Reagents. In a typical run, to a stirred solution of sulfoxide 15 (251 mg, 1.0 mmol) in THF (10 mL) was added 1.58 M *n*-butyllithium (0.13 mL, 0.2 mmol) under N_2 atmosphere at -78 °C. The mixture was stirred for 15 min at -78 °C. After hydrolysis and extraction with dichloromethane (3 × 20 mL), the extract was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, hexane/EtOAc = 7/3) to give *n*-butyl *p*-tolyl sulfoxide (**5a**) in 13% and recovered sulfoxide 15 in 83% yield. Optical rotation ($[\alpha]_D^{25}$) of the recovered sulfoxide 15 is 0° (*c* = 1.0, acetone).

Reactions of ^{18}O-Labeled Phenyl *p*-Tolyl Sulfoxide (4c) with *n*-Butyllithium. The reaction was carried out according to the same procedure of the optically active sulfoxide **4b** with *n*-butyllithium. The products were separated by column and preparative liquid chromatography, and their ^{18}O contents were determined by mass spectrometry. The ^{18}O content of each sulfoxide is 38 atom %.

Cross-Over Reaction of ^{18}O-Labeled Diphenyl Sulfoxide (7b) and Unlabeled Di-*p*-tolyl Sulfoxide (8) with Phenyllithium. To a solution of sulfoxide **7b** (101 mg, 0.5 mmol) and di-*p*-tolyl sulfoxide (8, 115 mg, 0.5 mmol) in THF (10 mL) under N_2 atmosphere at -78 °C was added 1.8 M phenyllithium (0.11 mL, 0.2 mmol) in ether/cyclohexane solution. After 15 min, water was added and the mixture was extracted with dichloromethane (3 × 20 mL). The extract was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by preparative liquid chromatography to afford diphenyl sulfoxide in 26%, phenyl *p*-tolyl sulfoxide in 51%, and di-*p*-tolyl sulfoxide in 17% yield. The ^{18}O contents of three sulfoxides are 19 atom % by mass spectrometry.

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Redox-Initiated Per(poly)fluoroalkylation of Olefins by Per(poly)fluoroalkyl Chlorides

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The per(poly)fluoroalkylation of olefins by per(poly)fluoroalkyl chlorides, initiated by ammonium persulfate/sodium formate ($(NH_4)_2S_2O_8/HCO_2Na$), is described. The reaction proceeds smoothly in polar aprotic solvents. The presence of functional groups like sodium carboxylate or sulfonate in the polyfluoroalkyl chloride appear to facilitate the reaction. The reaction appears to be initiated by a single-electron transfer, represents the first example of the reactivity of per(poly)fluoroalkyl chlorides, and also demonstrates their use as per(poly)fluoroalkylating agents. For α-chloro-ω-iodoperfluoroalkanes only the carbon–iodine bond is cleaved during the reaction. An explanation for the apparent stability of the carbon–chlorine bond in such compounds is given.

Introduction

The development of methods for introducing per(poly)fluoroalkyl groups into organic molecules is an important goal of synthetic organic chemistry. Traditional methods involve the addition of organofluorine compounds like R_fX (X = I, Br, CCl_3, SO_2Cl, SO_2Br, or SO_2Na) to alkenes and alkynes.[1] Such additions are commonly catalyzed by peroxides,[2] main-group metals,[3] transition-metal complexes,[4] or $Na_2S_2O_4$.[5] Whether the additions occur through a free-radical, ionic, or single-electron-transfer (SET) mechanism, the reactivity of $-CF_2X$ generally decreases in the following order:[6] $CF_2I > CCl_3 \sim CF_2Br > CFCl_2$. Until now, nearly all per(poly)fluoroalkylations have involved the use of R_fI, R_fBr, or R_fCCl_3.

Table I. Yields of the Adducts $R_fCH_2CH_2R$ (1-10) from the Per(poly)fluoroalkylation of Olefins (CH_2=CHR) by R_fCl

adduct[a]	R_fCl R_f =	CH_2=CHR R =	isolated yield (%)
1	$(CF_2)_8OCF_2CF_2SO_3Na$	*n*-C_4H_9	87
2	$(CF_2)_8OCF_2CF_2SO_3Na$	*n*-C_5H_{11}	79
3	$(CF_2)_8OCF_2CF_3$	*n*-C_5H_{11}	76
4	$(CF_2)_8OCF_2CF_3$	CH_2Br	52
5	$(CF_2)_8OCF_2CF_3$	CH_2OAc	74
6	$(CF_2)_6COONa$	*n*-C_5H_{11}	87[a]
7	$(CF_2)_7COONa$	CH_2OAc	74[a]
8	$(CF_2)_7COONa$	*n*-C_4H_9	85[a]
9	$(CF_2)_7COONa$	*n*-C_5H_{11}	67[a]
10	$(CF_2)_7COONa$	$CH_2Si(CH_3)_3$	69[a]

[a] The yield is that of the corresponding methyl ester $RCH_2CH_2(CF_2)_nCOOCH_3$ (*n* = 6, 7), formed by treating the initial product with methanolic H_2SO_4.

