Journal of Fluorine Chemistry, 64 (1993) 129–149

Synthesis of functionalized polyfluoroalkyl hypochlorites and fluoroxy compounds and their reactions with some fluoroalkenes*

Bruce B. Randolph and Darryl D. DesMarteau**

Howard L. Hunter Chemistry Laboratory, Clemson University, Clemson, SC 29634-1905 (USA)

(Received August 11, 1992; accepted November 15, 1992)

Abstract

Several new polyfluoroalkyl hypochlorites and fluoroxy compounds containing Cl, H and Br in the alkyl group have been prepared and characterized by ^{19}F NMR, ^1H NMR and IR spectroscopies and by their reactions with fluoroalkenes to produce new polyfluoroethers. The novel compounds are prepared by the CsF-catalyzed addition of F_2 or ClF to the $C{=}O$ bond in $CF_3C(O)CF_2Cl$, $ClCF_2C(O)CF_2Cl$, and their derivatives $HCF_2C(O)CF_3$ and $HCF_2C(O)CF_2Cl$. Compounds containing an α-CF_3 group exhibit enhanced thermal stability.

New fluoroxy compounds and hypochlorites have also been prepared from the acid fluorides CF_3–CFX–C(O)F (X = Cl, Br), which are obtained by the ring-opening reaction of hexafluoropropene oxide with $(CH_3)_3SiCl$, LiBr and $(C_2H_5)_3SiBr$. These –OX compounds behave similarly to previously known materials with two α-F atoms, decomposing quickly at room temperature to COF_2 and haloalkanes.

Introduction

Highly fluorinated alkylhypochlorites and fluoroxy compounds R_fOX (X = Cl, F) have been known for many years and continue to be of synthetic value in the preparation of many fluorine-containing compounds [1–6]. Of these, CF_3OX (X = F, Cl) are two of the most extensively studied compounds with respect to their preparation and chemistry. For compounds other than CF_3OX, very much less is known about their reactivity. One reason for this is the fact that nearly all other polyfluoroalkyl derivatives of this type have a lower thermal stability than CF_3OX, and in most cases this instability is not easily defined or predictable.

In other investigations directed towards elucidating some of the factors affecting the stability of compounds of this type, we carried out the preparation of a variety of functionalized compounds according to eqn. (1) [7–9]:

$$R_fC(O)F + XF \xrightarrow{CsF} \underset{\mathbf{(1a{-}k)}}{R_fCF_2OX}(X = F, Cl) \qquad (1)$$

---

*Dedicated to Prof. N. Watanabe on the occasion of his 70th birthday.

**Author to whom all correspondence should be addressed.

0022-1139/93/$6.00

$R_f = ClCF_2$, X = F (**a**), X = Cl (**b**); $R_f = HCF_2$, X = F (**c**), X = Cl (**d**); $R_f = ClCF_2{-}CFCl$, X = F (**e**), X = Cl (**f**); $R_f = BrCF_2{-}CFBr$, X = F (**g**); $R_f = FSO_2CF_2$, X = F (**h**), X = Cl (**i**); $R_f = FSO_2C(F)CF_3$, X = F (**j**) X = C; (**k**)

The fluoroxy compounds **1** (X = F) show differing degrees of stability. For example, **a**, **e** and **j** can be handled at room temperature without extensive decomposition, but **g** and **h** readily decompose at −60 °C and 22 °C, respectively, and **c** exploded when attempts were made to purify it [10]. The hypochlorite derivatives **b**, **d**, **f** are all unstable at 22 °C, decomposing within minutes to COF_2 and the corresponding R_fCl compounds [7–9], whereas **i** and **k** are stable at 22 °C. If the hypochlorites are maintained below their decomposition temperature, they readily react with fluoroalkenes to give the respective ethers. The corresponding fluoroxy derivatives often undergo decomposition and only **j** gives good yields of the addition products. The apparent stabilizing effect of a CF_3– group α to the –OX function [7, 11], led us to attempt the preparation of new derivatives according to eqn. (2):

$$R_f{-}C(O){-}R_f' + XF \xrightarrow{CsF} \underset{\mathbf{(2a\text{–}h)}}{R_fCF(R_f')OX} \quad (X = F,\ Cl) \tag{2}$$

$R_f = CF_3$, $R_f' = CF_2Cl$, X = F (**a**), X = Cl (**b**); $R_f = CF_3$, $R_f' = CF_2H$, X = F (**c**), X = Cl (**d**); $R_f = R_f' = ClCF_2$, X = F (**e**), X = Cl (**f**); $R_f = ClCF_2$, $R_f' = HCF_2$, X = F (**g**), X = Cl (**h**)

In addition, it was also desirable to compare the stability of compounds **2** with the isomeric unbranched compounds **3**. Some of these compounds were prepared according to eqn. (3):

$$R_x{-}COF + XF \xrightarrow{CsF} \underset{\mathbf{(3a\text{–}d)}}{R_x{-}CF_2OX} \quad (X = F,\ Cl) \tag{3}$$

$R_x = CF_3CFCl$, X = F (**a**), X = Cl (**b**); $R_x = CF_3CFBr$, X = F (**c**), X = Cl (**d**)

The required acid fluorides for the reaction depicted in eqn. (3) can be prepared from hexafluoropropene oxide (HFPO) and either $(CH_3)_3SiCl$ [12] or LiBr [13]. An improved preparation of $CF_3CFBrCOF$ from HFPO and $(C_2H_5)_3SiBr$ is described herein.

Experimental

General methods

Volatile compounds were handled in a glass and/or stainless-steel vacuum system equipped with glass/Teflon or stainless-steel valves. Pressures were measured with a Wallace and Tiernan series 1500 differential pressure gauge. The addition reactions with alkenes were carried out in 50 or 100 ml glass bulbs fitted with glass/Teflon valves. Separation of volatile compounds was accomplished by vacuum distillation through a series of cold traps.

Infrared spectra were recorded in the gas phase using 10 cm cells fitted with KCl or AgCl windows. NMR spectra were obtained at 188.313 MHz for ^{19}F and 200.132 for ^{1}H. ^{19}F and ^{1}H chemical shifts are reported relative to internal $CFCl_3$ and TMS or residual hydrogen in deuterated solvents, respectively. The deuterated solvents $CDCl_3$, acetone-d_6 and benzene-d_6 were used as lock solvents in most cases. The low stability of the hypochlorites and some hypofluorites necessitated the use of special handling techniques for NMR sample preparation. We prepared the NMR samples as solutions in pure $CFCl_3$ at concentrations of *c.* 3 mol% as follows. A 5 mm NMR tube was joined to the bottom of a glass U-trap and the trap was immersed in a cold bath of appropriate temperature in order to trap the hypohalite. The hypohalite was then collected in the trap under dynamic vacuum as the sample container was allowed to warm in the air from −196 °C. After collecting an appropriate amount of compound, the trap was closed and the cold bath slowly lowered to allow the compound to flow into the NMR tube. The $CFCl_3$ was then added by vacuum transfer to the cold NMR tube and the tube sealed with a torch and stored at −111 °C until analysis was carried out.

Mass spectra were recorded in the EI (70 eV) and CI (CH_4) modes using direct insertion techniques.

Reagents

Chloropentafluoroacetone and 1,3-dichlorotetrafluoroacetone were obtained from commercial sources and used as received. Triethylphosphite was purchased from Aldrich Chemical Co. and distilled immediately prior to use. Activated charcoal was obtained from Aldrich Chemical Co. and used as received.

Fluorine was obtained from Air Products and was passed through an NaF scrubber before use. Chlorine monofluoride was prepared by heating equimolar amounts of Cl_2 and F_2 at 220 °C in a 150 ml Monel bomb. Cesium fluoride was activated by melting in a platinum crucible, followed by powdering in a ball mill under very anhydrous conditions. The fluoroalkenes were purchased from PCR, Inc. and used as received after passing through a −80 °C trap. LiBr was dried under vacuum at 80 °C for 24 h. Diglyme was distilled from CaH_2 before use.

Preparation of $HCF_2C(O)CF_3$

Only slight modifications were made from literature methods [14, 15]. Chloropentafluoroacetone (14.6 mmol) was condensed into a 250 ml three-necked round-bottom flask fitted with a dropping funnel, gas inlet and reflux condensor. Freshly distilled $P(OC_2H_5)_3$ (2.42 g, 14.6 mmol) was added dropwise to the $ClCF_2C(O)CF_3$ at −30 °C, allowing the effluent gas to bubble slowly through a mineral oil trap. After the addition, the reaction mixture was allowed to warm slowly to room temperature while stirring. At this time, 25 ml of 10% (vol.) H_2SO_4 was added and the mixture then heated to reflux for 20 h.

Into a three-necked round-bottom flask, fitted with an addition funnel and two gas inlet/outlet valves, was placed 65.0 g (229 mmol) P_4O_{10}. Concentrated H_2SO_4 (96%, 50 ml) was added slowly and this mixture was heated to 110 °C. The reaction mixture obtained above was then added dropwise to the P_4O_{10}/H_2SO_4 mixture and the effluent gases trapped at −111 °C. The contents of this trap were then distilled in a vacuum line through −111 °C and −196 °C traps. The −111 °C trap contained pure $CF_3C(O)CF_2H$ in 60% yield.

Preparation of $HCF_2C(O)CF_2Cl$

Only slight modifications from the literature method were employed [14]. In an essentially identical manner as above, 8.5 g (43 mmol) of $(ClCF_2)_2C{=}O$ gave $HCF_2C(O)CF_2Cl$ (36.5 mmol, 86%) upon collection of the effluent gases in a −65 °C trap, followed by vacuum distillation into a −80 °C trap.

Preparation of $CF_3CFClC(O)F$

The literature method of Heinrich [12] was used with some simple modifications. A 100 ml reactor containing an Ace threaded connection and Teflon stopcock was charged with 3.1 g of activated charcoal. The inner sleeve of the threaded connection was plugged with glass wool to prevent the charcoal from being pulled into the vacuum line. After evacuation, 2.0 mmol each of $(CH_3)_3SiCl$ and hexafluoropropene oxide (HFPO) were condensed into the reactor at −196 °C. The reactor was then allowed to warm slowly to room temperature. After 8 h at room temperature, the reactor was cooled to −196 °C and the contents distilled through traps at −111 °C and −196 °C. The −111 °C trap contained $(CH_3)_3SiF$, while the desired $CF_3CFClC(O)F$ collected in the −196 °C trap (1.6 mmol, 80% yield). IR (cm^{-1}): 1877 (vs); 1293 (s); 1241 (vs); 1230 (vs); 1137 (vs); 964 (s); 910 (m); 853 (m); 761 (w); 700 (m). ^{19}F NMR ($CDCl_3$) δ: CF_3^A–CF^MCl–$C(O)F^X$: $A = -79.4$ (d–t, 3F) ppm, $J_{AM} = J_{AX} = 7.3$ Hz; $M = -132.7$ (d–q, 1F) ppm, $J_{XM} = 16.3$ Hz; $X = +22.4$ (d–d–q, 1F) ppm.

