Thermal and BF₃ • Et₂O-catalyzed cleavage of 1-hydrohexafluoroisobutenyloxytrimethylsilane. Perfluoromethacrolein, its isomers, dimers, and homopolymers

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During vacuum pyrolysis in a quartz or steel tube, 1-hydrohexafluoroisobutenyloxytrimethylsilane (1) eliminates fluorotrimethylsilane to give perfluoromethacrolein, which was detected by NMR. Similar pyrolysis of silane 1 over KF results in *E*- and *Z*- β -hydrotetrafluoromethacryloyl fluorides. At 20 °C, perfluoromethacrolein undergoes homopolymerisation and/or cyclodimerization to yield 4,4-difluoro-2-pentafluoroisopropenyl-5trifluoromethyl-4*H*-1,3-dioxin, which rearranges into *E*-7,7,7-trifluoro-2,6-bis(trifluoromethyl)-4-oxahepta-2,5-dienoyl fluoride under the action of BF₃•Et₂O. The same fluoride is also formed, together with fluorotrimethylsilane, directly from silane 1 under the action of BF₃•Et₂O.

Key words: 1-hydrohexafluoroisobutenyloxytrimethylsilane, boron trifluoride—diethyl ether complex, pyrolysis, perfluoromethacrolein, *E*- and *Z*- β -hydrotetrafluoromethacryloyl fluorides, *E*- and *Z*-7,7,7-trifluoro-2,6-bis(trifluoromethyl)-4-oxahepta-2,5-dienoyl fluorides, 4,4-difluoro-2-pentafluoroisopropenyl-5-trifluoromethyl-4*H*-1,3-dioxin.

It has been reported^{1,2} that enol trimethylsilyl ethers and ketene trimethylsilyl acetals containing a CF₃ group in the β -position are thermally rather unstable and eliminate fluorotrimethylsilane at temperatures above 50 °C to give the corresponding α , β -unsaturated carbonyl compounds. This communication reports an attempt to extend this approach to 1-hydrohexafluoroisobutenyl trimethylsilyl ether (1) in order to synthesize perfluoromethacrolein (2), which has been suggested previously^{3,4} as an intermediate for some reactions.

Results and Discussion

It was found unexpectedly that trimethylsilyl ether 1, which has not been described in the literature and has been prepared by a slightly modified reported procedure,⁵ is distillable under atmospheric pressure without decomposition and withstands prolonged heating at 160 °C in a sealed glass tube.

Using alkylhexafluoroisobutenyl ethers $(CF_3)_2C=CXOR (X = F, OR', NR'_2, C_2F_5)$ similar in structure to silane 1, it has been shown⁶ that 1,4-elimination of alkyl fluorides is efficiently catalyzed by SbF₅ or BF₃·Et₂O. The addition of BF₃·Et₂O to silyl ether 1 also

[†] Deceased.

results in quantitative elimination of Me_3SiF , but this yields *E*-fluoride **3**^{*} as the second product rather than perfluoromethacrolein (**2**) (Scheme 1).



The time required for complete conversion of silyl ether 1 depends appreciably on the amount of the catalyst used. For instance, in the presence of $\geq 10 \text{ mol.}\%$ BF₃•Et₂O, the reaction is completed over 24 h at 20 °C, whereas with 2–4 mol.% BF₃•Et₂O, the reaction goes to completion in ~20 days at 20 °C or in several hours at 60 °C. A pronounced $E \rightarrow Z$ isomerization of fluoride **3**

* The corresponding dimethylamide is known.7

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in the presence of $BF_3 \cdot Et_2O$ takes place only after complete conversion of silane 1, its rate being rather low at 20 °C.

Fluoride *E*-3 is formally the dimer of perfluoromethacrolein (2); however, no such dimers are known for either methacrolein (*cf.* Refs 8, 9) or perfluoromethacryloyl fluoride (4) (*cf.* Ref. 10), which is a close perfluorinated analog of aldehyde 2. The stereospecificity of the reaction (see Scheme 1) indicates probably that the reaction proceeds *via* a cyclic intermediate (or a cyclic transition state) with *cis*-fixing of the H atom and the CF₃ group at the ring double bond, this fragment remaining intact during the subsequent ring opening.

It is $known^{11,12}$ that fluoride 4 as well as perfluoro(ethyl isopropenyl ketone) (5) readily form [4+2]-cycloadducts with aliphatic aldehydes. This gives grounds for hoping that intermediate perfluoromethacrolein (2) could be detected using compound 4 or 5. However, it was found that in the $1-BF_3 \cdot Et_2O-4$ (or 5) ternary mixtures, silane 1 and fluoride 4 (or perfluorovinyl ketone 5) behave absolutely independently of each other, in particular, silyl ether 1 eliminates Me₃SiF according to Scheme 1 to give a mixture of fluorides E,Z-3, while fluoride 4 is rearranged into bis(trifluoromethyl) ketene (cf. Ref. 13), and perfluorovinyl ketone 5 remains virtually unchanged. Moreover, fluoride 4 can itself catalyze the reaction shown in Scheme 1; however, its electrophilicity does not suffice to ensure $E \rightarrow Z$ -isomerization of acyl fluoride E-3. In the case of ketone 5, this type of catalysis is not involved, most likely, due to steric restrictions created by the bulky pentafluoroethyl group.

