Novel routes to fluorinated ethers containing a fluorosulfonyl group

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Abstract

The chloroxy compounds $ClOCF_2CFXSO_2F$ (X = F, CF_3) have been reacted with several simple olefins to give ethers. In the case of unsymmetrical olefins the reaction mainly follows an electrophilic *cis* addition with the positive polarized chlorine adding in a Markovnikov manner. One example of the conversion of a sulfonyl fluoride to its corresponding acid is given. The latter gives the respective sulfonyl chloride with phosphorus pentachloride.

Introduction

The insertion reaction of olefins into the ClO bond of organic hypochlorites is a well-known method of preparing stable ethers [1]. These reactions involve high regiospecificity with unsymmetrical olefins due to different electron density at the olefinic carbons. Several groups have been working on the synthesis of fluorinated ethers containing a fluorosulfonyl group [2–8], but the insertion reaction has not been described. In the following we report the synthesis of a number of ethers by addition of the new hypochlorites $ClOCF_2CFXSO_2F$ (X = F, CF_3) [9] to fluoro-olefins.

$$ClOCF_2CFXSO_2F + RR'C{=}CR''R''' \longrightarrow ClRR'C{-}CR''R'''{-}O{-}CF_2CFXSO_2F$$

(**1**) X = F; (**2**) X = CF_3

(R, R′, R″, R‴ = F, Cl, H)

Additionally, the hypochlorite C_2F_5OCl (**19**) has been reacted with C_2ClF_3 to form the regioisomers $C_2Cl_2F_3{-}OC_2F_5$ (**20**) for comparison with the above reactions.

Experimental

General methods

Gases and volatile materials were handled in a glass vacuum system fitted with glass–Teflon valves. Amounts of gases were determined either

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with a Wallace and Tiernan Series 1500 differential pressure gauge by PVT measurements, or by direct weighing. Reactions were carried out in Pyrex-glass reactors (100 ml) fitted with glass–Teflon valves and containing a magnetic stirring bar.

IR spectra were recorded on a Perkin-Elmer 1430 instrument with a 7500 data system, using KCl or AgCl windows for neat liquids or a 10-cm gas cell. NMR spectra were measured on a JEOL FX-90Q or on an IBM NR 200 AF spectrometer using generally $CDCl_3$ solutions of 1–2 mol l^{-1} concentrations. The chemical shift values are negative high field to $CFCl_3$ as the internal standard. Mass spectra were obtained from a Hewlett Packard 5985-B spectrometer at 70 eV and 200 °C source temperature for CI(CH_4) and EI; samples were introduced by gas injection.

Reagents

The compounds C_2H_4, C_2H_3F, $C_2H_2F_2$, C_2HF_3, C_2F_4, C_3F_6, C_2ClF_3, $C_2Cl_2F_2$, PCl_5, $Ba(OH)_2$ and H_2SO_4 were obtained from commercial sources. The hypochlorites $ClOCF_2CFXSO_2F$ (X = F, CF_3) were prepared according to our previously described methods [9] and C_2F_5OCl by a literature method [10, 11].

Reactions of $ClOCF_2CFXSO_2F$ (X=F, CF_3) with olefins

A glass reactor was charged with the respective hypochlorite, CFC-11 as the solvent, if used, and the olefin at −196 °C *in vacuo*. The amounts are given in Table 1. The mixture was usually warmed up to room temperature with stirring in a CFC-11 bath initially at −110 °C, during the time given in Table 1. Purification was done by trap-to-trap fractionation, where the ether compound was obtained in the trap cooled to −50 °C. Products due to the decomposition of the hypochlorites $FC(O)CFXSO_2F$, and the chloro-fluorination product of the olefin with released ClF, were trapped at −110 °C and −196 °C.

*Reaction of **11** with $Ba(OH)_2$: $[C_2Cl_2F_3OCF_2CF_2SO_3]_2Ba$ (**12**)*

The ether **11** (1.0 g; 2.9 mmol) was stirred with a solution of barium hydroxide (4 g of $Ba(OH)_2 \cdot 8H_2O$; 12.7 mmol) in water (40 ml) overnight at 22 °C. In the beginning **11** formed a second phase which disappeared after some hours, giving a foamy solution. This was acidified with dilute sulfuric acid to precipitate the excess barium hydroxide as $BaSO_4$, followed by neutralization with $BaCO_3$ (solid). After filtration, evaporation of the water and drying *in vacuo*, the solid was extracted with dry acetone, filtered, evaporated and dried. The barium salt (**12**) was obtained as a white powder (1.0 g; 83%).

*Preparation of the sulfonic acid $C_2Cl_2F_3OCF_2CF_2SO_3H$ (**13**)*

The barium salt **12** (1.0 g; 1.2) was heated with sulfuric acid (2 ml; 100%) to 150 °C in a distillation apparatus under high vacuum. At about 130 °C the acid distilled as a colorless viscous liquid (0.8 g; 2.3 mmol; 79%).

