Synthesis of Halogenated Esters of Fluorinated Carboxylic Acids by the Regio- and Stereospecific Addition of Acyl Hypochlorites to Olefins

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Addition reactions of the fluorinated acyl hypochlorites CF_3CO_2Cl, $C_2F_5CO_2Cl$, n-$C_3F_7CO_2Cl$, $ClCF_2CO_2Cl$, and HCF_2CO_2Cl with $CF_2{=}CF_2$ and $CF_2{=}CH_2$ form the respective esters in varying yields. The reactions are regiospecific with $CF_2{=}CH_2$. Additional reactions of CF_3CO_2Cl with $CF_2{=}CFCl$, $CF_2{=}CCl_2$, $CH_2{=}CH_2$, and *cis*- and *trans*-$CFH{=}CFH$ further illustrate the potential of the acyl hypochlorites for the synthesis of a variety of esters. In addition, the latter reactions provide further examples of the regiospecificity of these additions and two examples of their stereospecificity. A concerted cis addition is proposed. The new esters exhibit excellent thermal stability, but are unstable in the presence of KF.

Introduction

The synthesis of highly fluorinated esters of carboxylic acids is in general quite difficult. This is mainly due to the fact that while fluorinated carboxylic acids are readily available, highly fluorinated alcohols are not. The simplest perfluorinated ester, perfluoromethyl acetate, is known, but its synthesis by a photochemical reaction is difficult.[2]

$$[CF_3OC(O)]_2 + (CF_3)_2CO \xrightarrow{h\nu} CF_3C(O)OCF_3$$

No alternative synthesis has been found, and on the basis of properties of CF_3OH,[3] synthesis from CF_3CO_2H and CF_3OH is unlikely.

Shreeve and co-workers developed methods for synthesis of several fluorinated esters via fluoride ion catalyzed reactions of fluoro ketones and fluorinated alcohols (no α-fluorines) with acid fluorides.[4,5] A few other syntheses

$$R_fC(O)F + (CF_3)_2CO \xrightarrow[\text{low temp}]{\text{CsF}} R_fC(O)OCF(CF_3)_2$$

$$R_f = F, CF_3, C_2F_5, C_3F_7$$

$$CF_3C(O)F + ROH \xrightarrow{\text{CsF}} CF_3C(O)OR + HF$$

$$R = CF_3CH_2, (CF_3)_3C, (CF_3)_2CH_3C, (CF_3)_2HC, C_2F_5(CF_3)_2C$$

with $KOC(CF_3)_3$ and acid fluorides,[6] $KOC(C_2F_3)_3$ and acid chlorides,[7] and fluorinated alcohols (no α-fluorines) and acid chlorides provided several other examples.[8] An interesting aspect of the above work concerns the stability of these esters in the presence of fluoride. Those which contained α-fluorines in the carboalkoxy group were unstable.

The recent discovery of chlorine(I) derivatives of several fluorinated carboxylic acids provides a potential new route for the synthesis of highly fluorinated esters.[9,10] These electropositive halogen compounds can be expected to undergo addition reactions with a variety of alkenes, forming the respective esters. In this paper, reactions of HCF_2CO_2Cl, $C_2F_5CO_2Cl$, n-$C_3F_7CO_2Cl$, $ClCF_2CO_2Cl$, and CF_3CO_2Cl with several olefins are discussed. In most cases, good yields of the expected esters were obtained. During the course of this work, an independent investigation reported two related esters by a similar route.[10]

Experimental Section

General Procedures. All work was carried out in Pyrex and stainless-steel vacuum systems equipped with glass–Teflon or stainless-steel valves. Pressures were measured with a Wallace and Tiernan differential pressure gauge, Series 1500. Temperatures were measured with a digital copper–constantan thermocouple. Quantities of reactants and products were measured either by direct weighing or by PVT measurements assuming ideal gas behavior.

Routine IR spectra were taken on a Perkin-Elmer 337 spectrometer at 5 to 100 torr. A 10-cm Pyrex glass cell fitted with AgCl was employed. IR spectra for assignment were taken on a Perkin-Elmer 180 at ~5 torr. Unless otherwise noted, NMR spectra were recorded on a Varian XL-100-15 spectrometer by using 20 to 15 mol % solutions in $CFCl_3$. Spectra were at 94.1 MHz for ^{19}F and 100.1 MHz for ^1H with $CFCl_3$ and Me_4Si as internal and external references, respectively. ^{19}F chemical shifts are reported as ϕ^* values (δ relative to internal $CFCl_3$ not at infinite dilution).

Molecular weights were determined by vapor density measurements by using a calibrated Pyrex bulb fitted with a glass–Teflon valve. Determinations were made on successive fractions of each sample.