Since the low-temperature cleavage of silyl ether 1 induced by $BF_3 \cdot Et_2O$ did not result in perfluoromethacrolein (2), we attempted to carry out vacuum pyrolysis of silane 1 in a flow-type reactor. It was found that pyrolysis in a quartz tube starts at 550 °C and, at low degrees of conversion, results in a quantitative formation of Me₃SiF and perfluoromethacrolein (2), which was detected by NMR in the reaction products (Scheme 2).

Scheme 2



The complete conversion of silane 1 is attained only at 800 °C; however, at temperatures of >700 °C, this compound undergoes more extensive destruction, as indicated, first of all, by the appearance of perfluoromethylacetylene in the pyrolysate.

The use of a stainless-steel tube allows the temperature of pyrolysis to be lowered by 100–200 °C; however, in this case, the reaction is obviously catalytic. The nature of the catalysis is obscure, because both the temperature of the onset of the pyrolysis (300–400 °C) and the degree of conversion of silane 1 at the same temperature depend appreciably on the tube prehistory.

An even more pronounced lowering of the temperature was attained by carrying out the pyrolysis in the presence of anhydrous KF, which proceeds with a 100% conversion of silyl ether 1 even at 300 °C. However, perfluoromethacrolein (2) is no longer the major reaction product, being replaced by its isomers, *E*- and *Z*- β -hydrotetrafluoromethacryloyl fluorides (6) (NMR and GLC/MS data) (Scheme 3).

Scheme 3



Dilute (2-3%) solutions of perfluoromethacrolein (2)in silyl ether 1 are sufficiently stable to enable unambiguous identification of aldehyde 2 by NMR spectroscopy. Nevertheless, perfluoromethacrolein (2) enters into subsequent reactions over a period of several days at room temperature; the main of these reactions is cyclodimerization to give dioxin 7 (Scheme 4).



An increase in the concentration of perfluoromethacrolein (2) in the pyrolysis products sharply increases the rate of its further transformations, homopolymerization rather than cyclodimerization being the major reaction route in this case.* The cyclodimer 7 : polymer 8 ratio and the exact structure of the

^{*} Although the resulting pyrolysates always contained small amounts of α -hydrohexafluoroisobutyraldehyde, in none of the cases, was the formation of 2-hexafluoroisopropyl-substituted analog of dioxin 7 detected (*cf.* Ref. 4).

polymer depend on both the composition of the initial pyrolysate and the schedule of its heating from -196 °C to room temperature. This implies apparently that di- and polymerization of perfluoromethacrolein (2) starts with an electrophilic attack by the carbonyl C atom of one molecule of aldehyde 2 on the carbonyl O atom of another molecule to give betaine 9 (Scheme 5). When the concentration of perfluoromethacrolein (2) is low, most of betaine 9 undergoes intramolecular cyclization into dioxin 7, while at high concentrations of 2, the betaine is attacked predominantly by the next molecules of aldehyde 2, which finally results into homopolymer 8.

Scheme 5



After the complete conversion of perfluoromethacrolein (2), the pyrolysate formed in a quartz tube at 730 °C was subjected to vacuum distillation to give a mixture of low-boiling products consisting mainly of silyl ether 1, Me₃SiF, and cyclic dimer 7. After addition of BF₃•Et₂O in an amount nearly equimolar to dioxin 7, compound 7 rearranged over a period of 4 days at 20 °C to give acyclic dimer *E*-3, apparently, through a fluoride ion elimination—addition reaction sequence (Scheme 6).

Scheme 6



In addition to relatively fast opening of cyclic dimer 7, a slow decrease in the content of silyl ether 1 and $BF_3 \cdot Et_2O$ and an increase in the amount of Me₃SiF occur (NMR data). New NMR signals appear that can be attributed to difluoroborane **10** (Scheme 7).

Scheme 7



After complete conversion of dioxin 7, the concentration of difluoroborane 10 continues to increase gradually at 20 °C, which is accompanied by the corresponding change in the content of silane 1, $BF_3 \cdot Et_2O$, and Me_3SiF , whereas the content of acyclic dimer *E*-3 virtually does not change. Meanwhile, heating of the reaction mixture to 60 °C induces fast consumption of borane 10 with simultaneous restoration of the initial concentration of $BF_3 \cdot Et_2O$, which is followed by slower transformation of silyl ether 1 into dimer *E*-3 and Me_3SiF according to Scheme 1. A similar intermediate formation of difluoroborane 10 occurs upon mixing of pure silane 1 with ~3 mol.% $BF_3 \cdot Et_2O$ at 20 °C. In addition, the reaction mixture was found to contain cyclic dimer 7.