TABLE 1

Details of $ClOCF_2CFXSO_2F$ (X = F, CF_3) reactions with olefins

Reactants (mmol)	$CFCl_3$ (mmol)	Temp. (°C/h)	Product (mmol; %)
1 (3.0), C_2F_4 (3.1)	none	−196/3	$ClCF_2CF_2OCF_2CF_2SO_2F$ **(3)** (2.7; 89)
1 (2.1), CH_2=CHF (2.5)	none	−110/18	$ClCH_2CHFOCF_2CF_2SO_2F$ **(4)** (1.3; 62)
1 (2.0), CH_2=CF_2 (2.5)	none	−110/18	$ClCH_2CF_2OCF_2CF_2SO_2F$ **(5)** (0.9; 47)
1 (1.0), CHF=CHF (1.1)[a]	none	−110/15	$ClCHFCHFOCF_2CF_2SO_2F$[c] **(6)** (1.0; 100)
1 (1.0), CHF=CF_2 (1.1)	none	−110/24	$ClCHFCF_2OCF_2CF_2SO_2F$ **(7)** (1.0; 100)
1 (8.5), C_2F_4 (8.6)	14	−115/24	$ClCF_2CF_2OCF_2CF_2SO_2F$ **(8)** (3.0; 35)
1 (6.4); C_3F_6 (6.5)	15	−110/26	$CF_3CFClCF_2OCF_2CF_2SO_2F$ **(9)** (2.1; 33)
1 (2.6), CFCl=CFCl (2.8)[b]	none	−110/15	$Cl_2CFCFClOCF_2CF_2SO_2F$ **(10)** (1.6; 63)
1 (1.5), CF_2=CFCl (1.7)	none	−110/18	$ClCF_2CFClOCF_2CF_2SO_2F$ **(11a)** $Cl_2CFCF_2OCF_2CF_2SO_2F$ **(11b)** (1.0; 66) ratio 9:1
2 (5.1), C_2H_4 (5.9)	none	−110/24	$ClCH_2CH_2OCF_2CF(CF_3)SO_2F$ **(15)** (4.8; 94)
2 (6.7), C_2F_4 (6.9)	10	−110/24	$ClCF_2CF_2OCF_2CF(CF_3)SO_2F$ **(16)** (2.9; 43)
2 (11.2), CF_2=CFCl (11.6)	44	−75/4	$ClCF_2CFClOCF_2CF(CF_3)SO_2F$ **(17)** (6.2; 56)
2 (7.4), C_3F_6 (7.6)	11	−110/5.5	$CF_3CFClCF_2OCF_2CF(CF_3)SO_2F$ **(18)** (3.7; 50)
19 (1.7), CF_2=CFCl (2.4)	15	−160/24	$Cl_2CFCF_2OC_2F_5$ **(20a)** $ClCF_2CFClOC_2F_5$ **(20b)** (0.7; 41) ratio 56:44

[a] *Cis* isomer.
[b] Mixture of *cis* and *trans* isomers.
[c] *Erythro* isomer.

*Reaction of **13** with PCl_5: $C_2Cl_2F_3OCF_2CF_2SO_2Cl$ **(14)***

A glass reactor (100 ml) was charged with PCl_5 (0.97 g; 4.65 mmol), carbon tetrachloride (1.9 g) and **13** (1.17 g; 3.4 mmol) at −196 °C. After evacuation, the bulb was warmed up to room temperature, while stirring, during a period of 10 min. Stirring was continued for 1 h, followed by evaporating the solvent and excess PCl_5 at 40 °C. The very low volatile sulfonic acid chloride **14** (1.24 g; 3.4 mmol; 100%) remained in the reactor as a pale yellow liquid.

Analytical data

$ClCH_2{}^{A}CH_2{}^{B}OCF_2{}^{C}CF_2{}^{D}SO_2F^{E}$ **(3)**: MS (CI): 277 [$(M+CH_3)^+$, 32.0]; 265/263 [$(M+H)^+$, 3.7/16.7]; 249/247 [$(M-CH_3)^+$, 5.5/14.3]; 235/233

[(M−CHO)$^+$, 2.0/17.1]; 227 [(M−Cl)$^+$, 17.6]; 226 [(M−HCl)$^+$, 17.1]; 213 [(M−CH_2Cl)$^+$, 83.1]; 199 [(M−C_2H_4Cl)$^+$, 61.4]; 181/179 [(M−SO_2F)$^+$, 35.7/100]. MS (EI): 199 [(M−C_2H_4Cl)$^+$, 53.9]; 169 [$C_3F_7^+$, 55.1]; 119 [$C_2F_5^+$, 36.1]; 100 [$C_2F_4^+$, 27.5]; 97 [$C_2F_3O^+$, 35.3]; 69 [CF_3^+, 92.7]; 67 [SOF^+, 92.7]; 65/63 [$C_2H_4Cl^+$, 45.3/100]; 64/62 [$C_2H_3Cl^+$, 16.2/39.0]; 51 [CHF_2^+, 8.1]; 49 [CH_2Cl^+, 11.6]; 47 [CCl^+, 13.5]. IR (liq. film, KCl cm^{-1}: 2967 (w); 1454 (vs); 1403 (m); 1335 (s); 1242 (vs); 1198 (vs); 1138 (vs); 1116 (vs); 1071 (m); 1012 (s); 982 (m); 966 (m); 808 (s); 782 (s); 752 (m); 735 (m); 679 (m); 655 (m); 612 (s); 542 (m). NMR: δ(A) 3.26 (t); β(B) 2.66 (t); δ(C) −83.7 (q); δ(C) −111.5 (q); δ(E) 44.0 (pent.); ^3J(AB) = 5.4 Hz, ^3J(CD) = ^4J(CD) = ^4J(CE) = ^3J(DE) = 5.0 Hz.

$ClCH_2{}^ACH^BF^COCF^DF^ECF_2{}^FSO_2F^G$ (**4**): MS (CI): 263/261 [(M−F)$^+$, 26.4/76.3]; 243/241 [(M−HF_2)$^+$, 7.7/22.7]; 231 [(M−CH_2Cl)$^+$, 21.2]; 183 [$C_2F_4SO_2F^+$, 31.7]; 145 [(M−CF_2Cl)$^+$, 27.2]; 119 [$C_2F_5^+$, 31.4]; 100 [$C_2F_4^+$, 17.7]; 87/85 [$CClF_2$, 7.8/17.3]; 83/81 [$C_2H_3ClF^+$, 31.7/100]; 69/67 [$CHClF^+$, 6.9/17.9]. IR (5 Torr, AgCl) cm^{-1}: 2986 (w); 1468 (vs); 1339 (m); 1276 (m); 1244 (vs); 1210 (vs); 1154 (vs); 1082 (s); 1051 (m); 1031 (m); 991 (m); 898 (w); 811 (s); 715 (w); 660 (w); 613 (s). NMR: δ(A) 2.72 (d–d); δ(B) 5.16 (d–t); δ(C) −126.6 (d–d–d–t); δ(D) −82.3 (d–'sex.'); δ(E) −84.3 (d–'sep.') (AB-pattern), ^2J(DE) = 143.3 Hz; δ(F) −112.2 (d–t); δ(G) 44.7 (pent.); ^3J(AB) = 4.6 Hz, ^3J(AC) = 11.6 Hz, ^2J(BC) = 55.7 Hz, ^4J(CD) = 11.5 Hz, ^4J(CE) = 6.0 Hz, ^3J(DF) = ^3J(EF) = 4.0 Hz, ^4J(DG) = ^4J(EG) = 5.5 Hz, ^3J(FG) = 4.0 Hz.