Preparation of $CF_3CFBrC(O)F$

A very brief report of this reaction has appeared [13]. Using a three-necked 250 ml flask, a solution of 1.39 g (16 mmol) of LiBr in 20 ml diglyme was prepared under dry N_2. The flask was fitted with a gas dispersion tube and a gas outlet valve. By means of the dispersion tube, HFPO was slowly bubbled into the solution at room temperature, and effluent gases were trapped at −26 °C. After 1 h, the trap was disconnected from the system, cooled to −196 °C and the contents distilled into the vacuum line through traps at −105 °C and −196 °C. The −105 °C trap contained 7.1 mmol (46% yield) of $CF_3CFBrC(O)F$. The −196 °C trap contained some residual HFPO. IR (cm^{-1}): 1871 (vs); 1290 (vs); 1260 (vs); 1241 (vs); 1220 (vs); 1133 (vs); 1019 (w); 983 (m); 964 (s); 917 (s); 759 (w); 692 (m). ^{19}F NMR (C_6D_6) δ: CF_3^A–CF^MBr–$C(O)F^X$: $A = -78.2$ (d–d, 3F) ppm, $J_{AM} = 9.9$ Hz, $J_{AX} = 7.7$ Hz; $M = 137.5$ (d–q, 1F) ppm, $J_{MX} = 21.1$ Hz; $X = +21.1$ (d–q, 1F) ppm.

An improved method for the preparation of $CF_3CFBrC(O)F$ is as follows. A 250 ml flask fitted with an Ace threaded connection and Teflon/glass stopcock was charged with 3.2 g of activated charcoal. The flask was cooled to −196 °C and 5 mmol HFPO was condensed in, followed by a slight excess (0.2 mmol) of $(C_2H_5)_3SiBr$. The reaction mixture was allowed to warm slowly to room temperature, then cooled to −196 °C and the contents distilled into the vacuum line through traps at −60 °C and −196 °C. The $(C_2H_5)_3SiF$ was trapped in the −60 °C trap, leaving pure $CF_3CFBrC(O)F$ (4.7 mmol, 94%) in the −196 °C trap.

Preparation of fluoroxy compounds and hypochlorites

*Preparation of $CF_3CF(CF_2Cl)OF$ (**2a**)*

Into a 75 ml stainless-steel bomb, passivated with 0.5 atm F_2, was charged 1.17 g CsF in a dry box. After attachment to the vacuum line, evacuation and cooling to −196 °C, 1.93 mmol $CF_3C(O)CF_2Cl$ was condensed in, followed by 3.0 mmol of F_2. The vessel was removed from the line and placed into a CF_2Cl_2 bath at −145 °C and allowed to warm slowly to −40 °C, whereupon the CF_2Cl_2 bath was replaced with a $CFCl_3$ bath (F-11) at −40 °C and allowed to warm to −10 °C. At this time, the bomb was cooled to −196 °C and attached to the vacuum line. The excess F_2 was removed by vacuum and the bomb was allowed to warm slowly to room temperature while the contents distilled through a −111 °C trap into a −196 °C trap. Pure $CF_3CF(CF_2Cl)OF$ was trapped at −111 °C (1.54 mmol, 80% yield), while the −196 °C trap contained $CF_3C(O)F$ and CF_3Cl (decomposition products). IR (cm^{-1}): 1308 (s); 1257 (vs); 1220 (s); 1156 (vs); 1116 (vs); 1079 (s); 1050 (w); 976 (s); 915 (s); 865 (s); 778 (m); 752 (m); 686 (m); 640 (m); 458 (w). ^{19}F NMR ($CDCl_3$) δ: $ClCF_2{}^{AB}CF^{M}(CF_3{}^{X})OF^{Z}$: typical AB pattern, A = −62.0 ppm, B = −63.9 ppm, $J_{AB} = 181$ Hz, $J_{AM} = 10$ Hz, $J_{BM} = 10$ Hz; M = −133.1 (t–d, 1F) ppm, $J_{MZ} = 11$ Hz; X = −73.7 (m, 3F) ppm, $J_{XZ} = 21$ Hz, $J_{XA} = J_{XB} = 10$ Hz; Z = +153.8 (m, 1F) ppm.

*Preparation of $ClCF_2CF(CF_3)OCl$ (**2b**)*

Similar to **2a**, 2.0 mmol $ClCF_2C(O)CF_3$ was allowed to react with 3.0 mmol of ClF over 1.62 g CsF from −120 °C to −28 °C over 12 h. After cooling to −196 °C and distilling the products through traps at −111 °C and −196 °C, the desired $ClCF_2CF(CF_3)OCl$ collected in the −111 °C trap. The −196 °C trap contained unreacted ClF, as well as the decomposition products $ClCF_2C(O)F$, CF_3Cl, $CF_3C(O)F$ and CF_2Cl_2. The IR spectrum agreed well with the literature data [16]. The literature also reports the ^{19}F NMR spectrum as unresolved signals at −68.1, −79.5 and −139 ppm in the ratio 2:2.9:1. We report the following ^{19}F NMR data ($CFCl_3$, unlocked) δ: $ClCF_2{}^{AB}$–$CF^{M}(CF_3{}^{X})OCl$: AB = −63.4 ppm, −64.9 ppm (AB pattern, 2F), $J_{AB} = 179$ Hz; M = −133.3 ppm (d–q, 1F), $J_{MX} \leq 1.2$ Hz, $J_{MB} = 10.8$ Hz; X = −75.1 (m, 3F) ppm, J_{AX} or $J_{BX} = 9.8$ Hz, $J_{XM} = 1.2$ Hz.

*Preparation of $HCF_2CF(CF_3)OF$ (**2c**)*

As in **2a**, 1.8 mmol $HCF_2C(O)CF_3$, 2 mmol F_2 and 1.51 g CsF were reacted from −140 °C to −41 °C over 12 h. The bomb was then cooled to −196 °C, excess F_2 (trace) was removed and the contents were distilled through a −111 °C trap into a −196 °C trap. The product $HCF_2CF(CF_3)OF$ was stopped in the −111 °C trap. Due to the explosiveness of **2c**, only NMR characterization was possible. ^{19}F NMR ($CFCl_3$) δ: $HCF_2^{AB}CF^{C}(CF_3^{M})OF^{X}$: AB = −135 (complex m, 2F) ppm, $^2J_{HF} = 51.8$ Hz, $J_{AB} = 50$ Hz; C = −136.8 (d–m, 1F) ppm, $^3J_{FH} = 24.7$ Hz; M = −75.3 (d–t, 3F) ppm, $J_{MX} = 15.9$ Hz, J_{MA} or $J_{MB} = 8.3$ Hz; X = +143.8 (complex m, 1F) ppm.

*Preparation of $HCF_2CF(CF_3)OCl$ (**2d**)*

The method used in preparing **2b** was followed. Using 2.0 mmol $ClCF_2C(O)CF_3$ and 3.0 mol ClF over 1.1 g CsF, the mixture was allowed to react from −140 °C to −75 °C over 6 h, held there for 2 h and then cooled to −196 °C and distilled through traps at −111 °C and −196 °C. The −111 °C trap contained $HCF_2CF(CF_3)OCl$ (*c.* 90% yield) while the −196 °C trap contained excess ClF and small amounts of HCF_2COF, CF_3COF, HCF_2Cl and CF_3Cl. IR (5 Torr) (cm^{-1}): 1465 (m); 1393 (w); 1357 (w); 1131 (m); 1235 (vs); 1193 (m); 1139 (s); 1115 (s); 1096 (m); 1033 (m); 825 (m); 757 (w); 640 (m); 630 (m); 522 (w). ^{19}F NMR ($CFCl_3$) δ: HCF_2^{AB}–$CF^{M}(CF_3^{X})OCl$: AB = −134.9 (complex m, 2F) ppm, $^2J_{HF} = 49.0$ Hz, $J_{AM} = 8.7$ Hz, $J_{BM} = 9.0$ Hz, $J_{AC} = 3.2$ Hz, $J_{BC} = 4.5$ Hz; M = −137.6 (br, m, 1F) ppm; X = −77.4 (t–t, 3F) ppm.

*Preparation of $(ClCF_2)_2CFOF$ (**2e**)*

The procedure for **2a** was followed. A mixture of 1.0 mmol $(ClCF_2)_2C{=}O$ and F_2 (2.0 mmol) over 1.41 g CsF was allowed to warm slowly from −151 °C to −30 °C over 12h, then at −30 °C for 2 h. The bomb was then cooled to −196 °C, excess F_2 was removed and the volatile materials distilled through a −111 °C trap into a −196 °C trap. The product $(ClCF_2)_2CFOF$ collected in the −111 °C trap, while the decomposition products $ClCF_2C(O)F$ and CF_3Cl collected in the −196 °C trap. No IR data were obtained due to the instability of this compound at room temperature in the gas phase. ^{19}F NMR ($CFCl_3$, −50 °C) δ: $(ClCF_2^{AB})_2CF^{M}OF^{X}$: (although there was no asymmetric carbon present, the $ClCF_2$– fluorines exhibited a typical AB pattern) AB = −59.4 ppm, −62.1 ppm (m, 4F); M = −128.3 (d–t, 5 lines, 1F), $J_{MX} = 19.5$ Hz, $J_{MA} = 11.1$ Hz; X = +149.6 (6-line m, 1F) ppm, $J_{AX} = J_{BX} = 10.2$ Hz.

*Preparation of $(ClCF_2)_2CFOCl$ (**2f**)*

Following the procedure for the preparation of **2b**, 2.4 mmol $(ClCF_2)C{=}O$ were reacted with 2.5 mmol ClF from −140 °C to −65 °C over 6 h. The mixture was then held at −65 °C for 4 h, followed by cooling to −196 °C and separation through −70 °C and −196 °C traps. The product $(ClCF_2)_2CFOCl$ stopped in the −70 °C trap (*c.* 80% yield). The −196 °C trap contained some ClF and $ClCF_2C(O)F$ and CF_2Cl_2. No IR data were obtained due to the instability of this material at 22 °C. ^{19}F NMR ($CFCl_3$; −40 °C) δ: $(ClCF_2^{AB})_2CF^{X}OCl$: (there is some nonequivalence of the $ClCF_2$– fluorines as evidenced (as in **2e**) by the AB pattern) AB = -60.7 ppm, -62.3 ppm (m, 4F), $J_{AB} = 171$ Hz; X = -128.4 (t, 1F) ppm, J_{AX} or $J_{BX} = 10.7$ Hz. The NMR spectrum also showed the presence of $ClCF_2C(O)F$ [$+10.2$ (s, 1F) ppm, -65.1 (s, 2F) ppm] and CF_2Cl_2 (-6.9 ppm, s), indicating that $(ClCF_2)_2CFOCl$ is unstable at -40 °C since neither $ClCF_2C(O)F$ nor CF_2Cl_2 will stop in a -70 °C trap.

