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Table III

[chloramine], M	[sulfinate], M	ΔA
1.0×10^{-4}	9.9×10^{-4}	0.034
2.0×10^{-4}	9.6×10^{-4}	0.068
1.0×10^{-4}	1.9×10^{-3}	0.036
1.0×10^{-3}	1.0×10^{-4}	0.037
1.0×10^{-3}	2.0×10^{-4}	0.072

each solution were mixed and allowed to react. After an appropriate time the reaction solution was rapidly washed into a solution (10 mL) of KI (0.5 g) in deionized water containing 1 mL of a pH buffer solution. The resulting solution was diluted up to approximately 75 mL with deionized water, and the amount of iodine formed was determined by amperometric titration with 8.10×10^{-4} N sodium thiosulfate. Typical readings taken included the following [reaction time (volume of titrant)]: 0 min (3.13 mL), 0.5 min (2.82 mL), 1 min (2.52 mL), 1.5 min (2.37 mL), 2 min (2.35 mL), 2.5 min (2.44 mL), 3 min (2.20 mL), 5 min (2.17 mL), 6 h (1.85 mL). Scatter in the readings from multiple runs made it impossible to obtain a good rate constant.

Isolation of Benzenesulfonyl Chloride. A solution (500 mL) of *N*-chloropiperidine (1.0×10^{-4} M) in deionized water was mixed for 0.5 min in a separatory funnel with a solution (500 mL) of sodium benzenesulfinate (1.1×10^{-3} M). Concentrated sulfuric acid (30 mL) was added, and the solution was rapidly extracted with chloroform (1 × 100 mL and then 1 × 50 mL). The extract was dried over sodium sulfate, filtered, and concentrated on a rotary evaporator in a tared flask. The residue (22 mg) gave an IR spectrum and VPC retention time identical to those of benzenesulfonyl chloride. VPC indicated the presence of a small amount (<10%) of residual chloroform.

Yield of 1-(Phenylsulfonyl)piperidine at Low Concentrations of *N*-Chloropiperidine. An aqueous solution (500 mL) of sodium benzenesulfinate (2.0×10^{-3} M) was mixed with an aqueous solution (500 mL) of either 2.0×10^{-4} or 2.0×10^{-5} M *N*-chloropiperidine. The resulting solutions were allowed to react 2.5 and 15 h, respectively. They were then extracted with chloroform (4 × 50 mL). The extracts of the separate reactions were each dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The residue of the reaction of 10^{-4} M chloramine was diluted with acetonitrile to 100 mL in a volumetric flask. The residue from the reaction of 10^{-5} M chloramine was diluted with acetonitrile to 10 mL in a volumetric flask. Each sample was analyzed by HPLC, and peak heights were compared with equivalent injections of 1.0×10^{-3} M 1-(phenylsulfonyl)piperidine in acetonitrile. A yield of 8% was obtained in the reaction of 10^{-4} M chloramine, and no product was detected for the reaction of 10^{-5} M chloramine.

Kinetics of the Secondary Reaction of *N*-Chloropiperidine and Sodium Benzenesulfinate. Hydrolysis of Benzenesulfonyl Chloride. Stock solutions of *N*-chloropiperidine and sodium benzenesulfinate were prepared so that when 0.100 mL of a solution of one reagent was micropipetted into 2.90 mL of a solution of the other in a cuvette, the solutions indicated in Table III were obtained. The absorbance (at 269 nm) was read 12 s after mixing (A_I) and 132 s after mixing (A_F). From these $\Delta A = A_I - A_F$ was calculated.

The change in absorbance with time was measured for a solution of 1.0×10^{-4} M *N*-chloropiperidine and sodium benzenesulfinate in 0.05 M NaCl at 25 °C. A plot of log (absorbance at time t − absorbance at t_∞) vs. time gave a straight line of slope $(-3.6 \pm 0.9) \times 10^{-3}$ s^{-1}.

The rate of hydrolysis of benzenesulfonyl chloride at 25 °C in 0.05 M aqueous NaCl was determined spectrophotometrically at 269 nm as described above by using solutions prepared by the method of Rogne.[3] Instead of acetone, acetonitrile was used to disperse the benzenesulfonyl chloride. A rate of hydrolysis of $(3.14 \pm 0.8) \times 10^{-3}$ s^{-1} was obtained.