Because they apparently are stable in the presence of various initiators, few reports dealing with the use of R_fCFCl_2 as per(poly)fluoroalkylating agents have appeared in the literature. Perfluoroalkyl chlorides, R_fCF_2Cl, appear to be chemically inert and are thermally stable up to 600 °C, even in the presence of NO_2.[7] Thus, such compounds have never been reported to be useful for synthetic work.

Although the redox telomerization of fluorine-containing olefinic monomers is rather well-known, the redox-initiated

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Table II. Effect of X of $Cl(CF_2)_7X$ on the Per(poly)fluoroalkylation of 1-Heptene

R_fCl	temp (°C)	time (h)	conversion[a] (%)
$Cl(CF_2)_7COONa$	50	4	100
$Cl(CF_2)_7COOMe$	50	8	76
$Cl(CF_2)_7COOH$	60	15	45

[a] Determined by ^{19}F NMR.

radical addition of polyhaloalkanes to olefins has been little studied. For example, Burton reported the CuI–ethanolamine-catalyzed addition of polyhaloalkanes to 1-octene. Recent work by us[8] showed that, when initiated by the reaction of certain redox pairs, nearly chemically inert 1,1,2-trichlorotrifluoroethane ($ClCF_2CFCl_2$) can add to alkenes and alkynes under mild conditions. Such results encouraged us to test the effectiveness of various redox pairs in catalyzing the reactions of R_fCF_2Cl. We found that, in the presence of the redox pair $(NH_4)_2S_2O_8/HCO_2Na$, per(poly)fluoroalkyl chlorides undergo facile radical addition to olefins.

Results and Discussion

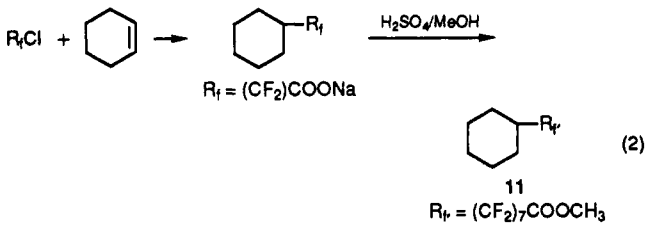
In the presence of an equimolar mixture of $(NH_4)_2S_2O_8$ and $HCO_2Na\cdot 2H_2O$, the per(poly)fluoroalkylation of olefins by R_fCl proceeded smoothly in DMF or DMSO suspension at 40–60 °C over 4–6 h to give the corresponding per(poly)fluoroalkanes (eq 1) in good yield. The results are shown in Table I.

$$R_fCl + CH_2{=}CHR \rightarrow R_fCH_2CH_2R \quad (1)$$
$$(1\text{–}10)$$

Addition does not occur below 40 °C. For example, when an equimolar mixture of 3-oxa-11-chloroperfluoroundecane sulfonyl fluoride ($Cl(CF_2)_8OCF_2CF_2SO_2F$), 1-hexene, $(NH_4)_2S_2O_8$, and $HCO_2Na\cdot 2H_2O$ in DMF was warmed at 35 °C for 6 h, only $Cl(CF_2)_8OCF_2CF_2SO_3Na$ was formed. However, at 40 °C, under otherwise identical conditions, the desired product (1) was formed in excellent yield.

The per(poly)fluoroalkylation of olefins by R_fCl is quite solvent sensitive. In aqueous CH_3CN, no reaction occurred, even after 10 h at 50 °C.

Disubstituted olefins like cyclohexene were also reactive (eq 2).



(2)

The presence of other functional groups in the polyfluoroalkyl chloride affects the reaction. Thus, when $Cl(CF_2)_7X$ (X = COONa, COOMe, COOH) was allowed to react with 1-heptene, the extent of conversion to the product depended on the nature of X (Table II).

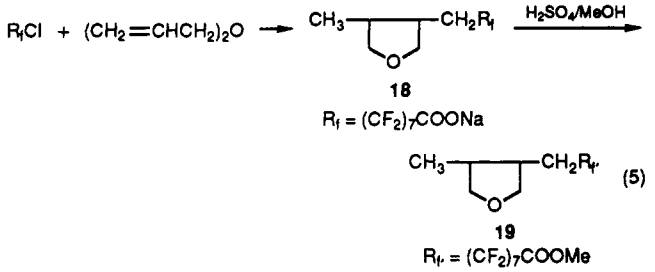
With α-chloro-ω-iodoperfluoroalkanes, only the carbon–iodine bond is cleaved. For example, in the presence of a catalytic amount of the redox pair, $Cl(CF_2)_nI$ (n = 4, 6) reacted smoothly with 1-heptene to give **12** (or **13**). The carbon–chlorine bond remained intact, even when the mole ratio $(NH_4)_2S_2O_8/HCO_2Na$/1-heptene/$Cl(CF_2)_nI$ was changed to 3:3:4:1 (eq 3). Cleavage of the carbon–chlorine bond was observed only after the iodine atom of $Cl(CF_2)_nI$ was replaced by SO_3Na. Thus, compounds **14** (n = 4) and **15** (n = 6) reacted with 1-heptene to yield **16** and **17** (eq 4). These phenomena will be explained later.