*Preparation of $HCF_2CF(CF_2Cl)OF$ (**2g**)*

The procedure for **2a** was followed, allowing 1.0 mmol $HCF_2C(O)CF_2Cl$ to react with 1.5 mmol F_2 over 1.45 g CsF from -150 °C to -40 °C over 6 h. The mixture was held at -40 °C for an additional 1 h, followed by cooling to -196 °C and distillation of the volatile material through traps at -105 °C and -196 °C. The product $HCF_2CF(CF_2Cl)OF$ collected in the -105 °C trap, while the -196 °C trap contained 1.0 mmol of $ClCF_2C(O)F$ and HCF_3, which were easily identified by their IR spectra. No IR data was obtained for $HCF_2CF(CF_2Cl)OF$ due to its instability at 22 °C. ^{19}F NMR ($CFCl_3$, -40 °C) δ: $ClCF_2^{AB}$–$CF^{M}(CF_2^{XY}H)OF^{Z}$: AB = -61.5 ppm, -62.3 ppm (m, 2F), $J_{AB} = 179.9$ Hz; M = -132.0 (m, overlaps XY) ppm; XY = -131.9 ppm, -134.2 ppm (d–m, 2F), $^2J_{HF} = 56.5$ Hz; Z = $+193.3$ (m, 1F) ppm.

*Preparation of $HCF_2CF(CF_2Cl)OCl$ (**2h**)*

Following the above procedure for **2b**, 1.0 mmol $HCF_2C(O)CF_2Cl$ was reacted with 1.2 mmol of ClF over 1.2 g CsF from -145 °C to -35 °C over 12 h. After 1 h at -35 °C, the bomb was cooled to -196 °C and the volatile material was distilled through traps at -80 °C and -196 °C. The product $HCF_2CF(CF_2Cl)OCl$ stopped in the -80 °C trap, whereas the -196 °C trap contained traces of ClF and the decomposition products $ClCF_2(O)F$, $HCF_2C(O)F$, Cl_2CF_2 and HCF_2Cl, which were identified by IR spectroscopy. No IR data were taken for $HCF_2CF(CF_2Cl)OCl$ due to its instability at 22 °C. ^{19}F NMR ($CFCl_3$, -40 °C) δ: $ClCF_2^{A}$–$CF^{B}(CF^{X}H)OCl$: A = -68.3 (t, 2F) ppm; $J_{AX} = 6.7$ Hz; B = -65.6 (s, 1F) ppm; X = -127.8 (d–t, 2F) ppm, $^2J_{HF} = 52.1$ Hz, $J_{XA} = 6.7$ Hz. ^1H NMR δ: 6.37 (t) ppm, $J = 52.0$ Hz. For comparison, ^{19}F NMR δ: $ClCF_2^{A}C(O)CF_2^{X}H$ showed A = -67.1 (t) ppm, $J = 8.8$ Hz; X = -134.0 (d–t) ppm, $^2J_{HF} = 54.0$ Hz. ^1H NMR δ: 6.1 (t) ppm, $^2J_{HF} = 54.0$ Hz.

*Preparation of $CF_3CFClCF_2OF$ (**3a**)*

Following the procedure for **2a**, 2.0 mmol of $CF_3CFClC(O)F$ was reacted with 3.0 mmol F_2 over 1.3 g CsF from -145 °C to -70 °C over 6 h. The bomb was then cooled to -196 °C and the volatile material was distilled through -130 °C and -196 °C traps. The -196 °C trap contained 0.9 mmol COF_2 and CF_3CF_2Cl, whereas the -130 °C trap contained $CF_3CFClCF_2OF$. This compound was so unstable that it could only be characterized by its decomposition products, COF_2 and CF_3CF_2Cl, which were formed in all attempts to obtain NMR spectroscopic samples or addition products to alkenes.

Preparation of $CF_3CFClCF_2OCl$ (3b)

Using the procedure for **2b**, 1.3 mmol of $CF_3CFClC(O)F$ was reacted with 3.0 mmol ClF over 1.26 g CsF from −140 °C to −70 °C over 6 h. The bomb was then cooled to −196 °C and the volatile material was distilled through traps at −125 °C and −196 °C. The −196 °C trap contained excess ClF, with no decomposition product observed in the IR spectrum. Upon expansion to allow an IR spectrum to be taken of the first five Torr of the −125 °C trap material, the appearance of CF_3CFCl_2 and COF_2 was observed, and all of the bands could be assigned to these species. Essentially complete decomposition occurred within minutes. Hence **3b** could only be characterized by its addition to alkenes.

Preparation of $CF_3CFBrCF_2OF$ (3c)

The method of **3a** was followed, using 2.0 mmol $CF_3CFBrC(O)F$ and 2.4 mmol F_2 over 1.46 g CsF from −140 °C to −70 °C. After reaching −70 °C, the bomb was cooled to −196 °C and the volatile material distilled under vacuum through traps at −111 °C and −196 °C. The −196 °C trap contained 2.7 mmol COF_2 and CF_3CF_2Br, as determined by the IR spectrum. The −111 °C trap contained $CF_3CFBrCF_2OF$, and because of its low stability it could only be characterized by its addition to alkenes and its decomposition products, COF_2 and CF_3CF_2Br.

Preparation of $CF_3CFBrCF_2OCl$ (3d)

Following the method for **3b**, 2.0 mmol $CF_3CFBrC(O)F$ was allowed to react with 2.4 mmol ClF over 1.32 g CsF from −140 °C to −70 °C over 6 h. The bomb was then cooled to −196 °C and the volatile materials were distilled through traps at −111 °C and −196 °C. The −196 °C trap contained COF_2, some ClF and smaller amounts of $CF_3CFBrCl$. The −111 °C trap contained $CF_3CFBrCl$ and $CF_3CFBrCF_3OCl$, and the hypochlorite could only be characterized further by its addition to alkenes.

Addition reactions of the fluoroxy compounds

Reaction of 2a with $CF_2{=}CFCl$

All of the addition reactions described below were undertaken in a similar manner. In those cases where the thermal stability of the fluoroxy compound was a problem, the following modification was made. During the separation of the fluoroxy compound from the other reaction product(s) by distillation through a −111 °C trap, the contents thus stopped were vacuum-transferred to the glass reactor containing the alkene held at −196 °C without allowing the pressure to build up as the −111 °C trap warmed in the air. In this fashion, the partial pressure of the fluoroxy compound was kept at a very low level, thus inhibiting decomposition. A Pyrex vessel of 50–100 ml capacity, fitted with a glass/Teflon stopcock and a ground glass joint, was attached to the vacuum line and evacuated while heating with a soft flame. After cooling to 22 °C, followed by immersion in liquid nitrogen, 2.0 mmol $CF_2{=}CFCl$ was condensed into the reactor, followed by 2.5 mmol $CFCl_3$ as the solvent.

The mixture was allowed to warm to room temperature then cooled to −196 °C, whereupon 2.0 mmol $CF_3CF(CF_2Cl)OF$ was added as noted above. The vessel was then placed in a $CFCl_3$ bath at −111 °C and allowed to warm up slowly to −35 °C over a period of 6–12 h.

At this temperature, the bath was replaced with a Dewar flask precooled to −196 °C and the vessel allowed to warm slowly to room temperature. The reactor was then cooled to −196 °C and the contents were distilled through traps at −80 °C and −196 °C. The addition products collected in the −80 °C trap (1.5 mmol, 80% yield). The −196 °C trap contained unreacted $CF_2{=}CFCl$, $ClCF_2C(O)F$ and CF_3Cl (by IR spectroscopy). The addition products were examined by IR and ^{19}F NMR spectroscopy and by mass spectrometry. The spectral data agree very well with those acquired previously [8]. The yield of 80% for the addition product represents an increase from 40% for the original preparation. This is probably due to the low pressure transfer of the $ClCF_2CF(CF_3)OF$ for addition to the alkene.

*Reaction of **2a** with $CF_2{=}CH_2$*

$ClCF_2CF(CF_3)OF$ and $CF_2{=}CH_2$ (1.0 mmol of each) were allowed to react from −140 °C to 22 °C in a CF_2Cl_2 bath, using 3.0 mmol $CFCl_3$ as the solvent. Distillation of the reaction contents through traps at −78, −111 and −196 °C gave the addition product as a mixture of regio isomers in the −78 °C trap (1.4 mmol, 70%). The −111 °C trap contained $CFCl_3$ and the −196 °C trap contained unreacted $CF_2{=}CH_2$, $CF_3C(O)F$ and CF_3Cl. IR (cm^{-1}): 2977 (w); 1459 (w); 1422 (w); 1322 (s); 1302 (s); 1294 (s); 1273 (s); 1224 (vs); 1173 (vs); 1133 (vs); 1043 (s); 969 (m); 931 (m); 874 (m); 765 (w); 721 (w); 636 (w); 617 (vw). ^{19}F NMR (C_6D_6) δ: $ClCF_2^{A}CF^{B}(CF_3)^{C}OCH_2CF_3^{D}$ (major isomer, 57%): A = −67.3 (m, 2F) ppm; B = −139.5 (m, 9 lines, 1F) ppm; C = −75.1 (t–d, 3F) ppm, $J_{AC} = 9.0$ Hz, $J_{BC} = 3.0$ Hz; D = −77.6 (t–d, 3F) ppm, $^3J_{HF} = 9.8$ Hz, $J_{BD} = 1.0$ Hz. ^1H NMR δ: 3.6 (m) ppm. ^{19}F NMR (C_6D_6) δ: $ClCF_2^{A}CF^{B}(CF_3)^{C}OCF_2^{D}CH_2F^{E}$: A = −68.4 (m, 2F) ppm; B = −140.8 (m, 1F) ppm; C = −78.3 (d–t, 3F) ppm, $J_{BC} = 11.2$ Hz, $J_{AC} = 5.0$ Hz; D = −75.74 (d–t, 2F) ppm, $J_{DE} = 16.8$ Hz, $^3J_{HF} = 8.4$ Hz; E = −235.4 (t–t, 1F) ppm, $J_{DE} = 16.8$ Hz, $^2J_{HF} = 45.8$ Hz. ^1H NMR δ: 3.6 (t–t) ppm, $^2J_{HF} = 45.8$ Hz, $^3J_{HF} = 8.4$ Hz. MS (CI) (*m/e*): 265 $(M+H)^+$ 100%; 249 $[(M+H)^+-HCl]^+$ 45%; 199 $(CF(CF_3)OCF_2CH_2F)^+$ 21%. MS (EI) (*m/e*): 199 $(CF(CF_3)OCF_2CH_2F)^+$ 19%; 185 $(CF(CF_3)CF_2Cl)^+$ 11%; 83 $(CF_2CH_2F)^+$ 100%; 69 $(CF_3)^+$ 23%.