To summarize the foregoing, one can propose the following sequence of transformations of silane 1 in the presence of $BF_3 \cdot Et_2O$ (Scheme 8).

First, $BF_3 \cdot Et_2O$ cleaves the Si-O bond of silvl ether 1 in a usual way to give Me₃SiF and difluoroborane 10 (cf., for example, Ref. 14). The F atoms of the trifluoromethyl groups in borane 10 remain fairly mobile, and the next $BF_3 \cdot Et_2O$ molecule detaches the allylic F atom; the resulting tetrafluoroborate salt 11 decomposes to give perfluoromethacrolein (2) and two recovered BF₃ molecules. Subsequently, perfluoromethacrolein (2) cyclodimerizes to give dioxin 7, which, in turn, rearranges to fluoride E-3 (see Schemes 4 and 6). Moreover, BF₃ · Et₂O apparently participates directly in the cyclodimerization of perfluoromethacrolein (2), which suppresses its polymerization. On the one hand, BF₃ • Et₂O activates the carbonyl group of aldehyde 2 and accelerates the formation of betaine 12, thus decreasing the concentration of perfluoromethacrolein (2) in the solution. On the other hand, it appears likely that betaine 12, which retains the possibility of intramolecular cyclization, is much less prone to intermolecular addition of the next molecule of aldehyde 2 than betaine 9 (see Scheme 5).

In conclusion, it should be noted that the susceptibility of perfluoromethacrolein (2) for the electrophilic attack by the carbonyl C atom with the C=C bond remaining intact discovered in this study makes this compound similar to standard aldehydes and emphasizes its essential difference from a close analog, fluoride 4.

Scheme 8



Experimental

¹H and ¹⁹F NMR (CF₃COOH as the external standard) and ¹⁹F{¹H} NMR spectra were recorded on Perkin—Elmer R-32 and Bruker WP-200SY spectrometers, IR spectra were measured on a UR-20 spectrometer, the Raman spectrum was recorded on a Ramanor HG-2S instrument, and mass spectra and GC/MS analysis were run on a VG 7070E mass spectrometer (EI, 70 eV).

The starting compounds and solvents were purified and dried by standard procedures; the experiments were carried out under dry argon. The molar ratios of the main components are always given for mixtures. The NMR and MS spectral data for the synthesized compounds are presented in Table 1.

1-Hydrohexafluoroisobutenyloxytrimethylsilane (1). Bis(trifluoromethyl) ketene (122 mL at −78 °C; ~200 g, ~1.12 mol)¹⁰ was passed with stirring through liquid trimethylsilane (88.4 g, 1.19 mol) precooled to −78 °C and containing crystalline H₂PtCl₆·6H₂O (0.0876 g, 1.69·10⁻⁴ mol) at such a rate that boiling of the reaction mixture (reflux condenser, −78 °C) was not too vigorous and the temperature did not rise above 35−40 °C (for passing of the last 30 mL, water cooling at intervals was required). After completion of the ketene addition, the mixture was stirred for 1 h for cooling down to ~20 °C. Distillation of the reaction mixture gave 271.1 g (~96%) of silane 1, b.p. 59−61 °C (50 Torr) (130−132 °C (760 Torr)), purity ≥99% (NMR and GLC data). Found (%): C, 33.4; H, 3.95; F, 45.3; Si, 10.7. C₇H₁₀F₆OSi. Calculated (%): C, 33.3; H, 4.00; F, 45.2; Si, 11.1. IR (Raman), v/cm⁻¹: 1670 s (1670 s) (C=C).

The impurities present were as follows:

1-Hydrohexafluoroisobutenyl 2-hydrohexafluoroisobutyrate, (CF(1)₃)₂CH(1)COOCH(2)=C(CF(2)₃)(CF(3)₃) (0.4%). ¹H NMR, δ: 4.52 (hept, 1 H, H(1), ${}^{3}J_{H(1),F(1)} = 7.1$ Hz); 8.53 (br.s, 1 H, H(2)). ¹⁹F NMR, δ: 12.7 (d, 6 F, F(1), ${}^{3}J_{F(1),H(1)} = 7.1$ Hz); 13.8 (q, 3 F, F(3), ${}^{4}J_{F(3),F(2)} = 6.2$ Hz); 17.2 (q, 3 F, F(2), ${}^{4}J_{F(2),F(3)} = 6.2$ Hz).

Trimethylsilyl 2-hydrohexafluoroisobutyrate, (CF₃)₂CHCOOSiMe₃ (0.2%). ¹H NMR, δ: 4.21 (hept, CH, ³J_{H,F} = 7.5 Hz); the signal of the Me₃Si group coincides with that in the spectrum of silane 1. ¹⁹F NMR, δ: 12.2 (d, ³J_{F,H} = 7.4 Hz).