$$Cl(CF_2)_nI + n\text{-}C_5H_{11}CH{=}CH_2 \rightarrow Cl(CF_2)_nCH_2CH(I)(CH_2)_4CH_3 \quad (3)$$
12 (n = 4); **13** (n = 6)

$$Cl(CF_2)_nI \xrightarrow[NaHCO_3]{Na_2S_2O_4} Cl(CF_2)_nSO_2Na \xrightarrow{Cl_2} Cl(CF_2)_nSO_2Cl \xrightarrow{NaOH} Cl(CF_2)_nSO_3Na$$
14 (n = 4); **15** (n = 6)

$$Cl(CF_2)_nSO_3Na + n\text{-}C_5H_{11}CH{=}CH_2 \rightarrow CH_3(CH_2)_6(CF_2)_nSO_3Na \quad (4)$$
16 (n = 4); **17** (n = 16)

Diallyl ether has been widely used as a probe to show that a reaction proceeds by a radical mechanism.[9] The reaction of $Cl(CF_2)_7COONa$ with allyl ether, initiated by the reaction of the redox pair, produced the cyclic adduct **18** (eq 5). This result implies that a radical intermediate is formed during the reaction.



(5)

Ammonium persulfate is a one-electron oxidant that spontaneously decomposes to $SO_4^{\bullet-}$. When $(NH_4)_2S_2O_8$ and HCO_2Na are mixed together, $CO_2^{\bullet-}$ is formed.[10] Experiments showed that the presence of both $(NH_4)_2S_2O_8$ and $HCO_2Na\cdot 2H_2O$ was necessary for the per(poly)fluoroalkylation of olefins by R_fCl to occur. It thus seems likely that the reaction is initiated by the transfer of a single electron to R_fCl from $CO_2^{\bullet-}$ rather than from $SO_4^{\bullet-}$. The intermediate $R_f^{\bullet}$ radical could be trapped by t-BuNO. Mixtures of the redox couple and R_fCl that also contained t-BuNO displayed a strong, persistent, and well-resolved (α_N = 11.87 G, α_F = 18.94 G) ESR spectrum attributable to the nitroxide radical $t\text{-}Bu_2N(O^{\bullet})R_f$. Because the carbon–chlorine bond of perfluoroalkyl chlorides is strong, $R_fCH_2\dot{C}HR$, the product of the addition of $R_f^{\bullet}$ to the olefins cannot abstract a chlorine atom from R_fCl to form $R_fCH_2CH(Cl)R$. Instead, it abstracts a hydrogen atom, presumably from the solvent, to form $R_fCH_2CH_2R$. The best results were obtained when the mole ratio $R_fCl/(NH_4)_2S_2O_8/HCO_2Na\cdot 2H_2O$ was 1:0.5–1:1. It is thus obvious that the reaction is not a conventional radical chain process. A tentative mechanism for the addition is shown in Scheme I.

Scheme I

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-}$$

$$SO_4^{\bullet-} + HCO_2^- \rightarrow HSO_4^- + CO_2^{\bullet-}$$

$$R_fCl + CO_2^{\bullet-} \rightarrow R_f^{\bullet} + CO_2 + Cl^-$$

$$R_f^{\bullet} + CH_2{=}CHR \rightarrow R_fCH_2\dot{C}HR \xrightarrow{H} R_fCH_2CH_2R$$

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On the other hand, when $Cl(CF_2)_nI$ was allowed to react with an olefin in the presence of $(NH_4)_2S_2O_8/HCOONa$, the carbon–iodine bond was cleaved to begin a classic radical chain process (Scheme II). Thus, only a catalytic amount of initiator was required.

Scheme II

$$CO_2^{\bullet-} + R_fI \rightarrow R_f^{\bullet} + CO_2 + I^-$$

$$R_f^{\bullet} + CH_2{=}CHR \rightarrow R_fCH_2\dot{C}HR \xrightarrow{R_fI} R_fCH_2CH(I)R + R_f^{\bullet}$$

According to Scheme II, iodide ion would be formed during the course of an $(NH_4)_2S_2O_8/HCO_2Na{\cdot}2H_2O$-initiated addition of $Cl(CF_2)_nI$ to an alkene. Because iodide ion is a one-electron reductant,[11] it would be oxidized by ammonium persulfate to iodine (Scheme III). Thus, the formation of the carbon dioxide anion radical would be suppressed. Because the presence of $CO_2^{\bullet-}$ is necessary for the carbon–chlorine bond to be cleaved (Scheme I), in its absence the carbon–chlorine bond of an α-chloro-ω-iodoperfluoroalkane remains intact.