Melting points were taken in a Pyrex tube fitted with a glass–Teflon valve. The compound was pumped under vacuum onto the wall of the tube cooled by liquid N_2 to form a crystalline ring. The tube was placed in an ethanol bath, which was cooled to −112 °C prior to the measurement and then warmed slowly with proper agitation.

Vapor pressures and boiling points of the products were measured by a static method. Equations describing pressure as a function of temperature were obtained by a least-squares fit of the data to both linear and quadratic equations and the best fit is reported.

For further purifications, the reaction products were separated via GLC on a Victoreen Series 4000 gas chromatograph equipped for gas injection, TCD, and low-temperature collection. A 2 ft × 3/8 in. column which was packed with 40% Halocarbon 11-21 polymer oil on acid-washed Chromosorb P was used in most cases. For less volatile products, a 1-ft column of similar condition was used.

Reagents. Fluorine, chlorine, CF_3COOH, $CClF_2COOH$, CF_2HCOOH, C_2F_5COOH, n-C_3F_7COOH, and NaOH were obtained from commercial sources. Sodium salts of the acids were prepared by reactions between the acids and NaOH and then were dried under vacuum. ClF was prepared by a reaction between equimolar amounts of fluorine and chlorine (90 mmol) in a 150-mL

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Table I. Addition Reactions of RCO_2Cl to Olefins[a]

R	olefin	product	% yield	
			method A	method B
CF_3	$CF_2=CF_2$	$CF_3CO_2CF_2CF_2Cl$	54	47
CF_3	$CF_2=CH_2$	$CF_3CO_2CF_2CH_2Cl$	94	56
CF_3	$CF_2=CFCl$	$CF_3CO_2CFClCF_2Cl$		65
CF_3	$CF_2=CCl_2$	$CF_3CO_2CCl_2CF_2Cl$		81
CF_3	$CH_2=CH_2$	$CF_3CO_2CH_2CH_2Cl$		33
CF_3	*cis*-CFH=CFH	*erythro*-$CF_3CO_2CFHCFHCl$		64
CF_3	*trans*-CFH=CFH	*threo*-$CF_3CO_2CFHCFHCl$		65
C_2F_5	$CF_2=CF_2$	$C_2F_5CO_2CF_2CF_2Cl$	65	53
C_2F_5	$CF_2=CH_2$	$C_2F_5CO_2CF_2CH_2Cl$	80	50
n-C_3F_7	$CF_2=CF_2$	*n*-$C_3F_7CO_2CF_2CF_2Cl$	66	49
n-C_3F_7	$CF_2=CH_2$	*n*-$C_3F_7CO_2CF_2CH_2Cl$	64	80
$ClCF_2$	$CF_2=CF_2$	$ClCF_2CO_2CF_2CF_2Cl$	17	42
$ClCF_2$	$CF_2=CH_2$	$ClCF_2CO_2CF_2CH_2Cl$	43	93
HCF_2	$CF_2=CF_2$	$HCF_2CO_2CF_2CF_2Cl$(?)	<1	<1
HCF_2	$CF_2=CH_2$	$HCF_2CO_2CF_2CH_2Cl$	17	95

[a] For details of reactions see Experimental Section. Blank indicates reaction was not tried.

Monel vessel (5000 psi) at 250 °C for 12 h. (**Caution**: Contained explosions are observed under these conditions as the temperature approaches ~100 °C). ClF for reactions was removed from the storage vessel at -111 °C to eliminate contamination by any ClF_3 present. Fluorinated olefins were obtained from PCR and were used as received.

The hypochlorites were prepared by reactions of the sodium salts of the acids with ClF at -111 to -78 °C or by reactions of the acid with ClF in the presence of NaF at -111 to -78 °C. Details for these preparations are given below.[9] (**Caution**: The hypochlorites described in this work are explosive. Considerable care must be used in the preparation and handling of these compounds. Please see ref 9 for details.)

Reactions of R_fCO_2Cl with Alkenes. Two related methods, differing mainly in the way the hypochlorite was prepared, were used for the reactions of the hypochlorites with the alkenes.