*Reaction of **2c** with $CF_2{=}CFCl$*

$CF_3CF(CF_2H)OF$ (2.3 mmol) was combined with 2.8 mmol of $CF_2{=}CFCl$ in 3 mmol $CFCl_3$ from −135 °C to −40 °C over 12 h. Distillation through traps at −80, −111 and −196 °C gave the addition product(s) in the −80 °C trap (1.0 mmol, 35% yield), whereas the −111 °C trap contained $CFCl_3$ and the −196 °C trap contained 2.6 mmol of $CF_2{=}CFCl$, HCF_3 and CF_3COF (as determined by IR spectroscopy). IR (cm^{-1}): 1379 (m); 1332 (m); 1312 (m); 1281 (s); 1231 (vs); 1189 (vs); 1147 (vs); 1043 (m); 1020 (m); 973

(vs); 889 (m); 861 (s); 805 (m); 739 (w); 705 (w); 665 (w); 636 (w). ^{19}F NMR (acetone-d_6) δ: $HCF_2{}^{A}CF^{B}(CF_3{}^{C})OCF_2{}^{D}CF_2Cl^{E}$: A = −135.9 (m, 2F) ppm, $^2J_{HF}=51$ Hz, $J_{AB}=4.3$ Hz, $J_{AC}=4.4$ Hz; B = −137.6 (t, 1F) ppm; C = −80.2 (t–d (4 lines), 3F) ppm, $J_{CB}=4.0$ Hz; D = −83.7 (m, 2F) ppm; E = −73.6 (t, 2F) ppm, $J=2.2$ Hz. ^{1}H NMR δ: 6.9 (t–d–q) ppm, $^2J_{HF}=51.0$ Hz, $^3J_{HF}=3.7$ Hz, $^4J_{HF}=1.0$ Hz. The other regio isomer was observed in only trace amounts.

*Reaction of **2c** with $CF_2{=}CH_2$*

As above, the reaction mixture was distilled through traps at −78 °C and −196 °C. The addition products collected in the −78 °C trap, while unreacted $CF_2{=}CH_2$ and $CFCl_3$ collected in the −196 °C trap. An isolated yield of 25% was observed based on the starting amount of ketone. IR (cm^{-1}): 2978 (w); 1813 (w); 1458 (w); 1423 (w); 1395 (w); 1362 (w); 1305 (w); 1282 (s); 1234 (vs); 1211 (vs); 1183 (vs); 1132 (vs); 1068 (s); 1019 (m); 968 (m); 861 (w); 818 (w); 744 (w); 630 (w); 525 (w). ^{1}H NMR (acetone-d_6) δ: $H^{A}CF_2CF(CF_3)OCF_2{-}CH_2{}^{B}F$ (23%): A = 6.60 (t–d–q, 1H) ppm, $^2J_{HF}=51.48$ Hz, $^3J_{HF}=3.79$ Hz, $^5J_{HF}=0.92$ Hz; B = 4.80 (t–t, 2H) ppm, $^2J_{HF}=45.23$ Hz, $^3J_{HF}=9.09$ Hz. $H^{A}CF_2CF(CF_3)OCH_2{}^{B}{-}CH_3$ (76%): A = 5.97 (t–d, 2H) ppm, $^2J_{HF}=53.89$ Hz, $^3J_{HF}=0.78$ Hz; B = 4.69 (q, 2H) ppm, $^3J_{HF}=8.21$ Hz.

*Reaction of **2e** with $CF_2{=}CFCl$*

$CF_2{=}CFCl$ (2.0 mmol) and $(ClCF_2)_2CFOF$ (**2e**) (1.5 mmol) were allowed to react in 5 mmol of $CFCl_3$ from −140 °C to 22 °C over 8 h. Distillation through traps at −78, −111 and −196 °C showed some unreacted $CF_2{=}CFCl$ in the −196 °C trap as well as smaller amounts of $ClCF_3$ and $ClCF_2C(O)F$. The −111 °C trap contained $CFCl_3$ and the −78 °C trap contained the addition products (0.8 mmol, 53%). IR (cm^{-1}): 1332 (m); 1273 (m); 1229 (s); 1192 (vs); 1024 (m); 972 (s); 841 (m); 802 (w); 757 (w); 619 (w). ^{19}F NMR (acetone-d_6) δ: $(ClCF_2{}^{A})_2CF^{B}OCF_2{}^{C}{-}CF_2{}^{D}Cl$ (65%): A = −65.4 (m, 4F) ppm; B = −135.4 (t–t, 1F) ppm, $J_{AB}=21.7$ Hz, $J_{BC}=4.5$ Hz; C = −83.0 (d–m, 2F) ppm, $J_{CD}=2.5$ Hz; D = −73.5 (t, 2F) ppm. $(ClCF_2{}^{A})_2CF^{B}OCF^{C}Cl{-}CF_3{}^{D}$ (35%): A = −68.3 (m, 4F) ppm, $J_{AB}=4.6$ Hz; B = −140.1 (m, 1F) ppm, $J_{BC}=8.7$ Hz; C = −134.2 (m, 1F) ppm; D = −83.5 (m, 3F) ppm, $J_{DC}=2.5$ Hz.

*Reaction of **2e** with $CF_2{=}CH_2$*

As above, the reaction mixture was distilled through traps at −80, −111 and −196 °C. The addition products (0.6 mmol, 30% yield) collected at −80 °C, whereas the −111 °C trap contained $CFCl_3$ and the −196 °C trap contained unreacted $CF_2{=}CH_2$ and the decomposition products CF_3Cl and $ClCF_2C(O)F$. ^{19}F NMR ($CDCl_3$) δ: $(ClCF_2{}^{A})_2CF^{B}OCH_2CF_3{}^{C}$ (75%): A = −64.7 (m, 4F) ppm; B = −135.7 (m, 1F) ppm; C = −75.2 (t–d, 3F) ppm, $^3J_{HF}=7.6$ Hz, $J_{BC}=2.9$ Hz. ^{1}H NMR ($CDCl_3$) δ: 4.34 (q) ppm, $^3J_{HF}=7.7$ Hz. $(ClCF_2{}^{A})_2CF^{B}OCF_2{}^{C}{-}CH_2F^{D}$ (25%): A = −65.7 (m, 4F) ppm; B = −136.5 (m, 1F) ppm; C = −77.6 (m, 2F) ppm; D = −235.9 (t–t, 1F) ppm, $^2J_{HF}=45.71$

Hz, $J_{CD}=16.1$ Hz. ^1H NMR ($CDCl_3$) δ: 4.71 (d–t) ppm, $^2J_{HF}=45.71$ Hz, $^3J_{HF}=8.5$ Hz.

*Reaction of **2g** with $CF_2{=}CFCl$*

As above, the product mixture was distilled through traps at −78, −111 and −196 °C. The −111 °C trap contained $CFCl_3$ and the −196 °C trap contained unreacted $CF_2{=}CFCl$, HCF_3 and $ClCF_2C(O)F$. The −78 °C trap contained 0.71 mmol (42% yield) of the addition product $HCF_2CF(CF_2Cl)OCF_2CF_2Cl$. No evidence of the other regio isomer was found. IR (cm^{-1}): 2999 (w); 1390 (w); 1332 (m); 1273 (m); 1192 (vs); 1145 (s); 972 (s); 896 (w); 804 (w); 602 (w). ^1H NMR (acetone-d_6) δ: 6.87 (t–d) ppm, $^2J_{HF}=51.1$ Hz, $^3J_{HF}=3.81$ Hz. ^{19}F NMR (acetone-d_6) δ: $HCF_2{}^ACF^B(CF_2{}^CCl)$-$OCF_2{}^DCF_2{}^ECl$: A = −134.0 ppm, −134.8 ppm (AB pattern, 2F), $J_{AB}=306$ Hz; B = −140.1 (m, 1F) ppm; C = −68.2 (m, 2F) ppm; D = −83.5 (m, 2F) ppm; E = −73.5 (t, 2F) ppm, $J_{De}=2.2$ Hz. Other coupling constants could not be readily determined.

*Reaction of **2g** with $CF_2{=}CH_2$*

As in the previous reaction, the −111 °C trap contained $CFCl_3$, the −196 °C trap contained unreacted $CF_2{=}CH_2$ as well as the decomposition products HCF_2COF, $ClCF_3$, HCF_3 and $ClCF_2COF$ in smaller quantities. The addition products stopped in the −78 °C trap (0.89 mmol, 44% yield). IR (cm^{-1}): 3002 (w); 2976 (w); 1458 (w); 1424 (w); 1390 (w); 1355 (w); 1300 (s); 1278 (s); 1235 (s); 1182 (vs); 1133 (vs); 1043 (m); 968 (m); 939 (m); 888 (m); 834 (w); 806 (w); 734 (w); 614 (w); 561 (w).

The assignments of the regio isomers could be made on the basis of the H NMR spectra alone. ^1H NMR ($CDCl_3$) δ: $H^ACF_2CF(CF_2Cl)OCH_2{}^BCF_3$ (66%): A = 6.12 (t–d, 1H) ppm, $^2J_{HF}=52.67$ Hz, $^3J_{HF}=3.93$ Hz; B = 4.34 (q, 2H) ppm, $^3J_{HF}=7.88$ Hz. $H^CCF_2CF(CF_2Cl)OCF_2CH_2{}^DF$ (33%): C = 6.19 (t–d, 1H) ppm, $^2J_{HF}=52.46$ Hz, $^3J_{HF}=2.86$ Hz; D = 4.6 (t–t, 2H) ppm, $^2J_{HF}=45.32$ Hz, $^3J_{HF}=8.73$ Hz.