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Registry No. Ammonia, 7664-41-7; allyl amine, 107-11-9; aniline, 62-53-3; *n*-hexylamine, 111-26-2; *sec*-butylamine, 13952-84-6; ethylenediamine, 107-15-3; leucine, 61-90-5; glycine, 56-40-6; piperidine, 110-89-4; pyrrolidine, 123-75-1; morpholine, 110-91-8; tetrahydroisoquinoline, 91-21-4; diisobutylamine, 110-96-3; dimethylamine, 124-40-3; diethylamine, 109-89-7; sodium benzenesulfinate, 873-55-2; sodium *p*-toluenesulfinate, 824-79-3; *N*-chloropiperidine, 2156-71-0; 1-(phenylsulfonyl)piperidine, 5033-23-8; *N,N*-dimethyl-*p*-toluenesulfonamide, 599-69-9; *N,N*-diethyl-*p*-toluenesulfonamide, 649-15-0; 1-(phenylsulfonyl)morpholine, 5033-21-6; 1,2,3,4-tetrahydro-2-(phenylsulfonyl)isoquinoline, 79409-51-1; 1-(*p*-tolylsulfonyl)piperidine, 4703-22-4; 1-(*p*-tolylsulfonyl)morpholine, 6339-26-0; 1-(*p*-tolylsulfonyl)pyrrolidine, 6435-78-5; benzenesulfonamide, 98-10-2; *N*-phenylsulfonylglycine, 5398-96-9; *N,N′*-ethylenebis(benzenesulfonamide), 4392-52-3; *N*-*sec*-butylbenzenesulfonamide, 23705-41-1; *N*-allyl-*p*-toluenesulfonamide, 50487-71-3; *N*-(phenylsulfonyl)leucine, 68305-76-0; *N*-phenylbenzenesulfonamide, 1678-25-7; *N,N*-diisobutylbenzenesulfonamide, 41178-58-9; *N*-hexylbenzenesulfonamide, 7250-80-8.

Synthesis and Reactions of Perfluorobutanesulfonyl Hypohalites

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Two new hypohalites, perfluoro-*n*-butanesulfonyl hypochlorite and hypobromite, are reported. The hypochlorite is prepared by the low-temperature reaction of ClF with the acid $C_4F_9SO_2OH$. The hypobromite is prepared by reaction of the hypochlorite with bromine. The new compounds contain very electrophilic halogen atoms and exhibit reactions similar to the analogous trifluoromethanesulfonates, CF_3SO_2OX (X = Cl, Br). The new hypohalites exhibit somewhat greater stability than the trifluoromethanesulfonates but form analogous decomposition products. Characterization of the new compounds is given along with several reactions with olefins and halides to yield a variety of new esters.

The synthetic utility of the halogen derivatives of several strong oxyacids has now been well established.[1] The primary reaction for these halogen derivatives involves electrophilic addition across an olefinic bond which gives rise to a variety of esters and ethers. Interestingly, the additions appear to stereospecific and cis in many cases.[2] An additional important reaction type is exhibited by four

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[1] Aubke, F.; DesMarteau, D. D. *Fluorine Chem. Rev.* 1977, *8*, 73.

[2] See for example: Katsuhara, Y.; DesMarteau, D. D. *J. Org. Chem.* 1980, *45*, 2441.

of the hypohalites, FSO_3Cl, FSO_3Br, CF_3SO_3Cl, and CF_3SO_3Br, in substitutive electrophilic dehalogenation (eq 1). This reaction provides a new route to many esters

$$R_fSO_3X + YR \rightarrow R_fSO_3R + XY \qquad (1)$$

$R_f = F, CF_3$; R = alkyl or perfluoroalkyl; X = Cl, Br; Y = Cl, Br

inaccessible by other methods.[3] As part of a continuing study in the chemistry of very strong electrophiles, we were interested in the synthesis of new reagents bearing electrophilic halogens. The synthesis of halogen derivatives of higher homologues of perfluoroalkane sulfonic acids was undertaken to compare the effects of the perfluoroalkyl groups on the reactivity of these compounds. In this paper the synthesis of the hypochlorite and the hypobromite of perfluorobutanesulfonic acid is described. Like the lower analogues, CF_3SO_3X (X = Cl, Br), these new halogen derivatives are very reactive but have greater thermal stability than the trifluoromethanesulfonates.

The characterization of these new compounds is described along with a variety of reactions leading to new $C_4F_9SO_3$ derivatives.

Experimental Section

General Methods. All work was carried out in a Pyrex and stainless-steel vacuum system equipped with glass–Teflon or stainless-steel valves. Pressures were measured with a Wallace and Tiernan differential gauge, Series 1500. Amounts 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 PE-337 spectrometer at 5–10 torr. A 10-cm Pyrex cell fitted with AgCl windows and a small trap was employed. For less volatile compounds (vapor pressure less than 2 torr at 22 °C) some of the compound was condensed in the trap on the IR cell, and the spectrum was taken of the gas in equilibrium with the liquid in the trap after it had warmed to 22 °C. Spectra for assignment were recorded on a PE-180 spectrometer at 0.5–5 torr by using the same techniques.