Method A. Dry RCO_2Na (10.0 mmol) was placed in a passivated 75-mL stainless-steel reactor, evacuated, and cooled to -195 °C. ClF (3.0 mmol) was then added from an all stainless steel vacuum line. The reactor was then placed in a $CFCl_3$ bath containing solid CO_2 at -111 °C. It warmed slowly over ~6 h to -78 °C and was kept at this temperature for ~18 h. The pure hypochlorite was then collected in a -111 °C trap (R = CF_3, C_2F_5) or -78 °C trap (R = C_3F_7, HCF_2, $ClCF_2$). The hypochlorite was then vacuum transferred at low pressure into a 100-mL glass bulb fitted with a Teflon-glass valve cooled to -195 °C. $CF_2{=}CF_2$ or $CF_2{=}CH_2$ (3.0 mmol) was then added and the reactor was placed in a CF_2Cl_2 bath at -150 °C. It warmed slowly over 1 day to ~22 °C and the products were separated by trap-to-trap distillation. The traps were cooled to a temperature (-60 to -111 °C) to condense the addition product, but not the unreacted olefin and decomposition products of the hypochlorites. Final purification was accomplished by GLC, although the product was normally ca. 95% pure before GLC.

Method B. To a ~15-mL Kel-F reactor containing 2.0 g of dry NaF powder was added RCO_2H (3.0 mmol) by weight directly or by vacuum transfer. The reactor was cooled to -195 °C and 3.3 mmol of ClF were added. The reactor was then placed in a $CFCl_3$ bath at -111 °C and allowed to warm as in method A. After 1 day, the reactor was cooled to -111 °C and pumped on to remove ClF and decomposition products. Olefin (3.0 mmol) was then added by vacuum transfer to the reactor at -195 °C and the reaction was allowed to proceed as in method A. Products were separated as in method A.

The reactions carried out by methods A and B are summarized in Table I. Data for new compounds follow.

$CF_3{}^ACO_2CF_2{}^BCF_2{}^CCl$: bp 42.6 °C; mp -98.4 °C; mol wt 248.9, calcd 248.5; ^{19}F NMR ϕ^*_A 76.0 (s); ϕ^*_B 90.6 (t), ϕ^*_C 74.3 (t), $J_{AB} \leq 0.5$, $J_{BC} = 1.9$ Hz; IR 1847 (vs), 1331 (s), 1244 (vs), 1213 (vs), 1197 (w), 1183 (w), 1166 (w), 1125 (vs), 1088 (vs), 975 (vs), 850 (w), 798 (w), 757 (w), 730 (w), 705 (m), 645 (m), 630 (w), 615 (w), 552 (w), 458 (w) cm^{-1}; $\Delta H_{vap} = 7.42$ kcal/mol; $\Delta S_{vap} = 23.5$ eu; $\log P$ (torr) $= 8.0182 - 1622.4/T$.

$CF_3{}^ACO_2CF_2{}^BCH_2{}^CCl$: bp 73.1 °C; mp -119 °C; mol wt 209.8, calcd 212.5; NMR ϕ^*_A 76.1 (s), ϕ^*_B 76.1 (t), δ_C 4.31 (t), $J_{AB} \leq 0.5$, $J_{BC} = 9.3$ Hz; IR 2990 (w), 1827 (vs), 1432 (m), 1351 (w), 1319 (m), 1283 (s), 1242 (vs), 1220 (w), 1198 (vs), 1143 (m), 1127 (vs), 1100 (m), 1073 (vs), 1025 (m), 902 (m), 879 (w), 835 (m), 787 (w), 764 (w), 740 (m), 655 (w), 620 (m), 544 (m), 460 (w) cm^{-1}; $\Delta H_{vap} = 7.84$ kcal/mol; $\Delta S_{vap} = 22.7$ eu; $\log P(\text{torr}) = 6.26125 - (626.602/T) - (188349/T^2)$.

$CF_3{}^ACO_2CF^BClCF^CF^DCl$: bp 71.5 °C; mp -115.0 °C; mol wt 264.2, calcd 265.0; ^{19}F NMR ϕ^*_A 76.0 (s), ϕ^*_B 82.3 (t(d-d)), ϕ^*_C 71.04 (d), ϕ^*_D 71.09 (d), $J_{AB} \sim 0.5$, $J_{BC} = 5.4$, $J_{BD} = 6.3$, $J_{CD} =$? Hz; IR 1842 (vs), 1330 (m), 1246 (vs), 1197 (vs), 1146 (m), 1100 (vs), 1094 (s), 1032 (s), 943 (m), 846 (s), 804 (m), 764 (w), 700 (w), 687 (w), 666 (m), 617 (m), 578 (m), 462 (w) cm^{-1}; $\Delta H_{vap} = 7.56$ kcal/mol; $\Delta S_{vap} = 21.9$ eu; $\log P(\text{torr}) = 5.98490 - (487.210/T) - (200882/T^2)$.