$ClCH_2{}^ACF_2{}^BOCF_2{}^CCF_2{}^DSO_2F^E$ (**5**): MS (CI): 315/313 [(M+CH_3)$^+$, 1.9/3.0]; 281/279 [(M−F)$^+$, 5.1/14.5]; 183 [$C_2F_4SO_2F^+$, 24.5]; 135/133 [$C_2HCl_2F_2^+$, 10.1/18.7]; 119 [$C_2F_5^+$, 13.3]; 101/99 [$C_2H_2ClF_2^+$, 28.8/100]; 79/77 [$C_2H_2ClO^+$, 15.2/36.5]. IR (6 Torr, AgCl) cm^{-1}: 2988 (w); 1469 (vs); 1346 (s); 1319 (s); 1278 (vs); 1244 (vs); 1201 (vs); 1152 (vs); 1082 (vs); 994 (m); 900 (w); 809 (vs); 706 (w); 667 (w); 611 (s). NMR: δ(A) 2.75 (t); δ(B) −74.3 (m); δ(C) −82.6 (m); δ(D) −112.5 (q); δ(E) 45.1 (t–t); ^3J(AB) = 9.52 Hz, ^3J(CD) = 3.9 Hz, ^4J(CE) = 6.3 Hz, ^3J(DE) = 3.9 Hz.

$ClCH^AF^BCH^CF^DOCF^EF^FCF_2{}^GSO_2F^H$ (**6**): MS (CI): 319/317 [(M+F)$^+$, 6.0/16.4]; 281/279 [(M−F)$^+$, 39.8/100]; 261/259 [(M−F−HF)$^+$, 9.8/23.7]; 183 [$C_2F_4SO_2F^+$, 55.1]; 119 [$C_2F_5^+$, 10.5]; 117 [$C_2HF_4O^+$, 37.7]; 101 [$C_2HF_4^+$, 39.8]. MS (EI): 231 [(M−CHClF)$^+$, 16.0]; 183 [$C_2F_4SO_2F^+$, 23.1]; 145 [$C_2F_3O_2S^+$, 17.9]; 133 [$CF_2SO_2F^+$, 11.8]; 119 [$C_2F_5^+$, 97.8]; 101 [$C_2HF_4^+$, 33.9]; 100 [$C_2F_4^+$, 37.3]; 99 [$C_2H_2ClF_2^+$, 85.0]; 81/79 [C_2HClF^+, 9.1/23.9]; 69/67 [$CHClF^+$, 36.1/100]. IR (7 Torr, AgCl) cm^{-1}: 3000 (w); 1468 (vs); 1335 (m); 1307 (w); 1247 (vs); 1219 (vs); 1160 (vs); 1124 (m); 1094 (vs); 1077 (s); 1047 (s); 983 (m); 845 (m); 817 (s); 795 (s); 665 (w); 638 (w); 613 (m). NMR: δ(A) 6.16 (d–t); δ(B) −153.93 (d–d–d); δ(C) 6.04 (d–t); δ(D) −135.2 (d–m); δ(E) −82.31 (d–m); δ(F) −85.03 (d–m) (AB-pattern), ^2J(EF) = 142.2 Hz; δ(G) −112.26 (br. s); δ(H) 44.89 (d–t); ^2J(AB) = −48.8 Hz, ^3J(AC) = 4.5 Hz, ^3J(AD) = 4.5 Hz, ^3J(BC) = 4.5 Hz, ^3J(BD) = 16.5 Hz, ^2J(CD) = 55.5 Hz, ^4J(DE) ≃ ^4J(DF) = 10.0 Hz, ^4J(EH) = 10.0 Hz, ^3J(GH) = 4.5 Hz.

$ClCH^AF^BCF_2{}^COCF_2{}^DCF_2{}^ESO_2F^F$ (**7**): MS (CI): 319/317 [$(M+H)^+$, 5.84/9.84]; 398/396 [$(M-HF)^+$, 5.8/19.0]; 235/233 [$(M-SO_2F)^+$, 5.5/18.4]; 183 [$C_2F_4SO_2F^+$, 100]. IR (8 Torr, AgCl) cm^{-1}: 3000 (w); 1471 (vs); 1372 (m); 1334 (m); 1289 (s); 1248 (vs); 1214 (vs); 1156 (vs); 1111 (vs); 1029 (w); 994 (m); 882 (m); 815 (s); 726 (w); 648 (m); 615 (s). NMR: δ(A) 4.88 (d–t); δ(B) − 155.0 (d–t); δ(C) − 82.3 (m); δ(D) − 83.9 (m); δ(E) − 112.6 (d–t); δ(F) 45.3 (pent.); ^2J(AB) = 47.8 Hz, ^3J(AC) = 4.1 Hz, ^3J(BC) = 11.0 Hz, ^3J(DE) = 3.2 Hz, ^4J(DF) ≃ ^3J(EF) = 6.0 Hz.

$ClCF_2{}^ACF_2{}^BOCF_2{}^CCF_2{}^DSO_2F^E$ (**8**): MS (CI): 337/335 [$(M+H)^+$, 1.9/6.0]; 203/201 [$C_3ClF_6O^+$, 5.5/17.5]; 199 [$OC_2F_4SO_2F^+$, 38.1]; 183 [$C_2F_4SO_2F^+$, 100]; 137/135 [$C_2ClF_4{}^+$, 12.4/33.8]; 119 [$C_2F_5{}^+$, 13.2]; 101 [$C_2HF_4{}^+$, 10.4]; 100 [$C_2F_4{}^+$, 18.8]. MS (EI): 137/135 [$C_2ClF_4{}^+$, 11.0/33.9]; 133 [$CF_2SO_2F^+$, 4.8]; 119 [$C_2F_5{}^+$, 52.5]; 100 [$C_2F_4{}^+$, 16.2]; 97 [$C_2F_3O^+$, 7.3]; 87/85 [$CClF_2{}^+$, 13.9/–]; 85 [CF_3O or $H_2SO_2F^+$, 100]; 69 [CF_3, 18.7]; 67 [SOF^+, 45.4]; 64 [$SO_2{}^+$, 10.6]; 50 [$CF_2{}^+$, 6.4]. IR (10 Torr, AgCl) cm^{-1}: 1468 (vs); 1353 (s); 1316 (s); 1249 (vs); 1217 (vs); 1186 (vs); 1158 (vs); 1132 (vs); 1026 (s); 1003 (m); 977 (vs); 823/811 (s); 776 (m); 751 (m); 702 (w); 614 (m): NMR: δ(A) − 74.5 (br. s); δ(B) − 87.0 (d–d); δ(C) − 82.6 (m); δ(D) − 112.8 (d–t); δ(E) 45.4 (pent.); ^3J(AB) < 1 Hz, ^4J(BC) = 12.5 Hz, ^3J(CD) = 3.4 Hz, ^4J(CE) ≃ ^3J(DE) = 5.9 Hz.