The ^{19}F NMR spectrum of the mixture was complex and second order except for the $-CH_2F$ signal and the $-CH_2CF_3$ signal. The $-CH_2F$ signal was found at −237.0 (t–t) ppm, $^2J_{HF}=45.3$ Hz, $^3J_{HF}=8.73$ Hz; $-CH_2CF_3$ = −75.5 (t) ppm, $^3J_{HF}=7.0$ Hz.

*Reaction of **3a** with $CF_2{=}CFCl$*

No evidence of any addition products in the reaction of $CF_3CFClCF_2OF$ (**3a**) with either $CF_2{=}CFCl$ or $CF_2{=}CH_2$ was found under a variety of conditions. Only unreacted alkenes, and the decomposition products COF_2 and CF_3CF_2Cl, were found as identified by IR and NMR spectroscopy.

*Reaction of **3c** with $CF_2{=}CFCl$*

The reaction mixture was distilled through taps at −80 °C and −196 °C. The single addition product (0.2 mmol, 10% yield) stopped in the −80 °C trap, while the −196 °C trap contained unreacted $CF_2{=}CFCl$, $CFCl_3$ and the decomposition products of ***3c***, COF_2 and CF_3CF_2Br. IR (cm^{-1}): 1488 (w); 1380 (w); 1279 (m); 1241 (s); 1187 (m); 1145 (m); 1026 (m); 974 (m); 928 (w); 890 (w); 861 (w). ^{19}F NMR (acetone-d_6) δ: $CF_3^ACF^BBrCF_2^COCF^DClCF_3^E$: A = −75.8 (q, 3F) ppm, $J_{AB} \simeq J_{AC} = 9.3$, 8.8 Hz; B = −144.3 (m, 1F) ppm; C = −80.2 (m, 2F) ppm; D = −136.0 (m, 1F) ppm; E = −75.4 (d, 3F) ppm, $J_{DE} = 9.0$ Hz. The other regio isomer, $CF_3CFBrCF_2OCF_2CF_2Cl$, was present in only a very small amount (< 1%).

*Reaction of **3c** with $CF_2{=}CH_2$*

The reaction mixture was distilled through traps at −78, −111 and −196 °C. The addition product $CF_3CFBrCF_2OCH_2CF_3$ collected in the −78 °C trap (0.4 mmol, 20%). Ir (cm^{-1}): 2979 (vw); 1423 (w); 1303 (s); 1289 (s); 1235 (vs); 1183 (vs); 1132 (m); 1066 (m); 1043 (w); 968 (m); 947 (m); 923 (m); 846 (w). ^1H NMR ($CDCl_3$) δ: 4.34 (q) ppm, $^3J_{HF} = 7.73$ Hz. ^{19}F NMR ($CDCl_3$) δ: $CF_3^ACF^BBrCF_2^{CD}OCH_2CF_3^E$: A = −76.8 (q, 3F) ppm, $J_{AB} \cong J_{AC} \cong J_{AD} = 9.3$, 8.6 Hz; B = −142.3 (sextet, 1F) ppm, $J_{AB} = 9.3$ Hz, $J_{BC} = J_{BD} = 10.2$ Hz; CD = −81.8 ppm, −83.6 ppm (m, AB pattern, 2F), $J_{CD} = 137.5$ Hz; E = −74.9 (t, 3F) ppm, $^3J_{HF} = 7.7$ Hz. The other regio isomer, $CF_3CFBrCF_2OCF_2CH_2F$, was present only in very small amounts (< 1%).

Addition reactions of the hypochlorites

All of the addition reactions of the hypochlorites, prepared as described above, were carried out in a similar fashion to those of the fluoroxy compounds. Using 2 mmol of each reactant, the reactions were carried out from −111 °C to 22 °C over 12 h, followed by vacuum distillation through traps at −78, −111 and −196 °C.

*Reaction of **2b** with $CF_2{=}CFCl$*

The addition product $ClCF_2CF(CF_3)OCF_2{-}CFCl_2$ (1.4 mmol, 70% yield) was the only isomer found in the −78 °C trap. The −111 °C trap contained $CFCl_3$, and the −196 °C trap contained unreacted $CF_2{=}CFCl$ and small amounts of $ClCF_2COF$, CF_3COF, CF_3Cl and CF_2Cl_2, which are known decomposition products of $ClCF_2CF(CF_3)OCl$ [40]. IR (cm^{-1}): 1328 (s); 1286 (vs); 1237 (vs); 1118 (vs); 1152 (vs); 1131 (s); 1047 (s); 934 (vs); 920 (vs); 892 (s); 864 (s); 794 (m); 745 (m); 702 (m); 688 (m); 646 (w); 632 (w). ^{19}F NMR (C_6D_6) δ: $ClCF_2^ACF^B(CF_3^C)OCF_2^{DE}CF^FCl_2$: A = −64.5 (m, 2F) ppm; B = −141.0 (t–m, 1F) ppm, $J_{AB} = 21.4$ Hz; C = −78.3 (q–m, 3F) ppm, $J_{AC} \simeq J_{BC} = 10.0$ Hz; DE = −82.0 ppm, −82.8 ppm (m, AB pattern, 2F), $J_{DE} = 148.0$ Hz; F = −76.1 (t, 1F) ppm, $J_{EF} = 7.5$ Hz. MS (EI) (*m/e*): 69 $(CF_3)^+$ 100%; 85 $(CF_2Cl)^+$ 79%; 101 $(CFCl_2{}^+$ 35%; 151 $(CF_2{-}CFCl_2)^+$ 32%; 185 $(CF(CF_3)CF_2Cl)^+$ 44%. MS (CI) (*m/e*): 333 $[(M+H)^+ - HF]^+$ 50%; 317 $[(M+H)^+ - HCl]^+$ 53%; 185 $(CF(CF_3)CF_2Cl)^+$ 100%.

*Reaction of **2b** with $CF_2{=}CH_2$*

The single addition product $ClCF_2CF(CF_3)OCF_2CH_2Cl$ (1.4 mmol, 70% yield) stopped at −78 °C. The −111 °C trap contained $CFCl_3$, whereas the

-196 °C trap contained unreacted $CF_2{=}CH_2$ and traces of decomposition products. IR (cm^{-1}): 2980 (w); 1433 (w); 1320 (m); 1242 (vs); 1170 (s); 1138 (vs); 1112 (s); 1082 (s); 1042 (m); 934 (m); 865 (m); 804 (w); 744 (w); 722 (w). ^{1}H NMR (C_6D_6) δ: $ClCF_2^{AB}CF^{C}(CF_3^{D})OCF_2^{E}CH_2Cl$: 2.75 (t) ppm, $^3J_{HF}=9.0$ Hz. ^{19}F NMR δ: AB $= -71.7$ ppm, -72.6 ppm (m–m, 2F), $J_{AB}=143.5$ Hz, $J_{AC}=19.6$ Hz, $J_{BC}=19.1$ Hz, $J_{AD}\simeq J_{BD}=11.3$ Hz; C $= -141.1$ (t–m, 1F) ppm; D $= -78.2$ (q, 3F) ppm; E $= -80.2$ (t, 2F) ppm, $^3J_{HF}=9.0$ Hz. MS (EI) (*m/e*): 251 $(ClCF_2CF(CF_3)OCF_2)^+$ 15%; 185 $(CF(CF_3)CF_2Cl)^+$ 30%; 99 $(CF_2{-}CH_2Cl)^+$ 100%; 85 $(CF_2Cl)^+$ 47%; 69 $(CF_3)^+$ (82%); 49 $(CH_2Cl)^+$ 20%. MS (CI) (*m/e*): 281 $[(M+H)^+-HF]^+$ 100%; 283 $[(M+H)^+-HCl]^+$ 70%.

*Reaction of **2d** with $CF_2{=}CFCl$*

The single addition product $HCF_2CF(CF_3)OCF_2CFCl_2$ stopped at -78 °C (0.8 mmol, 40% yield). The -111 °C trap contained $CFCl_3$, and the -196 °C contained unreacted $CF_2{=}CFCl$ along with small amounts of the decomposition products HCF_2COF, CF_3COF, HCF_2Cl and CF_3Cl. IR (cm^{-1}): 2997 (w); 1449 (w); 1397 (w); 1318 (m); 1279 (s); 1239 (vs); 1221 (vs); 1185 (s); 1139 (vs); 1103 (s); 1063 (s); 1020 (m); 914 (s); 845 (m); 791 (w); 739 (w). ^{1}H NMR (acetone-d_6) δ: 6.91 (t–d) ppm, $^2J_{HF}=51.1$ Hz, $^3J_{HF}=3.5$ Hz. ^{19}F NMR (acetone-d_6) δ: $HCF_2^{AB}CF^{C}(CF_3)^{D}OCF_2^{E}{-}CFCl_2$: AB $= -135.6$ (m, 2F) ppm, $^2J_{HF}=51.1$ Hz, J_{AB} not readily determined; C $= -144.4$ (t–m, 1F) ppm, $J_{AC}=20.6$ Hz, $J_{BC}=18.2$ Hz; D $= -80.1$ (m, 3F) ppm, $J_{AD}\simeq J_{BD}=8.3$ Hz; E $= -82.0$ (m, 2F) ppm; F $= -75.7$ (t, 1F) ppm, $J_{EF}=7.4$ Hz. MS (CI) (*m/e*): 101 $(CFCl_2)^+$ 16%; 151 $(CF_2{-}CFCl_2)^+$ and $(CF(CF_3)CF_2H)^+$ 81%; 283 $[(M+H)^+-HCl]^+$ 91%; 299 $[(M+H)^+-HF]^+$ 100%. MS (EI) (*m/e*): 283 $[M^+-Cl]^+$ 7%; 151 $(CF_2CFCl_2)^+$ and $(CF(CF_3)CF_2H)^+$ 85%; 101 $(CFCl_2)^+$ 26%; 69 $(CF_3)^+$ 100%; 51 $(CF_2H)^+$ 18%.