^{19}F NMR spectra were recorded on a Varian XL-100-15 spectrometer by using 15–20 mol % solutions in $CFCl_3$. $CFCl_3$ was employed as an internal standard. ^1H spectra were recorded on a Varian T-60 under similar conditions but with Me_4Si as an external standard. Chemical shifts are positive when found to the low-field side of the reference and vice versa. ^{19}F chemical shifts are given as ϕ^* values (internal $CFCl_3$ reference not at infinite dilution).

Wherever possible, molecular weights were determined by vapor-density measurements using a calibrated Pyrex bulb fitted with glass–Teflon valve.

Melting points were taken in a Pyrex tube fitted with a glass–Teflon valve. The compounds were pumped under vacuum onto the wall of the tube cooled by liquid N_2 and formed a crystalline or solid 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. The collapse of the ring was taken as the melting point.

Vapor pressures and boiling points of the products were determined both by static and dynamic methods. 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. All boiling points are extrapolated to 760 torr.

Purification of some of the reaction products was carried out via GLC on a Victoreen Series 4000 gas chromatograph equipped for gas injection, TCD, and low-temperature collection. A 10 ft × $^3/_8$ in. column which was packed with 30–40% halocarbon 11-21 polymer oil on acid-washed Chromosorb P was used in most cases.

Reagents. F_2, Cl_2, Br_2, $C_4F_9SO_2F$, C_2F_4, CF_2CH_2, C_2F_3Cl, CF_2CCl_2, *cis*-CHFCHF, $SiMe_3Cl$, and CH_3Cl were obtained from commercial sources. $C_4F_9SO_3H$,[4] SiF_3Br,[5] SF_5Br,[6] and POF_2Br[7] were prepared according to the methods reported in the literature. $C_4F_9SO_3H$ was doubly distilled before use in reactions. Br_2 was dried over P_4O_{10} and distilled before use. ClF was prepared by heating equimolar amounts of Cl_2 and F_2 at 250 °C in a Monel bomb for 18 h. The ClF was taken out of the bomb at −111 °C to prevent contamination by ClF_3 and unreacted Cl_2.

Preparation of $C_4F_9SO_2OCl$. $C_4F_9SO_3H$ was vacuum transferred through a short glass connection into a 20-mL U-shaped FEP reactor cooled to −195 °C and fitted with a 304 stainless-steel valve. The amount of the acid transferred was determined by weighing the original acid container before and after transfer. The FEP reactor containing the transferred acid was warmed to room temperature to let all the acid flow down to the bottom. It was then cooled to −195 °C, and 10 mol% excess of ClF was condensed onto it. The reaction mixture was then warmed slowly from −111 to −30 °C in a cold freon bath and was held at −30 °C until the formation of the hypochlorite was complete as indicated by the appearance of two layers of liquid, a yellow colored layer at the bottom due to the hypochlorite and a clear HF layer on top of it. This process usually required ~24 h for preparation of 2.5–3.0 mmol of the hypochlorite. Larger amounts of acid required longer reaction times. HF was removed by holding the reactor at −50 °C and vacuum pumping through a liquid N_2 cooled Kel-F trap. Traces of HF were removed by letting the hypochlorite warm to −35 °C and pumping on it for a few minutes.

Preparation of $C_4F_9SO_2OBr$. In a typical preparation, onto $C_4F_9SO_2OCl$ (3.0 mmol) at −195 °C in an ~20-mL FEP reactor was condensed Br_2 (1.5 mmol) by vacuum transfer. The reaction mixture was allowed to warm slowly in a cold freon bath from −78 to −15 °C. During the course of the warm-up, the reaction mixture first liquified (~−27 °C), then solidified, and again liquified (−20 °C). The warm-up usually required 10–12 h, depending on the scale of the reaction. Larger amounts required longer reaction times. The Cl_2 formed was pumped out, after the reaction mixture was cooled to −35 °C and pumped on for 0.5 h, followed by brief pumping at −15 °C.

Properties of $C_4F_9SO_2OX$ (X = Cl, Br). $C_4F_9SO_3Cl$ is a pale yellow liquid which solidifies to a white crystalline solid on cooling with a melting point of −35 °C. It decomposes to C_4F_9Cl and SO_3 on being allowed to stand at room temperature for 2 h as evidenced by complete disappearance of the yellow color due to the hypochlorite. $C_4F_9SO_3Br$, on the other hand, was found to have a much higher thermal stability. Its decomposition was not complete even after 10 days when allowed to stand at room temperature in a Kel-F or an FEP tube. $C_4F_9SO_3Br$, like CF_3SO_3Br, is a wine-red liquid which solidifies to a deep brown solid. The hypobromite was found to have a melting point of −12 °C. Decomposition of $C_4F_9SO_3Br$ was carried out by allowing 10 mmol of the compound stand at room temperature in a Kel-F tube for 2 weeks. Products of decomposition were separated through −10, −40, and −195 °C traps. The −195 °C trap contained C_4F_9Br and Br_2, the −40 °C trap had $C_4F_9SO_3C_4F_9$ and a little Br_2, and in the −10 °C trap was a very heavy material, some of which also stayed behind in the reaction vessel. This heavy material was believed to be $C_4F_9SO_3SO_3C_4F_9$ by the analogy with the decomposition of CF_3SO_3Br.[8]