Scheme III

$$I^- + SO_4^{\bullet-} \rightarrow I^{\bullet} + SO_4^{2-}$$

$$2I^{\bullet} \rightarrow I_2$$

$$I_2 + HCO_2Na \rightarrow CO_2 + HI + NaI$$

In conclusion, a convenient and practical method for the per(poly)fluoroalkylation of olefins by per(poly)fluoroalkyl chlorides has been developed. Apparently, the reaction is initiated by $CO_2^{\bullet-}$, which is generated by a reaction between the two members of the redox pairs $(NH_4)_2S_2O_8$ and HCO_2Na.

Experimental Section

General. Melting and boiling points are uncorrected. Infrared spectra of liquid films or KBr pellets were recorded with a Perkin–Elmer 983 spectrometer. ^1H NMR spectra (60 Hz) were recorded with a Varian EM-360A instrument. TMS served as an internal standard. ^{19}F NMR spectra (56.4 Hz) were recorded with a Varian EM-360L instrument. $CFCl_3$ served as an external standard. Chemical shifts (in ppm) are negative in sign for upfield shifts. Mass spectra were recorded with a Finnigan GC-MS-4021 spectrometer.

Preparation of $Cl(CF_2)_8OCF_2CF_2SO_2F$.[12] A 200-mL pressure vessel was charged with anhydrous KF (12 g, 0.21 mol), diglyme (35 mL), tetrafluoroethane sulfone (30 g, 0.16 mol), and excess Cl_2. The mixture was shaken for 10 min, and then 6-chloroperfluoro-1-hexene (35.5 g, 0.11 mol) was added. The mixture was shaken at 40 °C for 6 h and then was poured into ice/water. The two liquid layers that formed were separated. The organic layer was washed with water, dried, and distilled to give 19.0 g of $Cl(CF_2)_8OCF_2CF_2SO_2F$ (62% yield, bp 182 °C).

Preparation of $CF_3CF_2O(CF_2)_8Cl$.[12] A mixture of CoF_3 (32.5 g) and $Cl(CF_2)_8OCF_2CF_2SO_2F$ (76 g) was heated, with stirring, at 195 °C for 6 h. The crude product was washed with water, dried, and fractionally distilled to give $CF_3CF_2O(CF_2)_8Cl$.

Preparation of $Cl(CF_2)_nI$.[13] An evacuated 2-L autoclave was charged with 1-chloro-2-iodotetrafluoroethane (1048 g, 4 mol) and tetrafluoroethene (250 g, 2.5 mol). The mixture was then heated at 170–180 °C for 5 h, during which time the pressure within the autoclave decreased from 36 kg/cm to 17.5 kg/cm. Fractional distillation of the crude mixture of telomeric products gave 405 g of $Cl(CF_2)_4I$ (bp 104–105 °C), 253 g of $Cl(CF_2)_6I$ (bp 68 °C (45 mmHg)), and 134 g of $Cl(CF_2)_8I$ (bp 72–73 °C (12 mmHg)).

$Cl(CF_2)_nCOONa$ was prepared from $Cl(CF_2)_nI$.[14]

Per(poly)fluoroalkylation of Olefins by $Cl(CF_2)_8OCF_2CF_2SO_2F$. General Procedure. A mixture of $Cl(CF_2)_8OCF_2CF_2SO_2F$ (6.4 g, 10 mmol), an olefin (12.5 mmol), $(NH_4)_2S_2O_8$ (2.3 g, 10 mmol), $HCO_2Na{\cdot}2H_2O$ (1.1 g, 10 mmol), and DMF (30 mL) was stirred at 40 °C for 4 h. The mixture was then poured into water, and the whole was extracted thrice with EtOAc. The extract was washed with aqueous $NaHCO_3$ and brine and dried (Na_2SO_4). Evaporation of the solvent and two recrystallizations of the residue from water gave the pure product (1 or 2).

1: mp 92–94 °C; ^{19}F NMR (CD_3COCD_3) −83.1 (s, 2 F, CF_2O), −84.1 (s, 2 F, CF_2O), −114.5 (t, 2 F, J = 18.8 Hz, CF_2CH_2), −119.5 (s, 2 F, CF_2SO_3Na), −122.1 (s, 8 F, 4×CF_2), −124.4 (s, 2 F, CF_2), −126.4 (s, 2 F, CF_2) ppm; ^1H NMR (CD_3COCD_3) 1.07 (t, 3 H, J = 4 Hz, CH_3), 1.57 (m, 8 H, 4×CH_2), 2.83 (m, 2 H, CH_2CF_2) ppm; IR 1070 (s, SO_3Na) cm^{-1}. Anal. Calcd for $C_{16}H_{13}F_{20}O_4SNa$: C, 27.27; H, 1.85; F, 53.89. Found: C, 27.08; H, 1.77; F, 52.59.