*Reaction of **2d** with $CF_2{=}CH_2$*

The addition products (0.6 mmol, 27%) collected in the -78 °C trap. The -111 °C trap contained $CFCl_3$, and the -196 °C trap stopped the unreacted $CF_2{=}CH_2$ as well as the decomposition products HCF_2Cl, CF_3OF, HCF_2COF and CF_3Cl. IR (cm^{-1}): 2982 (w); 1435 (w); 1396 (w); 1331 (m); 1238 (vs); 1211 (s); 1129 (vs); 1105 (s); 1019 (m); 899 (w); 842 (w); 807 (w); 740 (w); 695 (vw); 668 (vw); 634 (vw). ^{1}H NMR (acetone-d_6) δ: $H^{A}CF_2{-}CF(CF_3)OCF_2{-}CH_2^{B}Cl$ (35%): A $=6.76$ (t–q, 1H) ppm, $^2J_{HF}=51.27$ Hz, $^3J_{HF}=1.14$ Hz; B $=4.32$ (t, 2H) ppm, $^3J_{HF}=9.52$ Hz. $H^{A}CF_2CF(CF_3)OCH_2^{B}{-}CF_2Cl$ (65%): A $=6.82$ (t–m, 1H) ppm, $^2J_{HF}=51.09$ Hz; B $=6.85$ (t, 2H) ppm, $^3J_{HF}=5.19$ Hz. ^{19}F NMR (acetone-d_6) δ: $HCF_2^{A}{-}CF^{B}(CF_3^{C})OCF_2^{D}{-}CH_2Cl$: A $= -135.0$ ppm (complex AB pattern with signals from both isomers overlapping); B $= -143.6$ (m, 1F) ppm; C $= -79.8$ ppm (m complex, signals for both isomers overlap); D $= -77.1$ (m, 2F) ppm. $HCF_2^{A}CF^{B}(CF_3^{C})OCH_2{-}CF_2^{D}Cl$: B $= -142.0$ (t–m, 1F) ppm, $^3J_{AB}=19.4$ Hz; D $= -71.6$ (m, 2F) ppm.

Reaction of 2f with $CF_2{=}CFCl$

The reaction mixture was distilled through traps at -50, -111 and -196 °C. The -111 °C trap contained $CFCl_3$, and the -196 °C trap contained unreacted $CF_2{=}CFCl$ and the decomposition products $ClCF_2COF$ and CF_2Cl_2. The -50 °C trap contained the single addition product $(ClCF_2)_2CFOCF_2CFCl_2$ in 10% yield. IR (cm^{-1}): 3570 (vw); 1288 (m); 1261 (m); 1192 (vs); 1163 (s); 1144 (s); 1105 (m); 1061 (m); 1023 (m); 984 (m); 914 (m); 839 (w); 789 (vw); 758 (vw); 695 (vw); 620 (vw). ^{19}F NMR (C_6D_6) δ: $(ClCF_2^{A})_2CF^{B}OCF_2^{C}CF^{D}Cl_2$: $A = -65.6$ (m, 4F) ppm; $B = -136.2$ (t–pent., 1F) ppm, $J_{BC} = 21.3$ Hz, $J_{BA} = 5.3$ Hz; $C = -81.5$ (d–d, t, 2F) ppm, $J_{CD} = 7.6$ Hz; $D = -75.7$ (t, 1F) ppm. MS (CI) (*m/e*): 349 $[(M+H)^+ - HF]^+$ 6%; 201 $(CF(CF_2Cl)_2)^+$ 100%; 151 $(CF_2\text{–}CFCl_2)^+$ 69%; 101 $(CFCl_2)^+$ 80%. MS (EI) (*m/e*): 201 $(CF(CF_2Cl)_2)^+$ 11%; 151 $(CF_2\text{–}CFCl_2)^+$ 100%; 101 $(CFCl_2)^+$ 39%; 85 $(CF_2Cl)^+$ 83%.

Reaction of 2f with $CF_2{=}CH_2$

The reaction mixture (no solvent) was distilled through traps at -78 °C and -196 °C. The addition products stopped in the -78 °C trap (0.1 mmol, 5% yield), whereas the -196 °C trap contained the decomposition products $ClCF_2C(O)F$, Cl_2CF_2 and unreacted $CF_2{=}CH_2$. IR (cm^{-1}): 2970 (w); 1245 (m); 1191 (s); 1121 (s); 969 (m); 877 (m); 774 (m). ^1H NMR (acetone-d_6) δ: $(ClCF_2^{A})_2CF^{B}OCF_2^{C}\text{–}CH_2Cl$: 4.30 (t) ppm, $^3J_{HF} = 9.2$ Hz. ^{19}F NMR (acetone-d_6) δ: $A = -64.9$ (m, 4F) ppm; $B = -136.2$ (m, 1F) ppm; $C = -79.4$ (m, 2F) ppm. The other regio isomer, $(ClCF_2)_2CFOCH_2CH_2Cl$ was present in trace amounts (< 1%).

Reaction of 2h with $CF_2{=}CFCl$

The reaction products (no solvent) were distilled through traps held at -78 °C and -196 °C. The -78 °C trap stopped 0.11 mmol. (10% yield) of addition products, and the -196 °C trap contained unreacted $CF_2{=}CFCl$ and the decomposition products $ClCF_2COF$, HCF_2Cl, HCF_2COF and CF_2Cl_2. The major isomer was $HCF_2CF(CF_2Cl)OCF_2CFCl_2$ (> 95%). IR (cm^{-1}): 2999 (w); 1398 (w); 1355 (w); 1286 (m); 1266 (m); 1190 (vs); 1139 (s); 1048 (m); 963 (m); 914 (m); 789 (w); 602 (w). ^1H NMR (acetone-d_6) δ: $HCF_2^{A}CF^{B}(CF_2^{C}Cl)OCF_2^{D}CF^{E}Cl_2$: 6.95 (t–d) ppm, $^2J_{HF} = 50.9$ Hz, $^3J_{HF} = 3.6$ Hz. ^{19}F NMR (acetone-d_6) δ: $A = -133.9$ ppm, -134.3 ppm (complex ABX); $B = -140.1$ (m, 1F) ppm; $C = -68.1$ (m, 2F) ppm; $D = -81.5$ (m, 2F) ppm; $E = -75.5$ (t, 1F) ppm, $J = 7.5$ Hz. MS (CI) (*m/e*): 315 $[(M+H)^+ - HF]^+$ 95%; 299 $[(M+H)^+ - HCl]^+$ 80%; 167 $(CF(CF_2Cl)CF_2H)^+$ 100%; 151 (CF_2CFCl_2) 33%.

Reaction of 2h with $CF_2{=}CH_2$

The reaction products were separated by distillation through traps held at -60 °C and -196 °C. The addition product stopped in the -60 °C trap (0.22 mmol, 11%) and the -196 °C trap contained unreacted $CF_2{=}CH_2$ as well as $HCF_2C(O)F$, CF_2Cl_2, $ClCF_2COF$ and HCF_2Cl. In this case, significant amounts of both regio isomers were formed. IR (cm^{-1}): 2990 (w); 1433 (w); 1331 (m); 1248 (m); 1173 (s); 1144 (s); 1114 (s); 963 (m); 848 (w); 797 (m); 602 (w). ^1H NMR (benzene-d_6) δ: $H^ACF_2CF(CF_2Cl)OCF_2–CH_2{}^BCl$ (40%): A=5.31 (t–d, 1H) ppm, $^2J_{HF}$=54.21 Hz, $^3J_{HF}$=0.40 Hz; B=2.84 (t, 2H) ppm, $^3J_{HF}$=9.14 Hz. ^{19}F NMR ($CDCl_3$) δ: $HCF_2{}^ACF^B(CF_2{}^CCl)OCF_2{}^DCH_2Cl$: A= −134.2 (t–t, 2F) ppm, $^2J_{HF}$=54.3 Hz, $^3J_{AC}$=7.8 Hz; B= −138.4 (m, 1F) ppm; C= −67.8 (m, 2F) ppm; D= −72.0 (m, 2F) ppm. $H^ACF_2CF(CF_2Cl)OCH_2{}^B–CF_2Cl$ (60%): A=5.41 (t–d–q, 1H) ppm, $^2J_{HF}$=51.51 Hz, $^3J_{HF}$=2.66 Hz, $^3J_{HF}$=0.5 Hz; B=6.8 (t–m, 2H) ppm, $^3J_{HF}$=7.8 Hz. ^{19}F NMR δ: $HCF_2{}^ACF^B(CF_2{}^CCl)OCH_2CF_2{}^DCl$: A= −132.7 ppm (overlapping AB pattern); B= −127.9 (m, 1F) ppm; C= −65.29 (m, 2F) ppm; D= −68.4 (t, 2F) ppm, $^3J_{HF}$=7.8 Hz. MS (CI) (*m/e*): 263 $[(M+H)^+ - HF]^+$ 100%; 247 $[(M+H)^+ - HCl]^+$20%. MS (EI) (*m/e*): 99 $(CF_2–CH_2Cl)^+$ or $(CH_2–CR_2Cl)^+$ 100%; 85 $(CF_2Cl)^+$ 50%; 69 $(CF_3)^+$ 17%; 49 $(CH_2Cl)^+$ 8%.

*Reaction of **3b** with $CF_2{=}CFCl$*

The products (no solvent) were distilled through traps at −70 °C and −196 °C. The −70 °C trap held 0.41 mmol (22% yield) of a single addition product, and the −196 °C trap contained COF_2, CF_3CFCl_2 and unreacted $CF_2{=}CFCl$. IR (cm^{-1}): 1499 (w); 1295 (vs); 1242 (vs); 1185 (vs); 1130 (vs); 1031 (vs); 970 (vs); 917 (m); 867 (m); 852 (m); 770 (w); 733 (m); 633 (w). ^{19}F NMR ($CDCl_3$) δ: $CF_3{}^ACF^BClCF_2{}^{CD}OCF^ECl–CF_2{}^{FG}Cl$: A= −78.3 (d–t, 3F) ppm, J_{AB}=7.0 Hz, $J_{AC} \simeq J_{AD}$=9 Hz; B= −140.6 (q–m, 1F) ppm, J_{BC}=7.3 Hz, J_{BD}=7.3 Hz; CD= −80.9 ppm, −82.5 ppm (AB pattern), J_{CD}=140.1 Hz, J_{DE}=22.9 Hz, J_{CE}=0 Hz; E= −77.5 (d–m, 1F) ppm; FG= −71.0 (m, 2F) ppm, J_{FG}=17.9 Hz, J_{EF}=4.5 Hz, J_{EG}=7.1 Hz.

*Reaction of **3b** with $CF_2{=}CH_2$*

The products (no solvent) were distilled through traps held at −70 °C and −196 °C. The addition products stopped in the −70 °C trap (0.6 mmol, 31% yield). The −196 °C trap contained unreacted $CF_2{=}CH_2$ as well as COF_2 and CF_3CFCl_2. $CF_3{}^ACF^BClCF_2{}^COCF_2{}^DCH_2Cl$ was the major isomer (>99%). IR (cm^{-1}): 2981 (w); 1432 (w); 1338 (m); 1296 (s); 1262 (s); 1233 (vs); 1181 (s); 1137 (s); 1117 (s); 1086 (s); 1027 (m); 970 (s); 896 (w); 848 (w); 736 (m). ^1H NMR ($CDCl_3$) δ: 3.86 (t) ppm, $^3J_{HF}$=9.2 Hz. ^{19}F NMR ($CDCl_3$) δ: A= −78.3 (d–t, 3F) ppm, J_{AB}=7.3 Hz, J_{AC}=9.2 Hz; B= −140.3 (m, 1F) ppm, J_{BC}=6.8 Hz; C= −81.5 (m, 2F) ppm; D= −75.1 (m, 2F) ppm.