Characterization of the new hypohalites is partly based on the NMR and Raman data and partly on their chemical properties. For $CF_3^ACF_2^BCF_2^CCF_2^DSO_2OCl$: ^{19}F NMR ϕ^*_A −81.4 (t), ϕ^*_B −126.6 (m), ϕ^*_C −121.3 (m, br), ϕ^*_D −106.4 (br), J_{AC} = 9.8 Hz; Raman 1451 (w), 1365 (w), 1301 (w), 1229 (m), 1208 (m), 1125 (w), 1074 (m), 1037 (w), 842 (w), 800 (w), 761 (m), 748 (s), 710 (vs), 697 (s), 682 (s), 669 (m, sh), 655 (s), 649 (m, sh), 618 (w), 582 (vw), 560 (vw), 530 (vw), 510 (w), 477 (vw), 465 (vw), 412 (s), 405 (s), 388 (m), 375 (w, sh), 368 (w), 343 (w), 308 (s), 301 (s), 285 (w, sh), 255 (w), 205 (m), 182 (s), 153 (m), 119 (w), 67 (w) cm^{-1}.

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Table I. Reactions of $C_4F_9SO_2OX$ (X = Cl, Br)

X (amt, mmol)	other reactant (amt, mmol)	temp,^{a} °C	product(s) (amt, mmol)^c
Cl (~2.5)	CF_3Br (4.0)	−150 to +22	$C_4F_9SO_3CF_3$ (2.3); Cl_2, Br_2, BrCl (2.4)
Cl (~4)	C_4F_9Br (4.5)	−111 to −10,^{b} −10 to +22	$C_4F_9SO_3C_4F_9$; Br_2, BrCl, Cl_2 (3.7)
Cl (2.5)	C_2F_4	−130 to +22	$C_4F_9SO_3CF_2CF_2Cl$
Cl (~5)	$CF_2{=}CH_2$ (6)	−130 to +22	$C_4F_9SO_3CF_2CH_2Cl$, CF_2CH_2 (0.5)
Cl (~3)	C_2F_3Cl (4.0)	−130 to +22	$C_4F_9SO_3CFClCF_2Cl$, C_2F_3Cl, C_4F_9Cl (1.5)
Cl (~2.5)	*cis*-CHFCHF (2.5)	−150 to +22	$C_4F_9SO_3CHFCHFCl$, *cis*-CHFCHF (0.2),
Cl (~2.5)	CF_2CCl_2 (3.5)		$C_4F_9SO_3CCl_2CF_2Cl$, CF_2CCl_2 (1.3)
Br (~2.5)	CF_2CH_2 (3.5)	−111 to 0	$C_4F_9SO_3CF_2CH_2Br$, CF_2CH_2 (1.5)
Br (~2.5)	C_2F_3Cl (3.5)	−111 to 0	$C_4F_9SO_3CFClCF_2Br$, C_2F_3Cl (1.9)
Br (~2.5)	*cis*-CHFCHF (3.5)	−111 to 0	$C_4F_9SO_3CHFCHFBr$, *cis*-CHFCHF (1.2)
Br (~2.5)	CF_2CCl_2 (3.0)	−111 to 0	$C_4F_9SO_3CCl_2CF_2Br$, CF_2CCl_2
Cl (~4.0)	SiF_3Br (5.0)	−130 to +22	$C_4F_9SO_3SiF_3$; Br_2, BrCl, Cl_2 (3.4)
Cl (~5.0)	$SiMe_3Cl$ (6.0)	−111 to +22	$C_4F_9SO_3SiMe_3$, Cl_2 (5.1)
Cl (~3.5)	SF_5Br (5)	−111 to +0	$C_4F_9SO_2OSF_5$; Br_2, BrCl, Cl_2 (3.1)
Cl (~3.0)	POF_2Br (4)	−111 to +0	$C_4F_9SO_2OPOF_2$; Br_2, BrCl, Cl_2 (2.9)
Cl (~3.5)	CH_3Cl (5)	−111 to +22	$C_4F_9SO_2OCH_3$, Cl_2 (3.2)

^{a} Reaction time 12–16 h. ^{b} 48 h. ^{c} Amounts not determined in all cases. Yields are all estimated to be at least 80%.