2: mp 106–109 °C; ^{19}F NMR (CD_3COCD_3) −83.1 (s, 2 F, CF_2O), −84.1 (s, 2 F, CF_2O), −115.0 (t, 2 F, J = 18.8 Hz, CF_2CH_2), −119.1 (s, 2 F, CF_2SO_3Na), −122.8 (s, 8 F, 4×CF_2), −124.4 (s, 2 F, CF_2), −126.4 (s, 2 F, CF_2) ppm; ^1H NMR (CD_3COCD_3) 1.10 (t, 3 H, J = 4 Hz, CH_3), 1.62 (m, 10 H, 5×CH_2), 2.92 (m, 2 H, CH_2CF_2) ppm; IR 1065 (s, SO_3Na) cm^{-1}. Anal. Calcd for $C_{17}H_{15}F_{20}O_4SNa$: C, 28.41; H, 2.01; F, 52.92. Found: C, 28.76; H, 2.6; F, 51.89.

Per(poly)fluoroalkylation of Olefins by $CF_3CF_2O(CF_2)_8Cl$. General Procedure. A mixture of $CF_3CF_2O(CF_2)_8Cl$ (5.7 g, 10 mmol), olefin (12.5 mmol), $(NH_4)_2S_2O_8$ (2.3 g, 10 mmol), $HCO_2Na{\cdot}2H_2O$ (1.1 g, 10 mmol), and DMF (30 mL) was stirred at 50 °C for 7 h. The mixture was then poured into water, and the whole was extracted with Et_2O (3 × 30 mL). The extract was washed with brine and dried (Na_2SO_4). Evaporation of the solvent and distillation of the residue under reduced pressure gave the pure product (3, 4, or 5).

3: bp 135–137 °C (2 mmHg); ^{19}F NMR (neat) −82.4 (s, 3 F, CF_3), −84.1 (s, 2 F, CF_2O), −89.1 (s, 2 F, CF_2O), −118.1 (t, 2 F, J = 18.8 Hz, CF_2CH_2), −122.8 (s, 10 F, 5×CF_2), −126.4 (s, 2 F, CF_2) ppm; ^1H NMR (neat) 0.99 (t, 3 H, J = 3.8 Hz, CH_3), 1.48 (m, 10 H, 5×CH_2), 2.76 (m, 2 H, CH_2CF_2) ppm; mass spectrum m/e (relative intensity) 43 (C_3H_7, 100), 634 (M, 1.85). Anal. Calcd for $C_{17}H_{15}F_{21}O$: C, 32.18; H, 2.36; F, 62.93. Found: C, 32.34; H, 2.42; F, 61.96.

4: bp 154–155 °C (2 mmHg); ^{19}F NMR (neat) −81.8 (s, 3 F, CF_3), −83.5 (s, 2 F, CF_2O), −87.8 (s, 2 F, CF_2O), −117.1 (t, 2 F, J = 18.8 Hz, CF_2CH_2), −121.8 (s, 10 F, 5×CF_2), −129.4 (s, 2 F, CF_2) ppm; ^1H NMR (neat) 2.75–2.95 (m, 4 H, $CF_2CH_2CH_2$), 3.85 (m, 2 H, CH_2Br); mass spectrum m/e (relative intensity) 69 (CF_3, 100), 657 (M, 7.67). Anal. Calcd for $C_{13}H_6F_{21}OBr$: C, 23.74; H, 0.91; F, 60.73. Found: C, 23.58; H, 0.84; F, 61.22.

5: bp 146–148 °C (2 mmHg); ^{19}F NMR (neat) −82.8 (s, 3 F, CF_3), −84.5 (s, 2 F, CF_2O), −89.1 (s, 2 F, CF_2O), −119.8 (t, 2 F, J = 18.7 Hz, CF_2CH_2), −122.8 (s, 10 F, 5×CF_2), −127.4 (s, 2 F, CF_2) ppm; ^1H NMR (neat) 2.17 (s, 3 H, CH_3O), 2.22–2.85 (m, 4 H, $CH_2CH_2CF_2$), 4.40 (t, 2 H, J = 4 Hz, CH_2O) ppm; IR 1750 (s, C=O) cm^{-1}; mass spectrum m/e (relative intensity) 59 (CH_3COO, 100), 637 (M + 1, 62.45). Anal. Calcd for $C_{15}H_9F_{21}O_3$: C, 28.30; H, 1.42; F, 62.73. Found: C, 28.36; H, 1.45; F, 61.93.

Per(poly)fluoroalkylation of Olefins by $Cl(CF_2)_nCOONa$ (n = 6, 7). General Procedure. A mixture of $Cl(CF_2)_nCOONa$ (10 mmol), olefin (12.5 mmol), $(NH_4)_2S_2O_8$ (2.3 g, 10 mmol), $HCO_2Na{\cdot}2H_2O$ (1.1 g, 10 mmol), and DMF (30 mL) was stirred at 50 °C for 4 h. The mixture was then poured into water, and the whole was extracted with EtOAc (30 mL). The extract was washed with aqueous $NaHCO_3$ and then, repeatedly, with brine. Evaporation of the solvent from the extract gave a white solid. This was dissolved in CH_3OH (10 mL). Concentrated H_2SO_4 (10 mL) was added to the methanol solution and the mixture was stirred for 7–8 h at 70 °C. The mixture was then poured into water, and the whole was extracted with Et_2O. The extract was washed with aqueous $NaHCO_3$ and brine and then was dried (Na_2SO_4). Evaporation of the solvent and distillation of the residue under reduced pressure gave the pure product (6, 7, 8, 9, 10, 11, or 19).