$CF_3{}^ACF^BClCF_2{}^COCF_2{}^DCF_2{}^ESO_2F^F$ (**9**): MS (CI): 387/385 [$(M+H)^+$, 0.5/1.0]; 367/365 [$(M-F)^+$, 3.3/7.2]; 303/301 [$M-SO_2F)^+$, 12.0/40.3]; 211 [$C_3F_5O_3S^+$, 14.5]; 187/185 [$C_3ClF_6{}^+$, 14.7/57.6]; 183 [$C_2F_4SO_2F^+$, 100]; 137/135 [$C_2ClF_4{}^+$, 12.8/36.9]; 119 [$C_2F_5{}^+$, 15.3]. MS (EI): 187/185 [$C_3ClF_6{}^+$, 11.0/35.7]; 137/135 [$C_2ClF_4{}^+$, 7.8/23.7]; 119 [$C_2F_5{}^+$, 100]; 100 [$C_2F_4{}^+$, 18.2]; 87/85 [$CClF_2{}^+$, 11.8/40.7]; 69 [$CF_3{}^+$, 62.7]; 67 [SOF^+, 64.8]. IR (7 Torr, KCl) cm^{-1}: 1469 (vs); 1338 (vs); 1284 (vs); 1244 (vs); 1211 (vs); 1155 (vs); 1123 (vs); 1046 (m); 1000 (m); 972 (vs); 867 (w); 823/811 (vs); 771 (m); 755 (m); 731 (m); 715 (m); 650 (m); 612 (s); 561 (m). NMR: δ(A) − 78.41 ('q'); δ(B) − 140.61 (sex.); δ(C) − 80.75 (m); δ(D) − 82.64 (m); δ(E) − 112.71 (d–t); δ(F) 45.14 (pent.); ^3J(AB) ≃ 7.0 Hz, ^4J(AC) = 8.3 Hz, ^3J(BC) = 7.0 Hz.

$Cl_2CF^ACF^BClOCF^CF^DCF_2{}^ESO_2F^F$ (**10**): MS (CI): 349/347 [$(M-F)^+$, 1.92/1.76]; 335/333/331 [$(M-Cl)^+$, 1.01/5.41/7.67]; 249/247/245 [$C_4Cl_3F_4O^+$, 0.7/3.74/5.91]; 183 [$C_2F_4SO_2F^+$, 97.9]; 171/169/167 [$C_2Cl_3F_2{}^+$, 13.5/44.9/44.4]; 137/135 [$C_2F_4Cl^+$, 9.3/28.8]; 119 [$C_2F_5{}^+$, 51.1]; 103/101 [CCl_2F^+, 59.4/100]; 100 [$C_2F_4{}^+$, 53.4]; 87/85 [$CClF_2{}^+$, 15.0/59.4]; 69/67 [$CHClF^+$, 25.8/79.7]. IR (5 Torr, AgCl) cm^{-1}: 1468 (vs); 1324 (m); 1249 (s); 1213 (vs); 1189 (s); 1154 (vs); 1109 (m); 1026 (m); 983 (w); 913 (m); 810 (s); 612 (m). NMR: δ(A) − 72.35 (d); δ(B) − 74.0 (d–d–d); δ(C) − 82.28 (d–d–d–t); δ(D) − 83.32 (d–d–d–t) (AB-pattern), ^2J(CD) = 142.3 Hz; δ(E) − 112.6 (m); δ(F) 45.6 (pent.); ^3J(AB) = 12.0 Hz, ^4J(BC) = 21.0 Hz, ^4J(BD) = 10.0 Hz, ^3J(CE) = 4.4 Hz, ^3J(DE) = 3.5 Hz, ^4J(CF) = 6.0 Hz, ^4J(DF) = 6.0 Hz, ^3J(EF) = 4.2 Hz.

$C_2Cl_2F_3OCF_2CF_2SO_2F$ (**11**): Anal. for $C_4Cl_2F_8O_3S$, mol. wt., 315.04: Calcd. C, 13.69; F, 43.30; S, 9.14%. Found: C, 13.76; S, 9.05%. MS (CI): 183

[$C_2F_4SO_2F^+$, 100]; 105/103/101 [CCl_2F^+, 1.0/4.2/7.0]. MS (EI): 183 [$C_2F_4SO_2F^+$, 17.1]; 171/169/167 [$(M+H-C_2F_4SO_2F)^+$, 2.9/6.0/5.9]; 155/153/151 [$C_2Cl_2F_3^+$, 2.9/19.5/28.8]; 137/135 [$C_2F_4Cl^+$, 14.1/42.5]; 133 [$CF_2SO_2F^+$, 14.2]; 119 [$C_2F_5^+$, 100]; 105/103/101 [CCl_2F^+, 3.3/19.1/33.1]; 100 [$C_2F_4^+$, 38.1]; 87/85 [$CClF_2^+$, 10.3/34.6]; 69/67 [$CHClF^+$, 28.8/91.7]; 50 [CF_2^+, 9.0]; 49/47 [CCl^+, 0.8/7.0]. IR (7 Torr, AgCl) cm^{-1}: 1468 (vs); 1328 (s); 1283 (m); 1247 (vs); 1202 (vs); 1155 (vs); 1125 (vs); 1034 (s); 987 (m); 918 (m); 855 (m); 814 (s); 737 (w); 657 (m); 613 (s). NMR: $ClCF^AF^BCF^CClOCF^DF^ECF_2{}^FSO_2F^G$ (**11a**) (~90%): δ(A) −70.68 (d–d–m); δ(B) −71.46 (d–d–m) (AB-pattern), ^2J(AB) = 171.2 Hz; δ(C) −77.09 (m); δ(D) −81.90 (d–d–d–t–t); δ(E) −83.64 (d–d–d–t–t) (AB-pattern), ^2J(DE) = 142.46 Hz; δ(F) −112.7 (d–d–t); δ(G) 45.46 (pent.); ^3J(AC) = 5.0 Hz, ^3J(BC) = 7.0 Hz, ^4J(CD) = 21.9 Hz, ^4J(DG) = 6.2 Hz, ^3J(DF) = 3.6 Hz, ^5J(AD) = ^5J(BD) = 0.8 Hz, ^4J(CE) = 9.0 Hz, ^4J(EG) = 6.1 Hz, ^3J(EF) = 3.6 Hz, ^5J(AE) = ^5J(BE) = 0.7 Hz, ^3J(FG) = 5.5 Hz, ^5J(CF) = 0.7 Hz. NMR: $Cl_2CF^ACF_2{}^BOCF_2{}^CCF_2{}^DSO_2F^E$ (**11b**) (~10%): δ(A) −72.03; δ(B) −82.0; δ(C) −80.05; δ(D) −112.68; δ(E) 45.49.