The freshly distilled product almost does not contain $(CF_3)_2CHCHO$ or $(Me_3Si)_2O$.

At an evaporator temperature of ~150 °C, the results of GLC and GLC/MS are in good agreement with NMR data; however, an increase in the evaporator temperature to ≥ 200 °C is accompanied by partial thermal destruction of silane 1, as indicated by the sharp increase in the concentration of impurities having short retention time, in particular, a noticeable amount of Me₃SiF appears.

Study of the thermal stability of silane 1. After heating (6 h at 160 °C) in a sealed glass tube, silyl ether 1 remains unchanged (NMR data).

E-7,7,7-Trifluoro-2,6-bis(trifluoromethyl)-4-oxahepta-2,5dienoyl fluoride (E-3). A. A mixture of silyl ether 1 (1.5179 g, 6.018 mmol) with BF₃ • Et₂O (0.6408 g, 4.515 mmol) was kept at 20 °C to complete conversion of silane 1. After 24 h, the mixture consisted of fluoride E-3, Me₃SiF, BF₃·Et₂O (1.0 : 2.2 : 1.7), and a small amount (<5%) of other components (NMR and GLC data). The solution was cooled (-78 °C) and allowed to warm spontaneously to 20 °C, volatile products being distilled in *vacuo* into a trap (-78 °C). At 20 Torr, this gave 0.5433 g (98%) of Me₃SiF with 98% purity (NMR and GLC data); at 20 °C (1 Torr), 0.6085 g of a mixture mainly consisting of $BF_3 \cdot Et_2O$ (85-90%), some fluoride E-3 (5-7%), and unidentified substances (NMR and GLC data) was obtained. The solid residue was sublimed at 40 °C (1 Torr), the sublimate was dissolved in CH₂Cl₂, the solution was filtered, and the filtrate was diluted with hexane until it became turbid and left for 14 h at -10 °C. The cold solution was filtered and the precipitate was dried in vacuo over P2O5 to give 0.6095 g (63%) of fluoride E-3 as colorless crystals with m.p. 49-55 °C and 98% purity (GLC data). Repeated reprecipitation from CH₂Cl₂ with hexane gave a sample with m.p. 55-56.5 °C. Found (%): C, 29.9; H, 0.67; F, 59.7. C₈H₂F₁₀O₂. Calculated (%): C, 30.0; H, 0.63; F, 59.4. IR, v/cm^{-1} : 1815 vs (COF), 1710 m (C=C), 1650 vs (C=C).

B. A mixture of silyl ether 1 (~1.5 mmol) and $BF_3 \cdot Et_2O$ (~0.06 mmol) was heated at 60 °C in a sealed glass tube. After 5 h, the reaction mixture did not contain the starting silane 1 and consisted of fluoride *E*-3, Me₃SiF (1 : 2), and minor amounts of $BF_3 \cdot Et_2O$ and unidentified components (NMR data).

 $E \rightarrow Z$ -Isomerization of fluoride *E*-3. A solution of fluoride *E*-3 (0.0788 g, 0.246 mmol) and BF₃·Et₂O (0.0088 g, 0.062 mmol) in CH₂Cl₂ (0.1761 g) was heated at 90–95 °C in a sealed glass tube. After 7 h, the solution contained a mixture of fluorides *E*-3 and *Z*-3 in ~1 : 1 ratio (NMR data). Similar heating of a 25% solution of fluoride *E*-3 in CH₂Cl₂ for 17 h