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6: bp 134–135 °C (5 mmHg); ^{19}F NMR (neat) −115.1 (t, 2 F, J = 18.8 Hz, CF_2CH_2), 19.1 (s, 2 F, CF_2COOMe), −122.4 (s, 6 F, 3×CF_2), −124.1 (s, 2 F, CF_2) ppm; ^1H NMR (neat) 0.90 (t, 3 H, J = 4 Hz, CH_3), 1.30 (m, 10 H, 5×CH_2), 2.56–2.76 (m, 2 H, CF_2CH_2), 3.9 (s, 3 H, OCH_3) ppm; IR 1785 (s, C=O) cm^{-1}; mass spectrum m/e (relative intensity) 43 (C_3H_7, 100), 459 (M + 1, 1.35). Anal. Calcd for $C_{15}H_{18}F_{12}O_2$: C, 39.30; H, 3.93; F, 49.78. Found: C, 39.39; H, 3.91; F, 48.98.

7: bp 118–120 °C (2 mmHg); ^{19}F NMR (neat) −115.5 (t, 2 F, J = 18.6 Hz, CF_2CH_2), −119.8 (s, 2 F, CF_2COOMe), −122.4 (s, 10 F, 5×CF_2) ppm; ^1H NMR (neat) 2.06 (m, 7 H, CH_3CO + $CF_2CH_2CH_2$), 3.96 (s, 3 H, CH_3O), 4.4 (m, 2 H, CH_2O) ppm; IR 1780 (s, C=O) cm^{-1}; mass spectrum m/e (relative intensity) 59 (CH_3COO, 100), 511 (M + 1, 1.71). Anal. Calcd for $C_{14}H_{12}F_{14}O_4$: C, 32.94; H, 2.35; F, 52.16. Found: C, 32.84; H, 2.30; F, 53.06.

8: bp 105–106 °C (2 mmHg); ^{19}F NMR (neat) −114.8 (t, 2 F, J = 18.8 Hz, CF_2CH_2), −119.1 (s, 2 F, CF_2COONa), −122.1 (s, 6 F, 3×CF_2), −123.1 (s, 2 F, CF_2), −124.2 (s, 2 F, CF_2) ppm; ^1H NMR (neat) 0.95 (t, 3 H, J = 4 Hz, CH_3), 1.57 (m, 8 H, 4×CH_2), 2.56 (m, 2 H, CH_2CF_2), 3.97 (s, 3 H, CH_3O) ppm; IR 1788 (s, C=O) cm^{-1}; mass spectrum m/e (relative intensity) 43 (C_3H_7, 100), 495 (M + 1, 6.71). Anal. Calcd for $C_{15}H_{16}F_{14}O_2$: C, 36.44; H, 3.24: F, 53.85. Found: C, 37.14; H, 3.28; F, 52.92.

9: bp 108–109 °C (2 mmHg); ^{19}F NMR (neat) −115.1 (t, 2 F, J = 18.8 Hz, CF_2CH_2), −120.6 (s, 2 F, CF_2COOMe), −123.9 (s, 10 F, 5×CF_2) ppm; ^1H NMR (neat) 1.07 (t, 3 H, J = 4 Hz, CH_3), 1.72 (m, 10 H, 5×CH_2), 2.08 (m, 2 H, CH_2CF_2), 3.85 (s, 3 H, OCH_3) ppm; mass spectrum m/e (relative intensity) 43 (C_3H_7, 100), 509 (M + 1, 2.50). Anal. Calcd for $C_{16}H_{18}F_{14}O_2$: C, 37.79; H, 3.54; F, 52.36. Found: C, 36.97; H, 3.44; F, 51.08.

10: bp 145–147 °C (5 mmHg); ^{19}F NMR (neat) −115.1 (t, 2 F, J = 18.8 Hz, CF_2CH_2), −117.5 (s, 2 F, CF_2COOCH_3), −122.8 (s, 10 F, 5×CF_2) ppm; ^1H NMR (neat) 0.00 (s, 9 H, $Si(CH_3)_3$), 0.65–0.85 (m, 2 H, CH_2Si), 1.65–2.85 (m, 4 H, $CF_2CH_2CH_2$), 3.85 (s, 3 H, OCH_3) ppm; IR 1775 (s, C=O) cm^{-1}; mass spectrum m/e (relative intensity) 59 (CH_3COO, 100), 525 (M + 1, 2.50). Anal. Calcd for $C_{15}H_{18}F_{14}O_2Si$: C, 34.35; H, 3.44; F, 50.76. Found: C, 34.68; H, 3.69; F, 50.18.