$CF_3{}^ACO_2CCl_2CF_2{}^BCl$: bp 96.3 °C; mp -116 °C; mol wt 285.0, calcd 285.5; ^{19}F NMR ϕ^*_A 75.9 (s), ϕ^*_B 68.1 (s); IR 1836 (vs), 1382 (s), 1244 (vs), 1197 (vs), 1102 (vs), 1063 (s), 1019 (s), 995 (s), 935 (m), 913 (s), 890 (w), 864 (s), 792 (s), 760 (w), 731 (m), 659 (m), 605 (m), 549 (m), 460 (w) cm^{-1}; $\Delta H_{vap} = 7.83$ kcal/mol; $\Delta S_{vap} = 21.2$ eu; $\log P(\text{torr}) = 8.98200 - (2796.79/T) + (200489/T^2)$.

$CF_3{}^ACO_2CH_2{}^BCH_2{}^CCl$: bp 121.4 °C; mp -116.0 °C; mol wt 175.3, calcd 176.5; NMR ϕ^*_A 75.7 (s), δ_B 3.97 (t), δ_C 4.83 (t), $J_{BC} = 5.6$ Hz; IR 2976 (w), 1800 (vs), 1459 (w), 1437 (w), 1395 (m), 1348 (s), 1304 (w), 1235 (vs), 1186 (vs), 1147 (vs), 970 (w), 772 (m), 731 (m), 680 (m), 665 (w), 655 (w), 618 (w), 595 (w), 524 (w), 463 (w) cm^{-1}; $\Delta H_{vap} = 7.65$ kcal/mol; $\Delta S_{vap} = 19.4$ eu; $\log P(\text{torr}) = 7.1200 - (1672.4/T)$.

***erythro*-$CF_3{}^ACO_2CF^BH^CCF^DH^ECl$:** bp 77.3 °C; mp -109 °C; mol wt 215.3, calcd 212.5; NMR ϕ^*_A 75.9 (s), ϕ^*_B 141.4 (d-d-d), ϕ^*_D 153.9 (d-d-d), δ_C 6.69 (basic d-d-d), δ_E 7.00 (basic d-d-d), $J_{AB} < 0.5$, $J_{BC} = 53.0$, $J_{BD} = 15.4$, $J_{BE} = 4.8$, $J_{CD} = 3.9$, $J_{CE} = 5.3$, $J_{DE} = 46.4$ Hz ($ABMNX_3$ spin system, J_{BE} and J_{CD} are the average of two slightly different values); IR 3005 (w), 1825 (s), 1362 (w), 1336 (s), 1306 (w), 1242 (vs), 1194 (vs), 1144 (vs), 1117 (vs), 1094 (m), 1076 (m), 1041 (s), 1026 (w), 995 (w), 928 (w), 862 (s), 825 (s), 709 (m), 737 (s), 650 (m), 631 (m), 654 (w), 620 (w), 476 (vw), 458 (vw), 432 (vw) cm^{-1}; $\Delta H_{vap} = 8.60$ kcal/mol; $\Delta S_{vap} = 24.5$ eu; $\log P(\text{torr}) = 9.14975 - (2514.07/T) - (111109/T^2)$.

***threo*-$CF_3{}^ACO_2CF^BH^CCF^DH^ECl$:** mol wt 214.0, calcd 212.5; IR not distinguishable from erythro isomer; NMR ϕ^*_A 75.8 (s), ϕ^*_B 142.4 (d-d-d), ϕ^*_D 155.1 (d-d-d), δ_C 6.66 (basic d-d-d), δ_E 6.39 (basic d-d-d), $J_{AB} \sim 0.4$, $J_{BC} = 51.6$, $J_{BD} = 20.4$, $J_{BE} = 3.9$, $J_{CD} = 5.0$, $J_{CE} = 4.8$, $J_{DE} = 49.2$ Hz ($ABMNX_3$ spin system, J_{CD} and J_{BE} are the average of two slightly different values).

$CF_3{}^ACF_2{}^BCO_2CF_2{}^CCF_2{}^DCl$: bp 63.3; mp -124.3 °C; mol wt 299.7, calcd 298.5; ^{19}F NMR ϕ^*_A 83.4 (t), ϕ^*_B 122.1 (q), ϕ^*_C 90.6 (t), ϕ^*_D 74.3 (t), $J_{AB} = 1.6$, $J_{CD} = 2.1$ Hz; IR 1834 (s), 1330 (m), 1272 (s), 1233 (vs), 1200 (s), 1180 (s), 1155 (s), 1120 (vs), 1005 (s), 965 (s), 845 (w), 768 (w), 748 (w), 705 (m), 633 (m), 588 (w), 535 (w) cm^{-1}; $\Delta H_{vap} = 7.58$ kcal/mol; $\Delta S_{vap} = 22.5$ eu; $\log P(\text{torr})\ 7.5248 - (1469.5/T) - (31356/T^2)$.