The Raman spectrum of $C_4F_9SO_2OCl$ is quite different from that of C_4F_9Cl.[9] Characteristic bands in the $C_4F_9SO_3Cl$ spectrum are at 710 (δ_{OCl}), 412 ($\delta_{SO(Cl)}$) and 182 cm^{-1} (δ_{SOCl}). The Raman spectrum of $C_4F_9SO_2OBr$ could not be obtained because of its dark color. ^{19}F NMR spectrum of the hypobromite showed the characteristic peaks due to the C_4F_9 moiety. For $CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_3Br$: ϕ^*_A −82.1 (t), ϕ^*_B −126.9 (br t), ϕ^*_C −121.8 (m), ϕ^*_D −108.8 (m), $J_{AC} = 10.0$ Hz, $J_{BD} = 14.5$ Hz.

General Procedure for the Reactions of $C_4F_9SO_2OX$ (X = Cl, Br). $C_4F_9SO_2OCl$ and $C_4F_9SO_2OBr$ were freshly prepared for each reaction, and the reactions were performed in the same reactor. Onto the $C_4F_9SO_2OX$ (X = Cl, Br) in a FEP reactor at −195 °C was condensed the desired amount of the reactant. The reactor was then placed in a cold bath at the desired temperature and allowed to warm to an appropriate temperature over a period of time (Table I). Completion of the addition reactions was indicated by the disappearance of color due to the hypohalite. In the case of sustitutive dehalogenation reactions, the appearance of Br_2 or BrCl or Cl_2 was a good indicator of the extent of reaction. Products were separated by trap to trap distillation as the reaction mixture warmed slowly from −195 to +22 °C, followed by purification by GLC in some cases.

Reaction of $C_4F_9SO_2OCl$. C_2F_4. The products were separated through −78, −111, and −195 °C traps. The −78 °C trap had pure adduct while the −195 °C trap contained a little unreacted C_2F_4. $C_4F_9SO_3CF_2CF_2Cl$: colorless liquid; mp <−111 °C; bp 135.9 °C; $\Delta H = 8.5$ kcal mol^{-1}; $\Delta S = 20.8$ eu; $\log P\,(\text{torr}) = 7.4278 - 1860.008/T$; IR 1465 (s), 1432 (m), 1355 (s), 1323 (w), 1295 (w), 1250 (vs), 1220 (vs), 1188 (s), 1150 (s), 1140 (s), 1032 (m), 1000 (m), 974 (s), 920 (w), 879 (w), 855 (w), 800 (w), 780 (w), 765 (w), 745 (sh, w), 730 (m), 700 (m), 650 (w), 620 (sh, w), 610 (sh, w), 590 (m), 565 (sh, w), 530 (w), 505 (w) cm^{-1}; ^{19}F NMR ($CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_3CF_2{}^ECF_2{}^FCl$) ϕ^*_A −81.4 (2 t), ϕ^*_B −126.3 (m), ϕ^*_C −121.0 (m), ϕ^*_D −108.3 (m), ϕ^*_E −83.2 (m, t), ϕ^*_F −73.7 (br s), $J_{AC} = 10.0$ Hz, $J_{BD} = 14.0$ Hz, $J_{AD} = 2.2$ Hz, $J_{DE} = 8.0$ Hz, $J_{AB} \approx 0$ Hz.

C_2F_3Cl. The products were separated through −25, −60, and −195 °C traps. Most of the adduct collected in the −25 °C trap. The −195 °C trap contained 1.5 mmol of a mixture of C_2F_3Cl and C_4F_9Cl. $C_4F_9SO_2OCFClCF_2Cl$: colorless liquid; mp −95.2 °C; bp 159.2 °C; $\Delta H = 10.9$ kcal mol^{-1}; $\Delta S = 25.1$ eu; $\log P\,(\text{torr}) = 8.3767 - 2376.116/T$; IR 1495 (w), 1457 (s), 1351 (m), 1295 (w), 1250 (vs), 1216 (vs), 1182 (s), 1150 (s), 1140 (sh, s), 1125 (sh, w), 1082 (s), 1030 (sh, w), 1017 (vs), 1005 (sh, s), 928 (m), 880 (w), 850 (m), 782 (m), 750 (w), 738 (m), 700 (w), 675 (w), 650 (w), 585 (w), 570 (w), 525 (w) cm^{-1}; ^{19}F NMR ($CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_2OCF^ECl\text{-}CF_2{}^FCl$) ϕ^*_A −81.4 (2 t), ϕ^*_B −126.3 (m, t), ϕ^*_C −121.0 (br), ϕ^*_D −108.4 (br m), ϕ^*_E −73.1 (m), ϕ^*_F −70.5 (d), $J_{AB} = 0$ Hz, $J_{AC} = 10.0$ Hz, $J_{AD} = 2.2$ Hz, $J_{BD} = 14.0$ Hz, $J_{DE} = 7.5$ Hz, $J_{EF} = 5.5$ Hz.