11: bp 156–158 °C (5 mmHg); ^{19}F NMR (neat) −119.5 (s, 4 F, CF_2COOCH_3 and $CF_2C_6H_{11}$), −122.8 (s, 6 F, 3×CF_2), −123.4 (s, 4 F, 2×CF_2) ppm; ^1H NMR (neat) 1.20–2.20 (m, 11 H, C_6H_{11}), 3.8 (s, 3 H, $COOCH_3$) ppm; IR 1785 (s, C=O) cm^{-1}; mass spectrum m/e (relative intensity) 83 (C_6H_{11}, 100), 493 (M + 1, 3.47). Anal. Calcd for $C_{15}H_{14}F_{14}O_2$: C, 36.58; H, 2.85; F, 54.07. Found: C, 36.30; H, 2.84; F, 54.66.

19: bp 168–170 °C (5 mmHg); ^{19}F NMR (neat) −114.4 (t, 2 F, J = 18.8 Hz, CF_2CH_2), −119.5 (s, 2 F, CF_2COOCH_3), −122.4 (s, 6 F, 3×CF_2), −126.1 (s, 4 F, 2×CF_2) ppm; ^1H NMR (neat) 1.50 (t, 3 H, J = 4 Hz, CH_3), 2.73–3.30 (m, 4 H, CF_2CH_2, CHCH), 4.2–4.53 (m, 4 H, CH_2OCH_2), 4.6 (s, 3 H, $COOCH_3$) ppm; IR 1782 (s, C=O) cm^{-1}; mass spectrum m/e (relative intensity) 69 (C_4H_6O, 100), 509 (M + 1, 1.22). Anal. Calcd for $C_{15}H_{14}F_{14}O_3$: C, 35.43; H, 2.75; F, 52.36. Found: C, 35.32; H, 2.71; F, 53.02.

Addition of $Cl(CF_2)_nI$ (n = 4, 6) to 1-Heptene. General Procedure. A mixture of $Cl(CF_2)_nI$ (5 mmol), 1-heptene (1.9 g, 20 mmol), $(NH_4)_2S_2O_8$ (3.5 g, 15 mmol), $HCO_2Na{\cdot}2H_2O$ (1.6 g, 15 mmol), and DMF (30 mL) was stirred at 40 °C for 3–4 h. The mixture was then poured into water, and the whole was extracted thrice with Et_2O. The extract was washed with brine and dried (Na_2SO_4). Evaporation of the solvent and distillation of the residue under reduced pressure gave the pure product (12 or 13).

12: 92% yield; bp 76–78 °C (5 mmHg); ^{19}F NMR (neat) −68.5 (s, 2 F, CF_2Cl), −114.1 (t, 2 F, J = 18.8 Hz, CF_2CH_2), −120.1 (s, 2 F, CF_2), −123.4 (s, 2 F, CF_2) ppm; ^1H NMR (neat) 1.05 (m, 3 H, CH_3), 1.45 (m, 8 H, 4×CH_2), 2.85 (m, 2 H, CF_2CH_2), 4.35 (m, 1 H, CHI) ppm; IR 1445 (m, CHI) cm^{-1}. Anal. Calcd for $C_{11}H_{14}F_8ClI$: C, 28.67; H, 3.04; F, 33.00. Found: C, 28.72; H, 3.09; F, 33.23.

13: 86% yield; bp 107–108 °C (5 mmHg); ^{19}F NMR (neat) −68.5 (s, 2 F, CF_2Cl), −114.1 (t, 2 F, J = 18.8 Hz, CF_2CH_2), −121.1 (s, 2 F, CF_2), −122.4 (s, 4 F, 2×CF_2), −124.1 (s, 2 F, CF_2) ppm; ^1H NMR (neat) 0.98 (m, 3 H, CH_3), 1.40 (m, 8 H, 4×CH_2), 2.85 (m, 2 H, CF_2CH_2), 4.32 (m, 1 H, CHI) ppm; IR 1450 (m, CHI) cm^{-1}. Anal. Calcd for $C_{13}H_{14}F_{12}ClI$: C, 27.83; H, 2.49; F, 40.68. Found: C, 27.96; H, 2.35; F, 41.32.

Conversion of $Cl(CF_2)_nI$ (n = 4, 6) into $Cl(CF_2)_nSO_3Na$. General Procedure. A mixture of $Cl(CF_2)_nI$ (20 mmol), $Na_2S_2O_4$ (5.3 g, 30 mmol), $NaHCO_3$ (1.7 g, 20 mmol), CH_3CN (15 mL), and H_2O (45 mL) was stirred at 70 °C for 3 h. The mixture was then poured into a mixture of EtOAc (100 mL) and brine (50 mL). The two liquid layers that formed were separated. The organic layer was washed repeatedly with brine and dried (Na_2SO_4). Evaporation of the solvent gave a white solid. This was dissolved in H_2O (50 mL). Then Cl_2 gas was bubbled through the solution at rt for 1 h, during which time two liquid layers formed. The two were separated. Aqueous NaOH was added to the organic layer, and the mixture was stirred at rt for 1.5 h. Then, the mixture was poured into a mixture of EtOAc and brine. The two liquid layers that formed were separated. The organic layer was washed with brine and dried (Na_2SO_4). Evaporation of the solvent gave the pure product (14 or 15).