$CF_3{}^ACF_2{}^BCO_2CF_2{}^CCH_2{}^DCl$: bp 88.3 °C; mp -105.5 °C; mol wt 261.5, calcd 262.5; NMR ϕ^*_A 83.4 (t), ϕ^*_B 122.3 (q), ϕ^*_C 75.9 (t), δ_D 4.30 (t), $J_{AB} = 1.6$, $J_{CD} = 9.5$ Hz; IR 2980 (w), 1815 (vs), 1430 (m), 1325 (m), 1274 (s), 1230 (vs), 1144 (s), 1128 (s), 1069 (vs), 1024 (vs), 902 (m), 850 (m), 786 (w), 734 (m), 672 (m), 622 (m), 533 (w) cm^{-1}; ΔH_{vap} = 8.42 kcal/mol; ΔS_{vap} = 23.3 eu; log $P(\text{torr}) = 6.43311 - (728.647/T) - (200831/T^2)$.

$CF_3{}^ACF_2{}^BCF_2{}^CCO_2CF_2{}^DCF_2{}^ECl$: bp 85.7 °C; mp −113.0 °C; mol wt 350.2, calcd 348.5; ^{19}F NMR ϕ^*_A 81.4 (t), ϕ^*_B 127.1 (s), ϕ^*_C 119.5 (q), ϕ^*_D 90.4 (t), ϕ^*_E 74.3 (t), $J_{AC} = 8.5$, $J_{DE} = 2.0$ Hz; IR 1837 (vs), 1500 (w), 1340 (w), 1440 (w), 1350 (m), 1325 (m), 1285 (w), 1244 (vs), 1220 (s), 1178 (m), 1155 (s), 1132 (vs), 1060 (s), 1022 (vs), 977 (vs), 915 (s), 844 (w), 752 (m), 704 (m), 631 (w), 587 (w), 527 (w) cm^{-1}; ΔH_{vap} = 8.51 kcal/mol; ΔS_{vap} = 23.7 eu; log $P(\text{torr}) = 7.3186 - (1325.5/T) - (95799/T^2)$.

$CF_3{}^ACF_2{}^BCF_2{}^CCO_2CF_2{}^DCH_2{}^ECl$: bp 109.7 °C; mp −99.6 °C; mol wt 311.5, calcd 312.5; NMR ϕ^*_A 81.3 (t), ϕ^*_B 127.0 (s), ϕ^*_C 119.7 (q), ϕ^*_D 76.0 (t), δ_E 4.30 (t), $J_{AC} = 8.8$, $J_{DE} = 9.5$ Hz; IR 2975 (w), 1813 (s), 1430 (m), 1350 (w), 1323 (m), 1243 (vs), 1220 (s), 1133 (vs), 1070 (vs), 1024 (s), 970 (m), 940 (m), 900 (m), 835 (m), 790 (w), 750 (m), 723 (m), 622 (w), 535 (w) cm^{-1}; ΔH_{vap} = 9.51 kcal/mol; ΔS_{vap} = 24.8 eu; log P (torr) $= 7.6599 - (1580.8/T) - (95345/T^2)$.

$ClCF_2{}^ACO_2CF_2{}^BCF_2{}^CCl$: bp 74.2 °C; mp −84.2 °C; mol wt 263.9, calcd 265.0; ^{19}F NMR ϕ^*_A 65.6 (s), ϕ^*_B 90.9 (t), ϕ^*_C 74.2 (t), $J_{BC} = 2.0$ Hz; IR 1835 (vs), 1450 (w), 1325 (m), 1268 (m), 1205 (m), 1184 (vs), 1160 (s), 1120 (vs), 1096 (vs), 1022 (vs), 980 (vs), 954 (s), 844 (w), 763 (w), 700 (m), 610 (m), 475 (w) cm^{-1}; ΔH_{vap} = 7.79 kcal/mol; ΔS_{vap} = 22.4 eu; log $P(\text{torr}) = 6.48996 - (804.431/T) - (156042/T^2)$.

$ClCF_2{}^ACO_2CF_2{}^BCH_2{}^CCl$: bp 105.8 °C; mp −95.5 °C; mol wt 227.9, calcd 229.0; NMR ϕ^*_A 65.5 (s), ϕ^*_B 76.2 (t), δ_C 4.33 (t); $J_{BC} = 9.6$ Hz; IR 3000 (vw), 1835 (s), 1324 (w), 1265 (m), 1205 (m), 1188 (vs), 1160 (s), 1124 (vs), 1093 (vs), 980 (s), 955 (m), 838 (w), 763 (w), 705 (w), 610 (w) cm^{-1}; ΔH_{vap} = 8.40 kcal/mol; ΔS_{vap} = 22.2 eu; log $P(\text{torr}) = 8.57653 - (2481.04/T) - (122290/T^2)$.