$[C_2Cl_2F_3OCF_2SO_3]_2Ba$ (**12**): IR (Nujol mull, KCl) cm^{-1}: 3601 (m); 3497 (w); 1614 (m) (H_2O); 1333 (m); 1289–1233 (vs); 1157 (vs); 1134 (s); 1071 (s); 1027 (s); 997 (m); 958 (m); 914 (s); 856 (m); 674 (m); 645 (m). NMR: $[ClCF^AF^BCF^CClOCF^DF^ECF_2{}^FSO_3]_2Ba$ (**12a**) (81%): δ(A) −69.86 (d–d); δ(B) −70.66 (d–d) (AB-pattern), ^2J(AB) = 170.0 Hz; δ(C) −75.68 (m); δ(D) −81.26 (d–d); δ(E) −82.92 (d–d) (AB-pattern), ^2J(DE) = 145.5 Hz; δ(F) −117.49 (s); ^3J(AC) = 4.8 Hz, ^3J(BC) = 7.0 Hz, ^4J(CD) = 21.7 Hz, ^4J(CE) = 9.4 Hz. NMR: $[Cl_2CF^ACF_2{}^BOCF_2{}^CCF_2{}^DSO_3]_2Ba$ (**12b**) (19%) δ(A) −75.55; δ(B) −84.51; δ(C) −82.05 (t); δ(D) −117.43 (s).

$C_2Cl_2F_3$–O–$CF_2CF_2SO_3H$ (**13**): MS (CI): 353/351/349 [M^+, 1.3/7.0/11.2]; 333/331/329 [$(M-HF)^+$, 7.1/30.4/42.5]; 315/313 [$(M-HCl)^+$, 2.4/5.3]; 267/265 [$(M-CClF_2+H)^+$, 6.5/7.1]; 229 [$(M-CCl_2F_2)^+$, 7.0]; 212 [$(M-CCl_2F_3+2H)^+$, 13.9]; 210 [$(M-CCl_2F_3)^+$, 21.3]; 181 [$C_2F_4SO_3H^+$, 48.4]; 155/153/151 [$C_2Cl_2F_3^+$, 8.4/64.0/100]; 137/135 [$C_2F_4Cl^+$, 7.1/24.5]; 119 [$C_2F_5^+$, 15.2]; 117 [$C_2F_4OH^+$, 25.5]; 101 [$C_2F_4H^+$, 17.3]; 100 [$C_2F_4^+$, 16.9]. IR (liq. film, AgCl) cm^{-1}: 3500–2000 (br. s); 1622 (m); 1552 (w); 1412 (m); 1322 (s); 1252–1119 (vs, b); 1067 (s); 1026 (s); 966 (m); 919 (s); 864 (m); 785–772 (w); 661 (m); 621 (m); 554 (w); 494 (w). NMR: $ClCF^AF^BCF^CClOCF^DF^ECF_2{}^FSO_3H^G$ (**13a**) (~83%): δ(A) −70.24 (d–d); δ(B) 70.63 (d–d), (AB-pattern), ^2J(AB) = 171.3 Hz; δ(C) −76.12 (m); δ(D) −81.43 (d–d); δ(E) −83.25 (d–d) (AB-pattern), ^2J(DE) = 145.0 Hz; δ(F) −117.28 (s); δ(G) 12.84 (in CD_3CN); ^3J(AC) = 5.0 Hz, ^3J(BC) = 7.0 Hz, ^4J(CD) = 22.6 Hz, ^4J(CE) = 9.4 Hz. NMR: $Cl_2CF^ACF_2{}^BOCF_2{}^CCF_2{}^DSO_3H^E$ (**13b**) (~17%): δ(A) ~ −76.1; δ(B) −84.4; δ(C) −82.3; δ(D) −117.27.

$C_2Cl_2F_3OCF_2CF_2SO_2Cl$ (**14**): MS (CI): 333/331 [$(M-Cl)^+$, 0.9/1.1]; 319/317/315 [$(M-Cl-O)^+$, 0.6/2.4/3.8]; 271/269/267 [$(M-SO_2Cl)^+$, 10.8/72.3/100]; 203/201/199 [$(M-CF_3SO_2Cl+H)^+$, 3.9/13.6/16.9]; 183 [$C_2F_4SO_2F^+$, 2.6]; 155/153/151 [$C_2Cl_2F_3^+$, 1.3/9.2/12.5]; 137/135 [$C_2ClF_4^+$, 6.5/17.1]; 105/103/101 [CCl_2F^+, 0.9/4.6/8.6]; 100 [$C_2F_4^+$, 3.5]. IR (liq. film, KCl) cm^{-1}:

1466–1449 (vs); 1320 (s); 1305 (m); 1279–1116 (vs); 1025 (s); 973 (m); 929 (m); 909 (m); 867 (m); 850 (m); 790 (s); 742 (s); 655 (m); 589 (s); 489 (s). NMR: $ClCF^AF^BCF^CClOCF^DF^ECF_2{}^FSO_2Cl$ (**14a**) (65%): δ(A) − 70.75 (d–d); δ(B) − 71.52 (d–d) (AB-pattern), ^2J(AB) = − 170.5 Hz; δ(C) − 77.2 (d–d–d–); δ(D) − 80.9 (d–d); δ(E) − 82.7 (d–d–t) (AB-pattern), ^2J(DE) = 142.0 Hz; δ(F) − 112.6 (br. s); ^3J(AC) = 5.0 Hz, ^3J(BC) = 7.0 Hz, ^4J(CD) = 21.5 Hz, ^4J(CE) = 9.0 Hz, ^3J(DF) = ^{3}J(EF) = 4.0 Hz. NMR: $Cl_2CF^ACF_2{}^BOCF_2{}^CCF_2{}^DSO_2Cl$ (**14b**) (35%): δ(A) − 76.9 (t); δ(B) − 81.79 (d–t); δ(C) − 84.5 (t–t); δ(D) − 112.4 (br. s); ^3J(AB) = 7.1 Hz, ^4J(BC) = 12.5 Hz, ^3J(CD) = 6.0 Hz.