Com- pound	NMR, δ (J/Hz)		MS, <i>m</i> / <i>z</i>	
	¹ H	¹⁹ F	$(I_{\rm rel}(\%))$	
1 <i>a</i>	0.71 (s, 9 H, Me); 7.69 (m, 1 H, CH)	15.8 (qd, 3 F, F(2), ${}^{4}J_{F(2),F(1)} = 6.4$, ${}^{4}J_{F(2),CH} = 1.9$); 18.3 (qd, 3 F, F(1), ${}^{4}J_{F(1),F(2)} = 6.4$, ${}^{4}J_{F(1),CH} = 1.4$)	252 [M] ⁺ (0.8), 237 [M – Me] ⁺ (18.3), 179 $[C_4HF_6O]^+$ (2.4), 159 $[C_4F_5O]^+$ (1.3), 141 $[C_4HF_4O]^+$ (100), 113 $[C_3HF_4]^+$ (23.7), 77 $[Me_2SiF]^+$ (82.2), 73 $[Me_3Si]^+$ (43.7) ^b	
2 ^{<i>c</i>}	10.09 (br.dq, 1 H, CHO, ${}^{4}J_{H,F(2)} \approx {}^{4}J_{H,F(3)} \approx 2.3$)	8.7 (dq, 1 F, F(1), ${}^{2}J_{F(1),F(2)} = 31.0$, ${}^{4}J_{F(1),F(3)} = 9.0$); 17.6 (ddd, 3 F, F(3), ${}^{4}J_{F(3),F(2)} = 23.5$, ${}^{4}J_{F(3),F(1)} = 9.0$, ${}^{4}J_{F(3),H} = 3.0$); 20.0 (dqd, 1 F, F(2), ${}^{2}J_{F(2),F(1)} = 31.0$, ${}^{4}J_{F(2),F(3)} = 23.5$, ${}^{4}J_{C(2),H} = 1.8$)	_	
E-3 ^d	7.37 (qdq, 1 H, H(1), ${}^{4}J_{H(1),F(2)} =$ 1.6, ${}^{4}J_{H(1),F(1)} =$ ${}^{6}J_{H(1),F(4)} = 0.8$); 7.64 (dq, 1 H, H(2), ${}^{4}J_{H(2),F(4)} =$ 4.1, ${}^{4}J_{H(2),F(3)} = 1.6$)	14.0 (dd, 3 F, F(3), ${}^{4}J_{F(3),F(4)} = 10.3$, ${}^{4}J_{F(3),H(2)} = 1.6$); 14.6 (dd, 3 F, F(2), ${}^{4}J_{F(2),F(1)} = 6.4$, ${}^{4}J_{F(2),H(1)} = 1.6$); 17.6 (qdd, 3 F, F(1), ${}^{4}J_{F(1),F(2)} = 6.4$, ${}^{8}J_{F(1),F(4)} = 2.1$, ${}^{4}J_{F(1),H(1)} = 0.8$); 117.1 (qdqd, 1 F, F(4), ${}^{4}J_{F(4),F(3)} =$ 10.3, ${}^{4}J_{F(4),H(2)} = 4.1$, ${}^{8}J_{F(4),F(1)} = 2.1$, ${}^{6}J_{F(4),H(2)} = 0.8$);	320 $[M]^+$ (22.5), 301 $[M - F]^+$ (12.7), 163 $[C_4HF_6]^+$ (89.7), 159 $[C_4F_5O]^+$ (18.5), 141 $[C_4HF_4O]^+$ (40.1), 138 $[C_4HF_3O_2]^+$ (100), 110 $[C_3HF_3O]^+$ (55.2), 91 $[C_3HF_2O]^+$ (28.5), 90 $[C_3F_2O]^+$ (16.5), 82 $[C_2HF_3]^+$ (17.5), 75 $[C_3HF_2]^+$ (47.2), 69 $[CF_3, C_3HO_2]^+$ (95.5), 53 $[C_3HO]^+$ (13.5), 51 $[CHF_2]^+$ (15.3), 47 $[COFI^+$ (14.2), 29 $[CHOI^+$ (33.1) ^e	
Z-3 ^f	~7.37 (m, 1 H, H(1), $\Delta(\delta_Z - \delta_E) \approx 0.00$); 7.77 (m, 1 H, H(2))	^{14.55} (qd, 3 F, F(2), ${}^{4}J_{F(2),F(1)} = 6.5$, ⁴ $J_{F(2),H(1)} = 1.8$); 17.0 (br.d, 3 F, F(3), ${}^{4}J_{F(3),F(4)} = 10.5$); 17.5 (br.q, 3 F, F(1), ${}^{4}J_{F(1),F(2)} = 6.5$); 100.4 (br.q, 1 F, F(4), ${}^{4}J_{F(4),F(3)} = 10.5$)	$ \begin{array}{l} (201)^{+} (11.2), 2) \ [0110]^{+} (15.1)^{+} \\ 320 \ [M]^{+} (11.8), 301 \ [M-F]^{+} (10.1), 163 \\ [C_{4}HF_{6}]^{+} (75.8), 159 \ [C_{4}F_{5}O]^{+} (21.8), 141 \\ [C_{4}HF_{4}O]^{+} (39.1), 138 \ [C_{4}HF_{3}O_{2}]^{+} (100), 113 \\ [C_{3}HF_{4}]^{+} (12.7), 110 \ [C_{3}HF_{3}O]^{+} (46.1), 91 \\ [C_{3}HF_{2}O]^{+} (23.0), 90 \ [C_{3}F_{2}O]^{+} (10.8), 82 \\ [C_{2}HF_{3}]^{+} (12.6), 75 \ [C_{3}HF_{2}]^{+} (36.2), 69 \ [CF_{3}, \\ C_{3}HO_{2}]^{+} (71.8), 51 \ [CHF_{2}]^{+} (11.4), 29 \\ [CHO]^{+} (13.3) \end{array} $	
E-6 ^a	7.52 (ddq, 1 H, CH, ${}^{2}J_{H,F(1)} = 70.9$, ${}^{4}J_{H,F(3)} = 4.6$, ${}^{4}J_{H,F(2)} = 1.6$)	-13.1 (ddq, 1 F, F(1), ${}^{2}J_{F(1),H} = 71.2$, ${}^{4}J_{F(1),F(3)} = 58.5$, ${}^{4}J_{F(1),F(2)} = 6.4$); 13.0 (ddd, 3 F, F(2), ${}^{4}J_{F(2),F(3)} = 10.2$, ${}^{4}J_{F(2),F(1)} = 6.4$, ${}^{4}J_{F(2),H} = 1.9$); 116.6 (dqd, 1 F, F(3), ${}^{4}J_{F(3),F(1)} = 58.5$, ${}^{4}J_{exp} = a = 0.2$, ${}^{4}J_{exp} = a = 4.6$)	$ \begin{bmatrix} 160 & [M]^+ & (89.1), 159 & [M - H]^+ & (34.0), 141 \\ [M - F]^+ & (59.2), 140 & [M - HF]^+ & (11.8), 132 \\ [M - CO]^+ & (14.2), 113 & [M - COF]^+ & (29.6), \\ 112 & [C_3F_4]^+ & (10.2), 93 & [C_3F_3]^+ & (15.3), 91 \\ [M - CF_3]^+ & (78.7), 82 & [C_2HF_3]^+ & (47.1), 75 \\ [C_7HE_1]^+ & (18.1), 71 & [C_7E0]^+ & (11.2), 69 & [CE_1]^+ \\ \end{bmatrix} $	
Z-6 ^a	7.61 (d, 1 H, CH, ${}^{2}J_{H,F(1)} = 71.2$)	$-9.8 (dqd, 1 F, F(1), {}^{2}J_{F(1),H} = 71.4, {}^{4}J_{F(1),F(2)} = 26.0, {}^{4}J_{F(1),F(3)} = 5.9); 16.1 (dd, 3 F, F(2), {}^{4}J_{F(2),F(1)} = 26.0, {}^{4}J_{F(2),F(3)} = 10.2); 101.0 (qd, 1 F, F(3), {}^{4}J_{F(2),F(3)} = 10.2, {}^{4}J_{F(2),F(1)} = 5.9)$	$(100), 63 [C_2HF_2]^+ (11.8), 51 [CHF_2]^+ (77.7),$ 47 [COF] ⁺ (29.7), 44 [C_2HF] ⁺ (16.6), 31 [CF] ⁺ (48.2) ^g	
7 ^h	6.66 (br.s, 1 H, H(1)); 7.91 (m, 1 H, H(2))	$\begin{array}{l} -7(3), F(2) & -12(3), F(1) & -12(3), F(1) & -12(3), F(2) & -12(3), F(1) & -12(3), F(2) & -12(3), F(2), F(2) & -12(3), F(2), F(3) & -12(3), F(2), F(3), F$	320 $[M]^+$ (6.4), 301 $[M - F]^+$ (0.3), 163 $[C_4HF_6]^+$ (46.4), 161 $[C_4H_2F_5O]^+$ (68.3), 159 $[C_4F_5O]^+$ (71.1), 141 $[C_4HF_4O]^+$ (100), 113 $[C_3HF_4]^+$ (30.2), 112 $[C_3F_4]^+$ (21.0), 75 $[C_3HF_2]^+$ (15.1), 69 $[CF_3]^+$ (29.2)	