$H^ACF_2{}^BCO_2CF_2{}^CCH_2{}^DCl$: mp −67.0 °C; mol wt 188.2, calcd 194.5; NMR ϕ^*_B 128.2 (d), ϕ^*_C 76.0 (t), δ_A 6.17 (t), δ_D 4.36 (t), $J_{AB} = 52.6$, $J_{CD} = 9.5$ Hz; IR 2975 (w), 1817 (vs), 1433 (m), 1345 (w), 1320 (m), 1267 (s), 1222 (s), 1197 (m), 1127 (vs), 1105 (s), 1075 (vs), 942 (w), 900 (m), 820 (m), 617 (w), 515 (w) cm^{-1}.

Results and Discussion

The addition reactions of RCO_2Cl to olefins are summarized in Table I. Due to the thermal instability of the hypochlorites, the reported yields are only approximate. Substantial variation in the amount of hypochlorite actually used in the reactions may have occurred, and this fact especially precludes any real comparison between methods A and B. These reactions proceed in good yield in cases where the addition occurs readily at low temperatures. Comparing $CF_2{=}CF_2$ to $CF_2{=}CH_2$ indicates a higher yield for the latter in nearly every case. This may be due to the greater resistance of $CF_2{=}CF_2$ to electrophilic attack (see following discussion on mechanisms) which requires higher temperatures for the reactions to proceed. The relative thermal stability of the hypochlorites is $R = CF_3 > C_2F_2 > n\text{-}C_3F_7 > ClCF_2 > HCF_2$, and this ordering may also qualitatively represent the relative electrophilic character of the chlorine atom.[9] Thus only traces of $HCF_2CO_2CF_2CF_2Cl$ were observed on reaction of HCF_2CO_2Cl with $CF_2{=}CF_2$. This hypochlorite, being the least stable and least electrophilic, decomposed before addition to the olefin occurred.

The halogenated esters formed in the above reactions significantly extend the known examples of such compounds. The new esters are all stable, colorless liquids at 22 °C and exhibit excellent thermal stability at higher temperatures. Several of the compounds were compared under identical conditions at 200 °C in glass. These results are given in Table II.

Table II. Comparison of Thermal Stability of Halogenated Esters[a]

ester	% recovery (200 °C, 10 h)[b]
$CF_3CO_2CF_2CF_2Cl$	100
$CF_3CO_2CF_2CH_2Cl$	100
$CF_3CO_2CCl_2CF_2Cl$	100
$C_2F_5CO_2CF_2CF_2Cl$	100
$C_2F_5CO_2CF_2CH_2Cl$	100
$n\text{-}C_3F_7CO_2CF_2CF_2Cl$	100
$n\text{-}C_3F_7CO_2CF_2CH_2Cl$	100
$ClCF_2CO_2CF_2CF_2Cl$	~90[c]
$ClCF_2CO_2CF_2CH_2Cl$	~90[c]
$HCF_2CO_2CF_2CH_2Cl$	~90[c]

[a] New compounds not listed here but given in Table I were not investigated. [b] Checked by comparison of IR with pure sample and measured by pressure in a known volume. [c] Lower molecular weight carbonyl compounds were observed but not identified.

The identification of the new esters is adequately determined by their molecular weight and IR and NMR spectra. Their IR spectra exhibit a $\nu(C{=}O)$ stretch in the 1800–1850 cm^{-1} region, which is in the region expected for compounds of this type. The remainder of the spectra are qualitatively as expected and considerably different from that of the parent olefin and hypochlorites. Their complexity, however, precludes the assignment of additional group frequencies.

The NMR spectra provide the best basis on which to assign the structures. In each case specific resonances assignable to each of the magnetically nonequivalent nuclei are observed. Unfortunately, spin–spin coupling between the acyl group and the carboalkoxy group is very small. This fact necessitated a greater dependence on chemical shift values to determine which carbon of the olefin was attached to oxygen. Two examples will be discussed here to illustrate how the assignments were made. In $CF_3{}^ACO_2CF_2{}^BCF_2{}^CCl$, the assignment of A is obvious as a slightly broadened singlet, which is coupled very weakly to B. Fluorines A and B are triplets and one multiplet is somewhat broader than the other. This could be due to coupling with A or a chlorine isotope effect. The choice of which resonance to assign to B and C is easily made, however, by comparison with compounds such as $CF_3{}^ASO_3CF_2{}^BCF_2{}^CBr$ and $CF_3{}^AOOCF_2{}^BCF_2{}^CCl$.[11,12] In these and other compounds, J_{AB} is easily determined and the chemical shift of B is at higher field than that of C.