$ClCH_2{}^ACH_2{}^BOCF_2{}^CCF^D(CF_3{}^E)SO_2F^F$ (**15**): MS (CI): 333/331 [(M + F)$^+$, 8.7/11.7]; 281/279 [(M − F − CH_2)$^+$, 2.6/4.2]; 265/263 [(M − F − CH_2O)$^+$, 3.2/5.7]; 245 [(M − CHClF)$^+$, 70.7]; 233 [$C_3F_6SO_2F^+$, 21.5]; 231/229 [(M − SO_2F)$^+$, 5.6/14.8]; 185 [(M − $C_3H_2ClF_2O$)$^+$, 15.0]; 183 [$C_2F_4SO_2F^+$, 100]; 181/179 [(M − CF_2SO_2F)$^+$, 18.9/43.4]; 153 [$CHF_4O_2S^+$, 30.7]; 151 [$C_3HF_6^+$, 44.4]; 135 [$C_2F_5O^+$, 13.2]; 119 [$C_2F_5^+$, 381]; 103 [CF_2ClO^+, 39.4]; 101 [$CF_2ClO^+/C_2HF_4^+$, 69.9]. MS (EI): 226 [(M − $CHClF_2$)$^+$, 13.3]; 213 [(M − $C_2H_2ClF_2$)$^+$, 13.5]; 119 [$C_2F_5^+$, 24.4]; 100 [$C_2F_4^+$, 47.4]; 97 [$C_2F_3O^+$, 32.4]; 69/67 [$CHFCl^+$, 39.8/100]; 65/63 [$C_2H_4Cl^+$, 43.3/89.7]; 64/62 [$C_2H_3Cl^+$, 20.5/41.6]; 51/49 [CH_2Cl^+, 12.3/24.0]; 50 [CF_2^+, 17.7]; 49/47 [CCl^+, 24.0/23.7]. IR (liq. film, KCl) cm^{-1}: 2967 (w); 1458 (vs); 1403 (m); 1264–1236 (vs); 1184 (s); 1148 (s); 1105 (s); 1071 (m); 1018 (m); 965 (s); 811 (s); 784 (m); 735 (m); 680 (m); 613 (s); 540 (m). NMR: δ(A) 3.40 (t); δ(B) 2.78 (t–'d'); δ(C) − 76.68 (sex.); δ(D) − 165.23 (d–t–q); δ(E) − 71.87 (d–d–t); δ(F) 53.98 ('d–sex.'); ^3J(AB) = 5.6 Hz, ^4J(BC) = 0.6 Hz, ^3J(CD) = ^4J(CE) = ^4J(CE) = ^4J(CF) = 9.5 Hz, ^3J(DE) = 7.0 Hz, ^3J(DF) = 3.7 Hz, ^4J(EF) = 11.1 Hz.

$ClCF_2{}^ACF_2{}^BOCF_2{}^CCF^D(CF_3{}^E)SO_2F^F$ (**16**): MS (CI): 367/365 [(M − F)$^+$, 1.7/4.8]; 349 [(M − Cl)$^+$, 5.5], 303/301 [(M − SO_2F)$^+$, 5.9/20.1]; 233 [(M − C_2ClF_4)$^+$, 100]; 211 [$C_3F_4OSO_2F^+$, 14.5]; 169 [$C_3F_7^+$, 16.7]; 137/135 [$C_2ClF_4^+$, 18.7/51.7]. MS (EI): 169 [$C_3F_7^+$, 26.7]; 137/135 [$C_2ClF_4^+$, 19.5/58.8]; 119 [$C_2F_5^+$, 31.4]; 100 [$C_2F_4^+$, 25.3]; 87/85 [$CClF_2^+$, 15.7/55.1]; 69 [CF_3^+, 79.7]; 67 [SOF^+, 100]; 50 [CF_2^+, 10.0]. IR (8 Torr, AgCl) cm^{-1}: 1472 (vs); 1345 (s); 1290–1131 (vs); 992–970 (s); 820 (vs); 772 (m); 756 (m); 732–720 (m); 648 (m); 617 (s); 541 (w). NMR: δ(A) − 74.5 (t); δ(B) − 87.2 (t); δ(C) − 75.3 (d–t–'pent.'); δ(D) − 166.2 (m); δ(E) − 71.9 (d–d–t); δ(F) + 55.2 (d–sex.); ^3J(AB) = 1.6 Hz, ^4J(BC) = 12.7 Hz, ^3J(CD) ≃ 9.5 Hz, ^4J(CE) ≃ 9.5 Hz, ^4J(CF) = 10.2 Hz, ^3J(DE) = 7.3 Hz, ^3J(DF) = 4.0 Hz, ^4J(EF) = 10.2 Hz.