*Reaction of **3d** with $CF_2{=}CFCl$*

The products were separated by distilling through traps at −65, −111 and −196 °C. The −65 °C trap stopped the single addition product (0.57 mmol, 28% yield). The −111 °C trap contained $CFCl_3$ used as the solvent, and the −196 °C trap contained unreacted $CF_2{=}CFCl$ and the decomposition products COF_2 and $CF_3CFBrCl$. IR (cm^{-1}): 1287 (s); 1237 (s); 1188 (s); 1143 (s); 1121 (s); 1029 (m); 956 (m); 927 (m); 700 (w); 602 (w). ^{19}F

NMR ($CDCl_3$) δ: $CF_3^A–CF^BBr–CF_2^C–O–CF^DCl–CF_2^ECl$: A = −75.81 (d–t, 3F) ppm, $J_{AB} = 9.0$ Hz, $J_{AC} = 8.9$ Hz; B = −144.1 (m, 1F) ppm; C = −78.6 ppm, −79.5 ppm (AB pattern, 2F); D = −76.9 (m, 1F) ppm; E = −70.7 (d–d, 2F) ppm; $J_{DE} = 7.1$ Hz, J_{CE}(?) = 4.7 Hz.

*Reaction of **3d** with $CF_2{=}CH_2$*

The −111 °C trap contained only $CFCl_3$ used as the solvent (5 mmol), the −196 °C trap contained COF_2, $CF_3CFBrCl$ and unreacted $CF_2{=}CH_2$. The single addition product collected in the −78 °C trap (0.15 mmol, 8% yield). IR (cm^{-1}): 2981 (w); 1433 (w); 1337 (s); 1289 (vs); 1261 (vs); 1234 (vs); 1177 (s); 1157 (s); 1136 (vs); 1115 (s); 1084 (vs); 1026 (m); 964 (m); 931 (s); 899 (w); 846 (w); 803 (w); 733 (m). ^1H NMR (acetone-d_6) δ: 4.37 (t) ppm, $^3J_{HF} = 9.6$ Hz. ^{19}F NMR (acetone-d_6) δ: $CF_3^A–CF^BBr–CF_2^C–O–CF_2^D–CH_2Cl$: A = −75.8 (q, 3F) ppm, $J_{AB} = J_{AC} = 9.5$ Hz; B = −143.5 (q, 1F) ppm; C = −78.3 ppm, −79.4 ppm (AB pattern); D = −74.2 (m, 2F) ppm.

Results and discussion

The ^{19}F NMR spectra prove conclusively the existence of the fluoroxy compounds at low temperature (⩽ −40 °C). The characteristic large downfield shift of the –OF fluorine atoms is a general property of fluoroxy compounds [4], and indicates the relative lack of electron density around the fluorine atom. This is in accord with the electrophilic nature of –OF compounds in selected reactions [17]. All of the fluoroxy compounds described here have –OF resonances in the range 140–155 ppm, typical for an –OF group bound to a halogenated alkyl group.

For an –OF group bonded to an asymmetric carbon, the fluorine resonance is greatly complicated by the different coupling constants. For example, compounds **2a**, **2c** and **2g** all exhibit complex patterns for the –OF fluorines. In **2e**, the –OF signal is also complex due to the apparent nonequivalence of the $–CFCl_2$ groups. This is assumed to be a result of hindered rotation. In most cases, an asymmetric carbon renders the neighboring $–CF_2–$ fluorines diastereotopic and AB patterns of varying complexity result, complicating the assignments. The AB coupling constants for these fluorines range from 17 Hz to 306 Hz, depending upon their type and location in the molecule. Most of the $ClCF_2–$ groups bound to an asymmetric carbon have $^2J_{FF}$ values in the 130 –180 Hz range.

The spectra for the analogous hypochlorites are somewhat simpler due to the absence of coupling to the –OX group. However, AB patterns for $XCF_2–$ groups are the general rule when an asymmetric carbon atom was present in the molecule. An exception are the $ClCF_2–$ fluorines in **2h**. These fluorines appear as a single triplet. The AB patterns for X = H exhibited smaller $^2J_{FF}$ values. The $^2J_{HF}$ coupling and $^2J_{FF}$ values were both near 50 Hz for the $HCF_2–$ groups and the spectra are more properly considered as ABX spin systems, but no detailed analysis was made.

The majority of the NMR spectra were taken at low ($\leqslant -40$ °C) temperatures. Compounds **2e–h** and **3a–d** are all very unstable at room temperature, decomposing in minutes. Compounds **2a–d** can be handled at room temperature as long as the pressure is kept relatively low ($\leqslant 10$ Torr). No explosive decompositions were observed for these materials except for **2c**, but rapid spontaneous decompositions of **2b,d** were observed when the vapor pressure of the compounds exceeded ~ 10 Torr.

The decomposition pathways for the hypochlorites and fluoroxy compounds are easily predicted in most cases [7, 9, 16, 18–20]. In general, the O–X bond is broken homolytically, producing $X^{\bullet}$ and $R_xO^{\bullet}$ radicals in an initiation step. If two α-F atoms are present, COF_2 is eliminated from $R_xO^{\bullet}$, and the resulting $R_x^{\bullet}$ radical abstracts halogen from the hypohalite in a very efficient process, as evidenced by the lack of any products resulting from coupling of the two R_x groups. When only one α-F atom is present, an acyl fluoride is eliminated instead of COF_2 and the decomposition process is similar. When the two R_x groups in **2** are not equivalent, the elimination of both types of $R_x^{\bullet}$ radical from the intermediate $R_x(R_x')CFO^{\bullet}$ radical was generally observed.

Reactions of the fluoroxy and hypochlorite compounds were carried out in each case with $CF_2{=}CFCl$ and $CF_3{=}CH_2$ in order to compare their reactivities and their potential as useful sources of halogenated ethers with a variety of alkenes. These reactions also provided further verification of the existence of the respective –OX derivatives. Of particular interest was the effect of the substituents in compounds **2** and **3** on the yields in these reactions and on the regiospecificity of the reactions with the unsymmetrical alkenes.

The products of the addition reactions are summarized in Tables 1 and 2. The fluoroethers are very stable, inert, clear, colorless liquids at room temperature. As indicated in the experimental section, NMR spectroscopy allowed easy identification of the products and their ratios in the case of regio isomers, in spite of the complexity of many of the observed spectra. In the case of isomers in nonregiospecific reactions, these could not be separated practically. Infrared spectra provided supportive evidence for the addition products and mass spectra provided good evidence for the ethers. The latter are interesting in the complete lack of parent ions in either the EI or CI mass spectra. This seems to be quite general [8] for highly fluorinated ethers and very intense ions were found for $(M-X)^+$, especially in the CI spectra. We assume that this results from protonation at oxygen in the ethers to form an unstable oxonium ion, which immediately undergoes loss of HX involving the adjacent α-fluorine or chlorine atoms.

It is interesting to compare the isolated yields of the fluoroethers produced by these reactions. There seems to be no general trend for the reaction yields in $CF_2{=}CFCl$ versus $CF_2{=}CH_2$, but in the cases of **2a**, **2c**, **2d** and **2e** the yields in the reactions with $CF_2{=}CFCl$ were significantly higher than in those with $CF_2{=}CH_2$. For the other –OX derivatives, the yields were very similar for $X = Cl$ and F. The overall yields for the reactions of the fluoroxy

TABLE 1

Summary of reaction conditions and products of the fluoroxy compounds with $CF_2{=}CFCl$ and $CF_2{=}CH_2$

Fluoroxy compound	Alkene	Conditions [temp. range (°C), time (h)]	Products
$CF_3CF(CF_2Cl)OF$ (**2a**)	$CF_2{=}CFCl$	$-140 \sim 22$ (20)	$ClCF_2CF(CF_3)OCF_2CF_2Cl$ (80)^a, $ClCF_2CF(CF_3)OCFClCF_3$ (20) [80]^b
	$CF_2{=}CH_2$	$-140 \sim 22$ (20)	$ClCF_2CF(CF_3)OCF_2{-}CH_2F$ (43), $ClCF_2CF(CF_3)OCH_2CF_3$ (57) [70]
$CF_3CF(CF_2H)OF$ (**2c**)	$CF_2{=}CFCl$	$-142 \sim 23$ (22)	$HCF_2CF(CF_3)OCF_2CF_2Cl$ (>99), $HCF_2CF(CF_3)OCFClCF_3$ (<1) [35]
	$CF_2{=}CH_2$	$-138 \sim 23$ (20)	$HCF_2CF(CF_3)OCF_2CH_2F$ (23), $HCF_2CF(CF_3)OCH_2CF_3$ (76) [25]
$(ClCF_2)_2CFOF$ (**2e**)	$CF_2{=}CFCl$	$-140 \sim 20$ (24)	$(ClCF_2)_2CFOCF_2CF_2Cl$ (65), $(ClCF_2)_2CFOCFClCF_3$ (35) [53]
	$CF_2{=}CH_2$	$-140 \sim 22$ (18)	$(ClCF_2)_2CFOCF_2CH_2F$ (25), $(ClCF_2)_2CFOCH_2CF_3$ (75) [30]
$HCF_2CF(CF_2Cl)OF$ (**2g**)	$CF_2{=}CFCl$	$-137 \sim 20$ (22)	$HCF_2CF(CF_2Cl)OCF_2CF_2Cl$ (>99), $HCF_2CF(CF_2Cl)OCFClCF_3$ (~0) [42]
	$CF_2{=}CH_2$	$-144 \sim 21$ (24)	$HCF_2CF(CF_2Cl)OCF_2CH_2F$ (33), $HCF_2CF(CF_2Cl)OCH_2CF_3$ (66) [44]
$CF_3CFClCF_2OF$ (**3a**)	$CF_2{=}CFCl$	$-140 \sim 22$ (20)	no addition products
	$CF_2{=}CH_2$	$-135 \sim 21$ (19)	no addition products
$CF_3CFBrCF_2OF$ (**3c**)	$CF_2{=}CFCl$	$-139 \sim 22$ (21)	$CF_3CFBrCF_2OCF_2CF_2Cl$ (<1), $CF_3CFBrCF_2OCFClCF_3$ (<99) [10]
	$CF_2{=}CH_2$	$-141 \sim 19$ (19)	$CF_3CFBrCF_2OCF_2CH_2F$ (<1), $CF_3CFBrCF_2OCH_2CF_3$ (<99) [20]

[a] Relative % yield based on ^{19}F NMR spectroscopy (and ^1H NMR spectroscopy if appropriate) integration intensities.