A similar analysis for $CF_3{}^ACO_2CF_2{}^BCH_2{}^CCl$ or $CF_3{}^ACO_2CH_2{}^CCF_2{}^BCl$ allows a choice as to the direction of addition. Assignment of A, B, and C is of course trivial, but a choice between the two structural isomers is not. Again, A is weakly coupled to another nuclei and, in all probability, it is coupled to B. However, this cannot rule out either of the possible structural isomers because one does not know what values of J_{AB} to expect, except that J_{AB} should be larger in $CF_3CO_2CF_2CH_2Cl$. By comparison with $CF_3SO_3CF_2CH_2Cl$,[13] $CF_3OCF_2CH_2Cl$,[14] $CF_3OOCF_2CH_2Cl$,[12] and $SF_5OOCF_2H_2Cl$,[15] the chemical shift of B is reasonable for $CF_3CO_2CF_2CH_2Cl$. Similarly, by comparison with a variety of compounds of the type $ClCF_2CR_1R_2R_3$ (R_1, R_2, R_3 = halogen, alkyl, perfluoroalky, and others),[16] an upper limit for the chemical shift of a terminal $ClCF_2$–C group appears to be 71–73 ppm. In addition, the latter is considerably less than 70 ppm when

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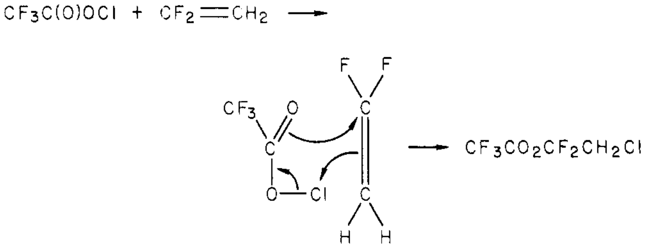
R_1, R_2, and R_3 are not all electronegative groups. On this basis, we are confident that $CF_3CO_2CF_2CH_2Cl$ is the only isomer formed.

On the basis of the NMR spectra, it is clear that the addition reactions are regiospecific. Four examples with CF_3CO_2Cl and one each with the other hypochlorites give only one of two possible structural isomers in every case. Also, the addition reactions of CF_3CO_2Cl and $ClCF_2CO_2Cl$ with $CF_3CF{=}CF_2$ carried out by Schack and Christe gave only one structural isomer, $RCO_2CF_2CFClCF_3$.[10] This regiospecificity is highly indicative of concerted polar addition. Because $CF_3CO_2^-$ and $R_fCO_2^-$ in general should be very weak nucleophiles, we believe the additions are electrophilic in nature. This is supported by the Markownikoff-like additions to $CF_2{=}CH_2$ and the relative reactivity of the olefins. The direction of addition of CF_3CO_2Cl to $CF_2{=}CFCl$ and $CF_2{=}CCl_2$ is also not that expected for a nucleophilic attack.[17] On the other hand, the additions to $CF_3CF{=}CF_2$ cited above are as expected for a nucleophilic attack. We favor calling these reactions electrophilic additions, since it is probably the positive chlorine atom that leads to initial interaction with the olefin.

Additional information about the mechanism of these reactions was obtained by the addition of CF_3CO_2Cl to *cis*- and *trans*-CFH=CFH. For each olefin, a single different diastereomer is obtained and the reaction is therefore stereospecific. We believe the cis olefin forms the erythro isomer and the trans olefin the threo isomer, which means the additions are cis (syn). This assignment of stereochemistry is based on the values of $^3J_{HH}$, $^3J_{HF}$, and $^3J_{FF}$. We have presented arguments for this in related work on the additions of CF_3SO_2OX (X = Cl, Br) to alkenes,[11,13,18] and the identical considerations apply here. If the reactions are indeed cis, a very reasonable mechanism can be written for the reactions; this is illustraed for the addition of CF_3CO_2Cl to $CF_2{=}CH_2$. This type of concerted addition is identical with that proposed for CF_3SO_2OX (X = Cl, Br),[13] whose additions parallel those of CF_3CO_2Cl in every case. This appears to be the simplest and best explanation of the observed facts.