Table 1. ¹ H and	l ¹⁹ F NMR and	mass spectra	of the products

^{*a*} Without a solvent.

^{*b*} For Si-containing ions, data only for the ²⁸Si isotope are given.

^{*h*} In a mixture of silyl ether **1** and Me₃SiF (1 : 2).

^c In silyl ether **1**.

^{*d*} In CD_2Cl_2 .

^e The assignment was done with allowance for analysis of metastable ions.

 $^{^{}f}$ In CH₂Cl₂.

^{*g*} For a mixture of E- and Z-isomers.

without a catalyst did not result in a change in the composition (NMR data).

Transformation of silane 1 in the presence of perfluoromethacryloyl fluoride (4). *A*. A mixture of silyl ether 1 (0.1361 g, 0.539 mmol), fluoride 4^{10} (0.0999 g, 0.561 mmol), and BF₃·Et₂O (0.0028 g, 0.020 mmol) was heated at 100 °C in a sealed glass tube. After 5 h, the mixture did not contain the starting silane 1 and consisted of Me₃SiF, fluorides *E*-3 and *Z*-3, perfluoromethacryloyl fluoride (4), bis(trifluoromethyl) ketene (1.0 : 0.30 : 0.15 : 0.72 : 0.37), and a small amount of impurities (¹⁹F NMR data). The composition of the mixture after 12 h was as follows: Me₃SiF : *E*-3 : *Z*-3 : 4 : (CF₃)₂C=C=O = 1.0 : 0.24 : 0.31 : 0.64 : 0.38 (¹⁹F NMR data). Further heating resulted in only an insignificant change in the *E*-3 : *Z*-3 and 4 : (CF₃)₂C=C=O ratios, but the amount of impurities in the mixture gradually increased (¹⁹F NMR data).