CF_2CCl_2. Products were separated through −25, −60, and −195 °C traps. Pure adduct collected in the −25 °C trap. $C_4F_9SO_2OCl_2CF_2Cl$: colorless liquid; mp −90.5 °C; bp 176.6 °C; $\Delta H = 11.8$ kcal mol^{-1}; $\Delta S = 26.3$ eu; $\log P\,(\text{torr}) = 8.6401 - 2590.5/T$; IR 1490 (w), 1453 (m), 1352 (m), 1295 (w), 1250 (s), 1240 (sh, m), 1215 (m), 1185 (m), 1150 (m), 1125 (w), 1062 (w), 1032 (w), 1010 (w), 988 (m), 970 (w), 940 (s), 900 (w), 878 (w), 853 (m), 835 (sh, w), 800 (w), 780 (w), 737 (w), 700 (w), 652 (w), 600 (w), 575 (sh, w), 553 (m), 520 (s) cm^{-1}; ^{19}F NMR ($CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_3Cl_2CF_2{}^ECl$) ϕ^*_A −81.4 (2 t), ϕ^*_B −126.4 (m, t), ϕ^*_C −121.6 (br), ϕ^*_D −108.4 (m, t), ϕ^*_E −67.6 (s), $J_{AC} = 10.0$ Hz, $J_{AD} = 2.2$ Hz, $J_{BD} = 14.0$ Hz.

CF_2CH_2. Products were separated through −35 and −195 °C traps. The adduct collected in the −35 °C trap. The −195 °C trap contained 0.5 mmol of unreacted CF_2CH_2. $C_4F_9SO_2OCF_2CH_2Cl$: colorless liquid; mp −53.2 °C; bp 154.4 °C; $\Delta H = 10.5$ kcal mol^{-1}; $\Delta S = 24.5$ eu; $\log P\,(\text{torr}) = 8.2295 - 2286.78/T$; IR 1485 (w), 1455 (m), 1440 (m), 1407 (m), 1335 (m), 1250 (s), 1218 (s), 1150 (s), 1135 (s), 1055 (w), 1032 (m), 1015 (sh, w), 980 (w), 950 (sh, w), 920 (s), 900 (sh, w), 875 (w), 845 (w), 800 (w), 732 (w), 700 (w), 656 (w), 590 (w), 535 (w) cm^{-1}; ^{19}F NMR ($CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^CSO_2OCF_2{}^ECH_2{}^FCl$) ϕ^*_A −81.5 (2 t), ϕ^*_B −126.3 (m), ϕ^*_C −121.4 (br), ϕ^*_D −110.0 (br m), ϕ^*_E −58.0, δ_F 2.5, $J_{AC} = 10.0$ Hz, $J_{AD} = 2.2$ Hz, $J_{BD} = 14.0$ Hz, $J_{EF} = 14.0$ Hz.

***cis*-CHFCHF.** Products were separated through −35 and −195 °C traps. Pure adduct stopped in the −35 °C trap. *erythro*-$C_4F_9SO_2OCHFCHFCl$: colorless liquid; IR 3000 (w), 1477 (m), 1355 (w), 1295 (w), 1252 (s), 1208 (sh, w), 1165 (s), 1152 (s), 1135 (w), 1102 (w), 1040 (s), 1060 (sh, w), 1050 (s), 1031 (s), 948 (w), 898 (m), 873 (w), 839 (sh, w), 825 (w), 788 (w), 780 (w), 749 (s), 700 (vw), 660 (s), 620 (w), 586 (m), 505 (w) cm^{-1}; ^{19}F NMR ($CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_2OCHF^ECHF^FCl$) ϕ^*_A −81.4 (2 t), ϕ^*_B −126.3 (m), ϕ^*_C −121.1 (br m), ϕ^*_D −110.0 (br), ϕ^*_E −131.9 (m), ϕ^*_F −153.9 (m), $J_{AC} = 9.8$ Hz, $J_{AD} = 2.2$ Hz, $J_{BD} = 14.0$ Hz, $J_{H^EF^E} = 49.4$ Hz, $J_{H^FF^F} = 45.6$ Hz, $J_{EF} = 16.8$ Hz, $J_{H^EF^F} = 5.0$ Hz.