$ClCF^AF^BCClF^COCF^DF^ECF^F(CF_3{}^G)SO_2F^H$ (**17**): MS (CI): 385/383/381 [(M − F)$^+$, 0.1/0.3/0.4]; 367/365[(M − Cl)$^+$, 0.1/0.2]; 333/331 [(M − CF_3)$^+$, 0.1/0.1]; 233 [$C_3F_6SO_2F^+$, 100]; 169 [$C_3F_7^+$, 11.1]; 155/153/151 [$C_2Cl_2F_3^+$, 2.2/14.2/21.0]. MS (EI): 233 [$C_3F_6SO_2F^+$, 100]; 169 [$C_3F_7^+$, 68.5]; 155/153/151 [$C_2Cl_2F_3^+$, 7.1/40.7/61.4]; 150 [$C_3F_6^+$, 16.7]; 131 [$C_3F_5^+$, 9.8]; 119 [$C_2F_5^+$, 9.8]; 105/103/101 [CCl_2F^+, 1.8/10.4/20.1]; 100 [$C_2F_4^+$, 29.1]; 87/85 [$CClF_2^+$, 8.5/26.7]; 83 [SO_2F^+, 8.6]; 69 [CF_3^+, 58.2]; 67 [SOF^+, 94.7]. IR (7 Torr, KCl) cm^{-1}: 1472 (vs); 1293 (vs); 1250 (vs); 1188 (vs); 1161 (vs); 1119 (vs); 1032 (vs); 973 (m); 922 (m); 854 (m); 819 (vs);

773–697 (w); 614 (s); 520 (m). NMR: δ(A)(B) − 71.26 (center of AB-pattern, not resolved); δ(C) − 77.21 (m); δ(D) − 74.66 (d–d–m); δ(E) − 76.64 (d–d–m) (AB-pattern), ^2J(DE) = 143.42 Hz; δ(F) − 166.06 (m); δ(G) = − 71.65 (m); δ(H) + 55.27 (m); ^3J(AC) = 8.0 Hz, ^3J(BC) = 9.0 Hz, ^4J(CD) = 23.5 Hz, ^4J(CE) = 19.0 Hz.

$CF_3{}^ACClF^BCF_2{}^COCF_2{}^DCF^E(CF_3)^FSO_2F^G$ (**18**): MS (CI): 451/449 [(M + CH_3)$^+$, 0.5/1.2]; 417/415 [(M − F)$^+$, 1.2/3.2]; 399 [(M − Cl], 0.9]; 353/351 [(M − SO_2F)$^+$, 0.6/1.8]; 233 [$C_3F_6SO_2F^+$, 100]; 211 [$C_3F_5O_3S^+$, 30.1]; 187/185 [$C_3ClF_6{}^+$, 14.7/51.6]. MS (EI): 233 [$C_3F_6SO_2F^+$, 80.5]; 187/185 [$C_3ClF_6{}^+$, 30.0/100]; 169 [$C_3F_7{}^+$, 84.1]; 150 [$C_3F_6{}^+$, 20.8]; 137/135 [$C_2ClF_4{}^+$, 8.1/24.2]; 119 [$C_2F_5{}^+$, 14.7]; 100 [$C_2F_2{}^+$, 33.5]; 87/85 [$CClF_2{}^+$, 13.2/43.0]; 83 [SO_2F^+, 9.2]; 69 [$CF_3{}^+$, 82.3]; 67 [SOF^+, 49.4]. IR (8 Torr, KCl) cm^{-1}: 1472 (vs); 1316–1261 (vs); 1163 (vs); 1134 (vs); 1117 (vs); 1046 (m); 976 (vs); 866 (w); 819 (vs); 764 (m); 741 (s); 701 (s); 616 (s); 539 (m). NMR: δ(A) − 78.41 (d–t); δ(B) − 140.66 ('sep.'); δ(C) − 80.87 (m); δ(D) − 75.20 (m); δ(E) − 166.21 (m); δ(F) − 71.86 (pent.); δ(G) + 55.18 ('sex.'); ^3J(AB) = 7.72 Hz, ^4J(AC) = 8.1 Hz, ^4J(DF) ≃ ^3J(EF) ≃ 8.7 Hz, ^4J(DG) ≃ ^4J(FG) ≃ 10.0 Hz.

$C_2Cl_2F_3OCF_2CF_3$ (**20**): 271/269/267 [(M − F)$^+$, 9.7/63.5/94.7]; 253/251 [(M − Cl)$^+$, 33.5/100]; 201/203 [$C_3F_6ClO^+$, 1.7/5.7]; 185 [$C_3F_7O^+$, 12.0]; 155/153/151 [$C_2Cl_2F_3{}^+$, 4.5/30.1/42.0]; 137/135 [$C_2F_4Cl^+$, 13.8/39.4]; 119 [$C_2F_5{}^+$, 19.3]. IR (10 Torr, AgCl) cm^{-1}: 1288 (vs); 1243 (vs); 1202 (vs); 1143 (vs); 1104 (vs); 1026 (s); 937 (s); 916 (s); 847 (s); 805 (m); 704 (s); 635 (w); 530 (w). NMR: $Cl_2CF^ACF_2{}^BOCF_2{}^CCF_3{}^D$ (**20a**) (56%): δ(A) − 76.72 (t); δ(B) − 85.40 (d–t); δ(C) − 89.39 (t); δ(D) − 87.16 (m); ^3J(AB) = 7.03 Hz, ^4J(BC) = 12.0 Hz, ^3J(CD) < 1 Hz. NMR: $ClCF^AF^BCF^CClOCF^DF^ECF_3{}^F$ (**20b**) (44%): δ(A) − 70.72 (d–d); δ(B) − 71.56 (d–d) (AB-pattern), ^2J(AB) = 170.0 Hz; δ(C) − 77.27 (d–d–d–d); δ(D) − 88.56 (d–d); δ(E) − 90.22 (d–d) (AB-pattern), ^2J(DE) = 144.8 Hz; δ(F) − 87.26 (m); ^3J(AC) = 4.0 Hz, ^3J(BC) = 7.0 Hz, ^4J(CD) = 21.0 Hz, ^4J(CE) = 10.0 Hz, ^3J(DF, EF) < 1 Hz.

Results and discussion

Olefins containing hydrogen or chlorine gave higher yields of the addition compounds than the fully fluorinated ethylene or propylene (see Table 1). Due to the partial decomposition of the hypochlorites **1** and **2**, the acid fluorides FC(O)CFXSO$_2$F (X = F, CF$_3$) and chlorofluorination adducts of the olefins are found as byproducts. The addition reactions of both **1** and **2** to unsymmetrical olefins are highly regiospecific and in the case of *cis*-CFH = CFH, the addition of **1** was stereospecific, forming a single diastereomer (see discussion of NMR spectral data). The diastereomer is assigned as the *erythro* isomer which implies the additions are *cis*. This result is consistent with previous work on related hypochlorites [12, 13].

The ethers are colorless liquids, stable at room temperature over a period of several years. Compounds **10, 11a** and **17** are potential precursors to

interesting, perhalogenated vinyl ethers, but this chemistry was not explored. The novel addition compounds were identified by their mass, infrared and NMR spectra.