[b] Total isolated yield by PVT measurements.

TABLE 2

Summary of reaction conditions and products of the hypochlorites with $CF_2{=}CFCl$ and $CF_2{=}CH_2$

Hypochlorite	Alkene	Conditions [temp. range (°C), time (h)]	Products
$ClCF_2(CF_3)CFOCl$ (**2b**)	$CF_2{=}CFCl$	−140 ~ 22 (20)	$ClCF_2CF(CF_3)OCF_2CFCl_2$ (>99)[a], $ClCF_2CF(CF_3)OCFClCF_2Cl$ (<1) [70][b]
	$CF_2{=}CH_2$	−139 ~ 20 (24)	$ClCF_2CF(CF_3)OCF_2CH_2Cl$ (>99), $ClCF_2CF(CF_3)OCH_2CF_2Cl$ (<1) [70]
$HCF_2CF(CF_3)OCl$ (**2d**)	$CF_2{=}CFCl$	−135 ~ 25 (18)	$HCF_2CF(CF_3)OCF_2CFCl_2$ (>99), $HCF_2CF(CF_3)OCFClCF_2Cl$ (<1) [40]
	$CF_2{=}CH_2$	−141 ~ 25 (24)	$HCF_2CF(CF_3)OCF_2CH_2Cl$ (35), $HCF_2CF(CF_3)OCH_2CF_2Cl$ (65) [27]
$(ClCF_2)_2CFOCl$ (**2f**)	$CF_2{=}CFCl$	−145 ~ 21 (24)	$(ClCF_2)_2CFOCF_2CFCl_2$ (>99), $(ClCF_2)_2CFOCFClCF_2Cl$ (<1) [10]
	$CF_2{=}CH_2$	−140 ~ 22 (20)	$(ClCF_2)_2CFOCF_2CH_2Cl$ (>99), $(ClCF_2)_2CFOCH_2CF_2Cl$ (<1) [5]
$HCF_2CF(CF_2Cl)OCl$ (**2h**)	$CF_2{=}CFCl$	−136 ~ 20 (18)	$HCF_2CF(CF_2Cl)OCF_2CFCl_2$ (>95), $HCF_2CF(CF_2Cl)OCFClCF_2Cl$ (<5) [10]
	$CF_2{=}CH_2$	−138 ~ 21 (20)	$HCF_2CF(CF_2Cl)OCF_2CH_2Cl$ (40), $HCF_2CF(CF_2Cl)OCH_2CF_2Cl$ (60) [11]
$CF_3CFClCF_2OCl$ (**3b**)	$CF_2{=}CFCl$	−141 ~ 22 (22)	$CF_3CFClCF_2OCF_2CFCl_2$ (<1), $CF_3CFClCF_2OCFClCF_2Cl$ (>99) [22]
	$CF_2{=}CH_2$	−140 ~ 21 (20)	$CF_3CFClCF_2OCF_2CH_2Cl$ (>99), $CF_3CFClCF_2OCH_2CF_2Cl$ (<1) [31]
$CF_3CFBrCF_2OCl$ (**3d**)	$CF_2{=}CFCl$	−141 ~ 22 (19)	$CF_3CFBrCF_2OCF_2CFCl_2$ (0), $CF_3CFBrCF_2OCFClCF_2Cl$ (99) [28]
	$CF_2{=}CH_2$	−138 ~ 20 (24)	$CF_3CFBrCF_2OCF_2CH_2Cl$ (>99), $CF_3CFBrCF_2OCH_2CF_2Cl$ (<1) [8]

[a] Relative % yield based on ^{19}F NMR spectroscopy (and ^{1}H NMR spectroscopy if appropriate) integration intensities.

[b] Total isolated yield by PVT measurements.

derivatives were generally higher than those for the hypochlorites and in general the yields parallel the thermal stabilities but not exclusively. In general, carbon branching in fluoroxy compounds usually leads to a decrease in stability, i.e. $CF_3CF_2CF_2OF > (C_2F_3)_2CFOF$, but for hypochlorites the opposite is usually true. The presence of substituents other than fluorine on carbon lowers the stability of both the –OF and –OCl derivatives. Hydrogen has a greater effect in this regard on fluoroxy compounds, chlorine is similar for both –OF and –OCl and bromine is equally destabilizing for both. The reactions leading to the highest isolated yields were those for **2a** and **2b**, which contain only one chlorine atom. Both were easily handled in the vacuum line at room temperature without extensive decomposition, whereas the analogs **2c** and **2d** containing hydrogen decomposed slowly over a period of several hours at 22 °C. All of the other hypochlorites and fluoroxy compounds prepared in this work decomposed within minutes at room temperature.

When one examines the distribution of regio isomers from the reaction of fluoroxy compounds and hypochlorites with $CF_2=CFCl$ and $CF_2=CH_2$, there is a pronounced tendency for the hypochlorite additions to show higher regioselectivity than the respective fluoroxy additions. This result was expected based on previous reports [4, 20]. In some cases, opposite regio isomers predominated for –OCl versus –OF additions, i.e. **2a**–**b**, **2e**–**f** and **3c**–**d** with $CF_2=CH_2$. The fluoroalkenes used in this study were somewhat deactivated towards electrophilic addition, $CF_2=CFCl$ more so than $CF_2=CH_2$. Trifluoromethyl hypochlorite is known to react very quickly with alkenes such as $CH_3–CH=CH_2$, but much more slowly with halogenated alkenes such as $CF_2=CFCl$ or $CF_2–CF=CF_2$ [20]. Fluoroxytrifluoromethane was very reactive with all the olefins and controlling the addition to activated alkenes such as 2-butene was impossible [20]. The regiochemistry of the addition of CF_3OCl and CF_3OF, and other R_fOX compounds, to alkenes is well established [20, 21], and the addition products here are consistent with the previously reported results.

We believe that these fluoroxy addition reactions probably proceed via a free-radical-type pathway. Although several fluoroxy addition reactions showed some selectivity, overall the selectivity was less than that for the hypochlorite additions. The R_fOCl derivatives probably react with olefins in a rather concerted manner, giving rise to Markovnikov-like addition products in most cases, although there were exceptions. For the latter, in the cases where the anti-Markovnikov isomer predominated, there were significant amounts of both isomers. In those which followed Markovnikov-like addition, one isomer was usually present in 95% or greater abundance.

In conclusion, it is apparent from this and other work that many different types of functionalized hypohalites can be prepared and characterized spectroscopically, but the stability of these compounds is not easily predicted. The presence of a CF_3 group α to the –OX function seems to enhance the stability, whereas other α groups such as HCF_2– or $–ClCF_2$ do not. Two α-F atoms give low thermal stability in many of these materials, with two exceptions being $ClCF_2CF_2OF$ [8, 10] and $ClCF_2CFClCF_2OF$ [8], which can be handled easily at ambient temperature. The corresponding –OCl derivatives are unstable. The presence of a CF_3 group γ to the –OX function (i.e. CF_3CFYCF_2OX, $\gamma = Cl$, Br) offers no enhancement of stability, with these compounds showing decomposition products even at −70 °C. In addition, $CF_3CFClCF_2OF$ showed no addition products when attempts were made to react it with $CF_2{=}CFCl$ and $CF_2{=}CH_2$. All others could be reacted with fluoroalkenes to give the corresponding ethers, although the yields in many cases were low. For enhanced yields of the ethers, the reaction of the R_f–OX compounds, immediately after preparation, with alkenes in a flow system seems to provide a better alternative [22]. This method also allowed larger scale preparations upon which industrial applications could be based.

Acknowledgements

The authors wish to thank Ausimont, SpA for their generous financial support of this work. Also we are indebted to Margaret Kotun for her invaluable help in obtaining the low-temperature NMR spectra.

References

1 G.H. Cady, *XVIIth International Congress of Pure and Applied Chemistry*, Butterworths, London, 1960, Vol. 1, p. 205.
2 C.J. Hoffman, *Chem. Rev.*, *64* (1964) 91.
3 M. Lustig and J.M. Shreeve, *Adv. Fluorine Chem.*, *7* (1973) 175.
4 J.M. Shreeve, *Adv. Inorg. Radiochem.*, *26* (1983) 119.
5 F.M. Mukhametshin, *Russ. Chem. Rev.*, *49* (1980) 668.
6 C.J. Schack and K.O. Christe, *Isr. J. Chem.*, *17* (1978) 20.
7 W. Storzer and D.D. DesMarteau, *Inorg. Chem.*, *30* (1991) 4821.
8 B.B. Randolph and D.D. DesMarteau, manuscript in preparation.
9 W. Storzer and D.D. DesMarteau, *Inorg. Chem.*, *30* (1991) 4122.
10 J.K. Ruff, A.R. Pitochelli and M. Lustig, *J. Am. Chem. Soc.*, *88* (1966) 4531.
11 D.E. Gould, L.P. Anderson, D.E. Young and W.B. Fox, *J. Am. Chem. Soc.*, *92* (1970) 2313.
12 L. Heinrich, *Z. Chem.*, *7* (1968) 257.
13 R. Watts, C.G. Allison, K.B. Barthold and P. Tarrant, *J. Fluorine Chem.*, *3* (1973) 7.
14 D.W. Wiley and H.E. Simmons, *J. Org. Chem.*, *29* (1964) 1876.
15 W.J. Middleton and R.V. Lindsey, *J. Am. Chem. Soc.*, *86* (1964) 4948.
16 D.E. Gould, L.P. Anderson, D.E. Young and W.B. Fox, *J. Am. Chem. Soc.*, *91* (1969) 1310.
17 S. Rozen, *Acc. Chem. Res.*, *21* (1988) 307.
18 J.H. Prager and P.G. Thompson, *J. Am. Chem. Soc.*, *87* (1965) 230.
19 C.J. Shack and A.W. May, *J. Am. Chem. Soc.*, *91* (1969) 2902.
20 K.K. Johri and D.D. DesMarteau, *J. Org. Chem.*, *48* (1983) 242.
21 J.M. Canich, G.L. Gard and J.M. Shreeve, *Inorg. Chem.*, *23* (1984) 441.
22 L. Conte, G. Gambaretto, M. Carbini and E. Legnaro, presented at the *12th Int. Symp. Fluorine Chem.*, Santa Cruz, CA, August 7–12, 1988, Abstract P. 223.