CF_3Br. Products were separated through −50, −78, and −195 °C traps. Most of $C_4F_9SO_2OCF_3$ collected in the −50 °C trap with a little collecting in the −78 °C trap. $C_4F_9SO_2OCF_3$: colorless liquid; mp −78.9 °C; bp 93.6 °C; $\Delta H = 8.75$ kcal mol^{-1}; $\Delta S = 23.87$ eu; $\log P\,(\text{torr}) = 7.5405 - 1504.675/T - 74\,850.805/T^2$; IR 1463 (s), 1354 (m), 1280 (s), 1250 (vs), 1218 (s), 1200 (sh, m), 1150 (s), 1135 (s), 1030 (m), 1008 (m), 952 (s), 876 (m), 855 (m), 808 (m), 770 (s), 747 (m), 738 (m), 700 (m), 650 (m), 620 (m), 575 (s), 553 (w), 528 (m), 503 (m), 433 (w) cm^{-1}; ^{19}F NMR ($CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_2OCF_3{}^E$) ϕ^*_A −81.4 (2 t), ϕ^*_B −126.2 (m, t), ϕ^*_C −121.0 (m), ϕ^*_D −108.2 (m), ϕ^*_E −53.2, $J_{AC} = 9.5$ Hz, $J_{AD} = 1.8$ Hz, $J_{BD} = 14.5$ Hz, $J_{DE} = 5.4$ Hz.

C_4F_9Br. Products were separated through −30, −111, and −195 °C traps. The −195 °C trap contained 0.4 mmol of C_4F_9Cl and Br_2, and $C_4F_9SO_2OC_4F_9$ was collected mainly in the −30 °C trap, while a little went to the −111 °C trap along with Br_2. $C_4F_9SO_3C_4F_9$

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[9] Raman spectra of C_4F_9Cl: 1363 (w), 1300 (w), 1271 (vw), 1210 (br, w), 1119 (vw), 1032 (w), 816 (w), 759 (sh, s), 755 (s), 740 (vs), 718 (m), 693 (m), 655 (m), 623 (w), 543 (w), 446 (s), 393 (m), 370 (vw), 380 (w, sh), 338 (m, sh), 330 (m), 272 (vw), 223 (m), 191 (w), 178 (w), 130 (vw) cm^{-1}.

was purified by condensing the mixture onto Hg and shaking this mixture for a few minutes at 22 °C. $C_4F_9SO_2OC_4F_9$: colorless liquid; mp −91.2 °C; IR 1455 (m), 1415 (m), 1352 (m), 1300 (s), 1250 (vs), 1225 (vs), 1200 (s), 1150 (s), 1135 (s), 1090 (m), 1062 (m), 1025 (m), 950 (m), 910 (sh, m), 900 (s), 875 (w), 860 (w), 822 (m), 805 (sh, w), 760 (sh, w), 740 (m), 722 (m), 700 (w), 685 (w), 650 (w), 610 (w), 590 (m), 540 (w) cm^{-1}; ^{19}F NMR $(CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_2OCF_2{}^ECF_2{}^FCF_2{}^GCF_3{}^H)$ ϕ^*_A, ϕ^*_H −81.5 (m), ϕ^*_D −108.3 (m), ϕ^*_E −79.4 (m), ϕ^*_C −121.0, ϕ^*_B, ϕ^*_F, ϕ^*_G −120.3 (m).

SiF_3Br. Products were separated through −78 and −195 °C traps. The −78 °C trap contained Br_2 and $C_4F_9SO_3SiF_3$. The contents of this trap were transferred to a bulb containing Hg and shaken at 22 °C for ∼5 min. Reseparation through −78 and −195 °C traps gave pure $C_4F_9SO_3SiF_3$ in the −78 °C trap. $C_4F_9SO_2OSiF_3$: colorless liquid; mp −51.3 °C; bp 92.1 °C; ΔH = 8.2 kcal mol^{-1}; ΔS = 22.5 eu; log P (torr) = 7.7933 − 1794.481/T; IR 1449 (s), 1352 (s), 1293 (m), 1250 (vs), 1212 (vs), 1150 (s), 1130 (sh, s), 1038 (sh, s), 1022 (vs), 990 (vs), 925 (w), 892 (m), 875 (w), 840 (s), 805 (m), 742 (m), 700 (m), 655 (m), 630 (w), 595 (s), 550 (w), 532 (m), 460 (m), 430 (s) cm^{-1}; ^{19}F NMR $(CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_2OSiF_3{}^E)$ ϕ^*_A −81.4 (2 t), ϕ_B −126.2 (m, t), ϕ^*_C −121.1 (m), ϕ^*_D −109.8, (br t), ϕ^*_E −154.6 (br s), J_{AC} = 9.7 Hz, J_{AD} = 2.0 Hz, J_{BD} = 14.5 Hz, J_{DE} ≤1.0 Hz.