Mass spectra

All compounds are identified by heavier fragments as M^+ (only for **13**), $[M+H]^+$, $[M-F]^+$, $[M-HF]^+$, $[M-Cl]^+$, $[M-HCl]^+$ or others. Furthermore, related fragmentation patterns strongly support the identity of the respective compounds; fragments with high abundance (many appeared as base peaks) were $[M-SO_2F]^+$ for **3, 9** and **16**, $[C_2F_4SO_2F]^+$ for **7, 8, 9, 10, 11** and **15**, $[C_3F_6SO_2F]^+$ for **18**, $[OC_3F_6SO_2F]^+$ for **16** and **17**, $[C_2H_3ClF]^+$ for **4**, $[C_2H_2ClF_2]^+$ for **5** and $[M-SO_2Cl]^+$ for **14**.

IR spectra

The compounds containing an SO_2F group have a very strong stretching vibration for $\nu(SO_2)$ in the range of 1454–1472 cm^{-1}. The vibration $\nu(SF)$ is found between 808 cm^{-1} to 820 cm^{-1} as a strong to very strong sharp band. Hydrogen-containing ethers show the $\nu(CH)$ stretching band in the range of 2967–3000 cm^{-1}. The sulfonyl chloride **14** shows a strong band for $\nu(SCl)$ at 589 cm^{-1}. A cluster of very strong broad bands in the region 1300 cm^{-1} to 1100 cm^{-1} is due to the usual CF vibrations and includes the symmetric $\nu(SO_2)$ vibration. The barium salt **12** and the acid **13** are found to contain water, as indicated by very broad $\nu(OH)$ bands in the expected regions.

NMR spectra

The expected chemical shift values were observed for the different fluorines and protons. In the case of the unsymmetrical olefins C_3F_6, C_2ClF_3, C_2HF_3, C_2H_3F and $CH_2=CF_2$, the ^{19}F NMR spectra of the ethers indicate a clear regiospecific reaction except for the adducts **11** and **20a, b**. Although the reaction of C_2F_3Cl is not regiospecific, the selectivity with **1** is clearly much greater than with **19**. As reported in previous papers [12, 13], the reactions follows Markovnikov's rule. Only C_2ClF_3 gives the anti-Markovnikov addition product $Cl_2CFCF_2OCF_2CF_2SO_2F$ (**11b**) in about 10% yield and $Cl_2CFCF_2OCF_2CF_3$ (**20a**) in 56% yield of the total ether yield in the reaction with **1** and **19**, respectively. The reaction of **1** with *cis*-CFH=CFH to form **6** is stereospecific. From the magnitude of the $^3J(FF)$ (16.5 Hz, $^3J(BD)$) in **6**, it can be argued that the *erythro* isomer has been formed. The *threo* isomer should have a value of ~25 Hz. However since *trans*-CFH=CFH was not available, we did not prepare both diastereomers and the assignment and conclusion that the addition reactions are *cis* must be regarded as somewhat tentative.

The ^{19}F NMR spectrum of **11b** as well as that of **12b**, **13b** and **14b**, prepared from **11b**, contain multiplets for which coupling constants are not assigned due to low concentrations and partial overlap with the respective

a isomers. All Markovnikov isomers **4, 6, 10, 11a–14a, 17** and **20b**, except **5, 7** and **9**, of the general structure Cl–CYY'–CZF–O–CF^AF^B–CFXSO_2F (Y, Y' = H, F or Cl; Z = H or Cl; X = F or CF_3) show an AB-pattern for the ^{19}F NMR signal of the CF_2 group bonded to the chiral (C*ZF) through the ether oxygen. These AB spectra are characterized for all the above listed compounds by the typical coupling constants in the range of $^2J(AB) = 142.0–145.5$ Hz and the ratio $^2J(AB)/[\delta(A) - \delta(B)] = 0.73 - 0.28$.

If Y-Y' = F as in **11a, 14a, 17** and **20b**, the CF_2 group directly bonded to the asymmetric C-atom also exhibits an AB-pattern with $^2J(AB) = 170.0–171.3$ Hz and $^2J(AB)/[\delta(A) - \delta(B)] = 2.1–2.4$. These values give a spectrum which is closer to an A_2-'pattern' in appearance than to a more typical AB-pattern as obtained for the CF_2 group bonded to the oxygen atom. This result gives an indication of a greater asymmetry effect on the OCF_2 group than on the neighboring CF_2 group. No effect was observed on the CH_2 group (for Y = Y' = H) in **4**. The asymmetric centers in **7, 9, 15, 16** and **18** do not give rise to any apparent second-order effects on the neighboring CF_2O groups and the observed spectra appear to be first order. Remarkable are the relatively large coupling constants $^4J(FF)$ across the ether linkage (observed with a comparable compound mentioned in [4]). These values vary between 9–24 Hz, presumably depending on the conformation.

The high-resolution AB-spectrum of F^D/F^E of **11a** contains the couplings to all other ^{19}F nuclei in the molecule, even to F^A and F^B, with long-range coupling constants of $^5J(AD) = {}^5J(BD) = 0.8$ Hz and $^5J(AE) = {}^5J(BE) = 0.7$ Hz. The respective AB-spectra of the derivatives **12a, 13a–14a** do not contain these couplings, even to the neighboring CF_2 and SO_2F groups.

*The barium salt **12**, sulfonic acid **13** and sulfonyl chloride **14***

The preparation of fluorinated sulfonic acids from their corresponding alkali or alkaline earth metal salts with 100% sulfuric acid is a well-known method [14].

$$R_fSO_3M \xrightarrow{H_2SO_4} R_fSO_3H$$

Also the saponification of sulfonyl fluorides to the salts by aqueous hydroxides is a common procedure.

$$R_fSO_2F \xrightarrow{MOH} R_fSO_3M$$

Both reactions were applied in one example in this work.

With barium hydroxide the isomeric mixture **11a/11b** gives the barium salts **12a/12b** in high yield. When heated above 200 °C the salts decompose without melting. The salts were converted in high yield to the sulfonic acids **13a/13b** by sulfuric acid. The ^1H NMR chemical shift of 12,8 ppm in acetonitrile-d_3 solution is typical for fluorinated sulfonic acids. The acids easily react with phosphorus pentachloride to give the corresponding sulfonyl chloride isomeric mixture **14a/14b**.

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