl ether **17** (1.0 : 0.65 : 0.73 : 0.03 : 0.07 : 0.04) (NMR, GLC). Distillation of the reaction mixture did not afford fractions containing more than 88.5% of divinyl ether **6**.

Reaction of silane 2a with *N*-(2-chloro-1,1,2-trifluoroethyl)dibutylamine (12d). Freshly distilled amine **12d** (21.4 g, 87.1 mmol) was added dropwise with stirring and cooling (−20 °C) to freshly distilled silyl ether **2a** (46.5 g, 184.4 mmol). The reaction mixture was allowed to slowly warm to room temperature. After one day (at 20 °C), the starting compounds and intermediates were absent in the reaction mixture (GLC and NMR), and the mixture contained Me_3SiF (**4a**), divinyl ether **6**, dibutylchlorofluoroacetamide (**13d**), aldehyde **1**, and chlorofluoroketene aminoacetal **16b** (1.0 : 0.40 : 0.44 : 0.08 : 0.08). Distillation afforded 22.54 g (75%) of divinyl ether **6** with a purity of >98% (NMR, GLC), b.p. 48—50 °C (8 Torr).

Reaction of *N*-(1,1,2,2-tetrafluoroethyl)diethylamine (12a) with trifluoroacetic anhydride. Trifluoroacetic anhydride (56.7 g, 0.270 mol) was added dropwise with stirring to freshly distilled amine **12a** (50.6 g, 0.292 mol) at 20 °C at such a rate that the liquid did not virtually condense in a water reflux condenser, and gaseous compounds were collected into a trap (−78 °C). After completion of the addition of the anhydride, the reaction mixture was warmed to 70 °C for a short period of time. Trifluoroacetyl fluoride was obtained in the trap (−78 °C) in a yield of 61.1 g (97.5%) with a purity of >97% (NMR), b.p. −55.5—−55.0 °C (*cf.* lit. data[26]: b.p. −59 °C).

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* An overstated yield of Me_3SiF (**4a**) and the formation of an insignificant amount of aldehyde **1** are, apparently, attributable to the presence of HF traces in amine **12b**.

** In the reaction mixture, δ 6.07.

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