Finally, the stability of several of the esters in the presence of KF was compared. Previous work had shown that esters of the type $R_fCO_2CF(CF_3)_2$ readily decomposed in the presence of KF to $R_fC(O)F$ and $(CF_3)_2C{=}O$.[4] On the other hand, esters containing no α-fluorine in the carboalkoxy group were stable.[5,6] The variety of compounds obtained in this work provided an apportunity to further test the generality of the above. In addition, this reaction could provide an indirect confirmation of structure for an ester such as $ClCF_2CO_2CF_2CH_2Cl$. If reaction with fluoride did not proceed, it might indicate that the ester is $ClCF_2CO_2CH_2CF_2Cl$ rather than $ClCF_2CO_2CF_2CH_2Cl$. Five of the esters were investigated by transferring a known amount of the ester into a 100-mL glass bulb containing ~10 g of dried KF at −195 °C. After the mixture was warmed to 22 °C and allowed to stand for 1 h, none of the parent ester was detectable by IR. An increase in pressure by a factor of ~2 was noted. IR and ^{19}F NMR analysis indicated the occurrence of the following reaction:

$$RCO_2CF_2R' \xrightarrow{KF} RC(O)F + R'C(O)F$$

The results are summrized in Table III. With active fluorides such as KF, the instability of any esters containing an α-fluorine in the carboalkoxy group is probably general. However, the fluoride source is very important. Sodium fluoride is inactive in this reaction under the same conditions, and all the esters in Table I were prepared in the presence of NaF via method B. This fluoride-catalyzed decomposition of fluorinated esters made by the addition of the hypochlorites to alkenes may be a useful method for the synthesis of certain acyl fluorides where the parent acid is not readily available. A variety of 1,1-difluoroalkenes are available via Wittig reactions and from other sources.

Table III. Reaction of Fluorinated Esters with KF[a]

RCO_2CF_2R'[b]		products,[c] % yield	
R	R′	RC(O)F	R′C(O)F
CF_3	CF_2Cl	90	100
$ClCF_2$	CH_2Cl	100	100
HCF_2	CH_2Cl	100	100
n-C_3F_7	CH_2Cl	100	100
n-C_3F_7	CF_2Cl	100	100

[a] ~10 g of KF for 1 h at 22 °C. [b] ~0.55 mmol. [c] Identified by IR and ^{19}F NMR. Relative amounts were determined by integration of $-C(O)F$ in the NMR spectra.

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Registry No. CF_3CO_2Cl, 65597-25-3; $C_2F_5CO_2Cl$, 71359-61-0; n-$C_3F_7CO_2Cl$, 71359-62-1; $ClCF_2CO_2Cl$, 68674-44-2; HCF_2CO_2Cl, 71359-63-2; CF_3CO_2H, 76-05-1; CF_3CO_2Na, 2923-18-4; $C_2F_5CO_2H$, 422-64-0; $C_2F_5CO_2Na$, 378-77-8; n-$C_3F_7CO_2H$, 375-22-4; n-$C_3F_7CO_2Na$, 2218-54-4; $ClCF_2CO_2H$, 76-04-0; $ClCF_2CO_2Na$, 1895-39-2; HCF_2CO_2H, 381-73-7; HCF_2CO_2Na, 2218-52-2; $CF_2{=}CF_2$, 116-14-3; $CF_2{=}CH_2$, 75-38-7; $CF_2{=}CFCl$, 79-38-9; $CF_2{=}CCl_2$, 79-35-6; $CH_2{=}CH_2$, 74-85-1; *cis*-CFH=CFH, 1630-77-9; *trans*-CFH=CFH, 1630-78-0; $CF_3CO_2CF_2CF_2Cl$, 72844-27-0; $CF_3CO_2CF_2CH_2Cl$, 72844-28-1; $CF_3CO_2CFClCF_2Cl$, 72844-29-2; $CF_3CO_2CCl_2CF_2Cl$, 72844-30-5; $CF_3CO_2CH_2CH_2Cl$, 40949-99-3; *erythro*-$CF_3CO_2CFHCFHCl$, 72844-31-6; *threo*-$CF_3CO_2CFHCFHCl$, 72844-32-7; $C_2F_5CO_2CF_2CF_2Cl$, 72844-33-8; $C_2F_5CO_2CF_2CH_2Cl$, 72844-34-9; n-$C_3F_7CO_2CF_2CF_2Cl$, 72844-35-0; n-$C_3F_7CO_2CF_2CH_2Cl$, 72844-36-1; $ClCF_2CO_2CF_2CF_2Cl$, 72844-37-2; $ClCF_2CO_2CF_2CH_2Cl$, 72844-38-3; $HCF_2CO_2CF_2CH_2Cl$, 72844-39-4; CF_3COF, 354-34-7; $ClCF_2COF$, 354-27-8; HCF_2COF, 2925-22-6; n-C_3F_7COF, 335-42-2; CH_2ClCOF, 359-14-8.

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