B. A mixture of silyl ether **1** (0.1412 g, 0.560 mmol) and fluoride **4** (0.1038 g, 0.583 mmol) was heated at 120 °C in a sealed glass tube. After 24 h, the degree of conversion of **1** was \geq 95% and the mixture consisted of fluoride *E*-**3**, Me₃SiF, perfluoromethacryloyl fluoride (**4**) (1.0 : 1.8 : 2.1), and a small amount of other components (¹⁹F NMR data).

The transformation of silane 1 in the presence of perfluoro(ethyl isopropenyl ketone) (5). *A*. A mixture of silyl ether 1 (0.2009 g, 0.796 mmol), vinyl ketone 5¹² (0.2102 g) with \geq 87% purity (0.66 mmol), and BF₃·Et₂O (0.0148 g, 0.104 mmol) was heated at 85 °C in a sealed glass tube. After 5 h, the mixture did not contain the initial silane 1 and mainly consisted of Me₃SiF, fluorides *E*-3 and *Z*-3, and vinyl ketone 5 (1.0: 0.47: 0.14: 0.9). In addition, the total amount of impurities slightly increased and their composition somewhat changed (¹⁹F NMR data).

B. A mixture of silyl ether **1** (0.1807 g, 0.716 mmol) and vinyl ketone **5** (0.1632 g) with $\ge 87\%$ purity (0.51 mmol) was heated at 150 °C in a sealed glass tube. After 7 h, the key composition of the mixture virtually has not changed (**1** : **5** = 1.0 : 0.69, total content **1** + **5** > 90%); however, the total amount of impurities slightly increased and their composition somewhat changed (¹⁹F NMR data).

Vacuum pyrolysis of silane 1. A. Silyl ether 1 (3.12 g, 12.4 mmol) was passed for 10 min in vacuo (1 Torr) through a quartz tube 8 mm in diameter preheated to 610 °C (a thermocouple on the outer side of the tube in the middle of the 25-cm long heated section), the pyrolysis products being collected in successively connected traps (-78 and -196 °C). The pyrolysates were heated to ~20 °C to give ~0.05 g (~0.5 mmol) of Me₃SiF with ~97% purity in the -196 °C trap (GLC data) and 3.05 g of a mixture of silvl ether 1, perfluoromethacrolein (2), Me₃SiF (1.0 : 0.03 : 0.02), and several minor components ((CF₃)₂CHCHO, $(CF_3)_2CHCOOCH=C(CF_3)_2,$ (Me₃Si)₂O, etc.) in the -78 °C trap (NMR data). After 20 days at 20 °C, the pyrolysate collected at -78 °C did not contain pentafluoromethacrolein (2) and consisted of silane 1, dioxin 7, Me_3SiF (1.0 : 0.01 : 0.02), and a number of minor components ((CF₃)₂CHCHO, (CF₃)₂CHCOOCH=C(CF₃)₂, etc.) (NMR data).

B. Silyl ether 1 (0.69 g, 2.7 mmol) was pyrolyzed in a similar way at 730 °C, the products being collected in a trap (-196 °C). After the completion, 0.69 g of the pyrolysate was carefully heated to melting and homogenization at the lowest possible temperature, transferred into a tube, sealed, and heated to -20 °C. After 1–2 min at 20 °C, the contents of the tube turned into a

gel and, according to NMR, consisted of silane 1, Me₃SiF, perfluoromethacrolein (2), 4,4-difluoro-2-pentafluoroisopropenyl-5-trifluoromethyl-4H-1,3-dioxin (7), polymer 8 (1.0: 1.7: 0.07: 0.05: 1.4), and several minor components, including F₃CC=CF (¹⁹F NMR, δ : -121.6 (q, 1 F, CF, ⁴J= 4.4 Hz); 28.0 (d, 3 F, CF₃, ${}^{4}J$ = 4.4 Hz) (cf. Ref. 15)). After 16 days, volatile substances consisting of silane 1, Me₃SiF, and dioxin 7 (1.0: 2.0: 0.07) with a small amount of other components (NMR data) were distilled in vacuo (1 Torr) at 20 °C from the mixture containing no perfluoromethacrolein (2) (NMR data) into a trap (-196 °C); the residue was a creamish-white waxy material. BF₃ · Et₂O (0.0054 g, 0.038 mmol) was added to 0.2318 g of the volatile products (1 : Me₃SiF : 7 : BF₃ · Et₂O = 1.0: 2.0: 0.07: 0.08 (NMR data)) and the mixture was left in a sealed glass tube at 20 °C. After 4 days, the mixture did not contain dioxin 7 and consisted of silvl ether 1, Me_3SiF , E-3, $BF_3 \cdot Et_2O$, and diffuoroborane **10** (1.0 : 2.5 : 0.06 : 0.04 : 0.04) (NMR data); the composition of the mixture after 7 days was as follows: $1 : Me_3SiF : E-3 : BF_3 \cdot Et_2O : 10 = 1.0 : 2.7 : 0.06 :$ 0.025 : 0.06 (NMR data). After 3 h at 60 °C, the mixture did not contain borane 10 and consisted of silane 1, Me₃SiF, E-3, and $BF_3 \cdot Et_2O$ (1.0 : 3.9 : 0.24 : 0.1) (NMR data), and after 24 h at 60 °C, the conversion of silyl ether 1 was >99% and the mixture contained Me₃SiF, fluoride E-3, and BF₃ · Et₂O (1.0 : 0.16 : 0.02) and also 5-7% of minor components (NMR data).