14: 72% yield; ^{19}F NMR ($CH_3COOC_2H_5$) −69.2 (s, 2 F, CF_2Cl), −113.3 (s, 2 F, CF_2SO_3Na), −119.8 (s, 2 F, CF_2), −121.8 (s, 2 F, CF_2) ppm; IR 1070 (s, SO_3Na) cm^{-1}.

15: 67% yield; ^{19}F NMR ($CH_3COOC_2H_5$) −68.1 (s, 2 F, CF_2Cl), −114.8 (s, 2 F, CF_2SO_3Na), −120.3 (s, 8 F, 4×CF_2) ppm; IR 1065 (s, SO_3Na) cm^{-1}.

Per(poly)fluoroalkylation of 1-Heptene by $Cl(CF_2)_nSO_3Na$ (n = 4, 6). General Procedure. Application of a method similar to that used for the addition of $Cl(CF_2)_8OCF_2CF_2SO_2F$ to olefins gave 16 and 17.

16: 64% yield; ^{19}F NMR (CD_3COCD_3) −114.1 (t, 2 F, J = 18.8 Hz, CF_2CH_2), −116.8 (s, 2 F, CF_2SO_3Na), −120.4 (s, 2 F, CF_2), −122.8 (s, 2 F, CF_2) ppm; ^1H NMR (CD_3COCD_3) 0.97 (m, 3 H, CH_3), 1.30–1.65 (m, 10 H, 5×CH_2), 2.70 (m, 2 H, CH_2CF_2) ppm; IR 1070 (s, SO_3Na) cm^{-1}. Anal. Calcd for $C_{11}H_{15}F_8O_3SNa$: C, 32.84; H, 3.73; F, 37.81. Found: C, 31.94; H, 3.70; F, 36.98.

17: 77% yield; ^{19}F NMR (CD_3COCD_3) −113.1 (t, 2 F, J = 18.8 Hz, CF_2CH_2), −114.8 (s, 2 F, CF_2SO_3Na), −121.4 (s, 6 F, 3×CF_2), −123.8 (s, 2 F, CF_2) ppm; ^1H NMR (CD_3COCD_3) 1.08 (m, 3 H, CH_3), 1.35–1.62 (m, 10 H, 5×CH_2), 2.96 (m, 2 H, CH_2CF_2) ppm; IR 1070 (s, SO_3Na) cm^{-1}. Anal Calcd for $C_{13}H_{15}F_{12}O_3SNa$: C, 31.08; H, 2.99; F, 45.42. Found: C, 30.79; H, 2.62; F, 46.72.

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Registry No. 1, 136176-28-8; 2, 136176-29-9; 3, 136176-30-2; 4, 136176-31-3; 5, 136176-32-4; 6, 136176-33-5; 7, 136176-34-6; 8, 136176-35-7; 9, 136176-36-8; 10, 136176-37-9; 11, 136176-38-0; 12 (n = 4), 103147-30-4; 13 (n = 6), 103190-37-0; 14 (n = 4), 136176-39-1; 15 (n = 6), 136176-40-4; 16 (n = 4), 136176-41-5; 17 (n = 6), 136176-42-6; 18, 136176-43-7; 19, 136176-44-8; $HO_3S(CF_2)_2O(CF_2)_8Cl{\cdot}Na$, 136176-45-9; $CF_3CF_2O(CF_2)_8Cl$, 84014-97-1; $Cl(CF_2)_6CO_2H{\cdot}Na$, 136176-46-0; $Cl(CF_2)_7CO_2H{\cdot}Na$, 136176-47-1; $H_2C{=}CH(CH_2)_3CH_3$, 592-41-6; $H_2C{=}CH(CH_2)_4CH_3$, 592-76-7; $H_2C{=}CHCH_2Br$, 106-95-6; $H_2C{=}CHCH_2OAc$, 591-87-7; $H_2C{=}CHCH_2TMS$, 762-72-1; $Cl(CF_2)_4I$, 5848-38-4; $Cl(CF_2)_6I$, 16486-97-8; $(CH_2{=}CHCH_2)_2O$, 557-40-4; $CHF_2CF_2SO_2F$, 82106-27-2; $Cl(CF_2)_4CF{=}CF_2$, 31001-56-6; $Cl(CF_2)_8O(CF_2)_2SO_2F$, 73606-15-2; $Cl(CF_2)_8I$, 16486-98-9; $Cl(CF_2)_2I$, 421-78-3; $F_2C{=}CF_2$, 116-14-3; $(NH_4)_2S_2O_8$, 7727-54-0; HCO_2Na, 141-53-7; cyclohexene, 110-83-8.