Polymer 8. ¹H NMR, δ : 6.90 (0.65 H); 7.71 (0.35 H); 7.80 (0.4 H); 7.97 (0.5 H); 8.05 (1 H) (all br.s). ¹⁹F NMR, δ : 6.4 (6.3 sh, 6.0 sh) (0.2 F); 8.3 (1 F); 8.6–9.1 (0.25 F); 9.25 (0.2 F); 9.4 (0.2 F); 9.8 (0.3 F); 10.2 (0.15 F); 10.5 (0.1 F); 10.7 (0.04 F); 11.0 (0.02 F); 14.5 (0.25 F); 15.1 (0.08 F); 17.7 (2.1 F); 18.0 (0.9 F) (all br.s); 19.1 (br.dd(q), 1 F, $J_d = 18.5$ Hz, $J_{d(q)} = 9$ Hz). The molar content was calculated from the total integral intensity of the signals for all H and F atoms of polymer **8** and converted for monomer C₄HF₅O.

(1-Hydrohexafluoroisobutenyloxy)difluoroborane (10). ¹H NMR, δ : 7.99 (br.s). ¹⁹F NMR, δ : -75.4 (br.s, 1.4 F, F(3)); 16.3 (m, 3 F, F(2)); 18.6 (m, 3 F, F(1)). The markedly reduced integral for the F(3) atom may indicate the partial formation of dialkoxy-substituted analog of borane **10**.

C. Silyl ether 1 (1.29 g, 5.11 mmol) was passed for 20 min *in vacuo* (1 Torr) through a stainless-steel tube 15 mm in diameter filled with a 15-cm long bed of anhydrous KF (1 mm < d < 2 mm)* and maintained at 310 °C (the heated length is 25 cm). During this period, 1.27 g of the pyrolysate containing no silane 1 was collected in a trap (-196 °C). The pyrolysate collected after 10 min at 20 °C consisted of Me₃SiF, fluorides *E*-6, *Z*-6, dioxin 7, polymer 8 (1.0 : 0.30 : 0.34 : 0.03 : 0.17) and a slight amount of minor components (NMR, GLC, and GLC/MS data).

Polymer 8. ¹⁹F NMR, δ : 6.7 (6.6 sh) (0.25 F); 8.5 (1.7 F); 8.8–9.6 (0.65 F); 10.1 (0.45 F); 10.4 (0.25 F); 14.6 (0.45 F); 17.7 (3.4 F); 18.0 (0.85 F) (all br.s); 19.3 (br.dd, 1 F, $J_1 = 19$ Hz, $J_2 = 10$ Hz).

Detection of intermediate products in the reaction of silane 1 with $BF_3 \cdot Et_2O$. A mixture of silyl ether 1 (0.3115 g, 1.235 mmol) with $BF_3 \cdot Et_2O$ (0.0049 g, 0.0345 mmol) was kept at 20 °C in a sealed glass tube and NMR spectra were recorded at intervals.

^{*} After filling the tube with preliminarily dried and sieved KF, the tube was heated for 1 h at 300-340 °C and for 1 h at 350-380 °C *in vacuo* (1 Torr).

After 8 h, a small amount of a white solid precipitated from the solution (apparently, the product of replacement of all F atoms in $BF_3 \cdot Et_2O$, and traces of diffuoroborane 10 appeared in the solution. The composition of the supernatant after 5 days was as follows: $1 : Me_3SiF : BF_3 \cdot Et_2O : 10 : 7 : E-3 = 1.0 : 0.1 : 0.007 :$ 0.01: 0.003: 0.02; the liquid contained also several minor components. After 6 days, the precipitate completely dissolved, the conversion of silane 1 was ~20%, borane 10 was not detected in the solution, and the content of BF3 · Et2O increased almost to the starting level (~1% of the total fluorine integral). After 7 days, with the conversion of silvl ether 1 equal to ~35%, cyclic dimer 7 was not detected in the solution either. After 18 days, conversion of silane 1 was 100%, and the mixture consisted of fluoride E-3, $Me_3SiF, BF_3 \cdot Et_2O(1.0: 2.2: 0.04)$, and a small amount (<5%) of minor components. After 26 days, the composition of the mixture almost did not change and traces of fluoride Z-3 were detected.

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