Me_3SiCl. Products were separated through −30 and −195 °C traps. Some of the $C_4F_9SO_3SiMe_3$ collected in the −30 °C trap. Most of it stayed behind in the reaction vessel as a very low volatile liquid. $C_4F_9SO_2OSiMe_3$: colorless liquid; IR 2920 (w), 1433 (s), 1352 (s), 1255 (s), 1218 (s), 1155 (s), 1002 (s), 796 (m), 748 (m), 616 (m) cm^{-1}; NMR $(CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_3SiMe_3{}^E)$ ϕ^*_A −81.5 (2 t), ϕ^*_B −126.5 (m, t), ϕ^*_C −121.1 (m), ϕ^*_D −112.9 (m, t), δ_E 0.5, J_{AC} = 10.0 Hz, J_{AD} = 2.0 Hz, J_{BD} = 14.0 Hz.

SF_5Br. Products were separated through −78 and −195 °C traps. The −78 °C trap contained $C_4F_9SO_2OSF_5$ and Br_2. Br_2 was removed by condensing the contents of the −78 °C trap onto Hg and shaking the mixture at 22 °C for a few minutes. $C_4F_9SO_2OSF_5$: colorless liquid; mp <−110 °C; bp 121.5 °C; ΔH = 10.0 kcal mol^{-1}; ΔS = 25.5 eu; log P (torr) = 8.614 − 2323.756/T + 25 074.8/T^2; IR 1458 (s), 1355 (s), 1295 (m), 1251 (vs), 1240 (sh, s), 1218 (vs), 1195 (sh, m), 1150 (s), 1130 (m), 1033 (m), 1012 (m), 940 (vs), 925 (sh, m), 880 (sh, s), 855 (vs), 800 (m), 750 (sh, m), 740 (m), 720 (m), 700 (m), 690 (w), 670 (m), 600 (m), 580 (sh, m), 565 (s), 532 (s), 520 (s) cm^{-1}; ^{19}F NMR $(CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_2OSF_4{}^EF^F)$ ϕ^*_A −81.4 (2 t), ϕ^*_B −126.3 (m), ϕ^*_C −121.0 (br m), ϕ^*_D −107.6 (br t), ϕ^*_E 77.3 (m, d) ϕ^*_F 53.9 (m), J_{AB} = 10.0 Hz, J_{AD} = 2.0 Hz, J_{BD} = 14.0 Hz, J_{EF} = 154 Hz.

POF_2Br. Products were separated through −50 and −195 °C traps. $C_4F_9SO_2OPOF_2$ and some Br_2 collected in the −50 °C trap. Br_2 was removed by shaking the contents with Hg for a few minutes. $C_4F_9SO_2OPOF_2$: colorless liquid; IR 1462 (s), 1405 (s), 1352 (m), 1292 (m), 1250 (vw), 1218 (vs), 1200 (sh, m), 1150 (s), 1125 (m), 1030 (m), 988 (s), 928 (vs), 873 (m), 855 (w), 845 (w), 845 (sh, w), 800 (m), 740 (m), 708 (m), 680 (m), 650 (m), 620 (sh, w), 610 (sh, w), 590 (m), 555 (w), 525 (m), 485 (s), 408 (m) cm^{-1}; ^{19}F NMR $(CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_2OPOF_2{}^E)$ ϕ^*_A −81.3 (2 t), ϕ^*_B −126.1 (m, t), ϕ^*_C −120.8 (m), ϕ^*_D −106.9 (m, t), ϕ^*_E −77.2 (t, d), J_{AC} = 10.0 Hz, J_{AD} = 2.0 Hz, J_{BD} = 14.0 Hz, J_{DE} = 2.0 Hz, J_{PF^E} = 1090 Hz.

CH_3Cl. Products were separated through −30 and −195 C traps. Pure $C_4F_9SO_2OCH_3$ stopped in the −30 °C trap. $C_4F_9SO_2OCH_3$: colorless liquid; mp −13.5 °C; bp 155.1 °C; ΔH = 9.2 kcal mol^{-1}; ΔS = 21.4 eu; log P (torr) = 4.8907 + 278.89/T − 488025.95/T^2; IR 2985 (m), 1450 (m), 1430 (s), 1352 (m), 1290 (w), 1250 (vs), 1235 (sh, s), 1210 (s), 1180 (sh, w), 1148 (s), 1135 (sh, m), 1040 (m), 1015 (sh, m), 1000 (s), 922 (w), 878 (w), 855 (w), 812 (w), 780 (m), 770 (sh, m), 745 (m), 730 (m), 695 (m), 650 (m), 590 (m), 530 (w) cm^{-1}; ^{19}F NMR $(CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_2OCH_3{}^E)$ ϕ^*_A −81.4 (2 t) ϕ^*_B −126.4 (m), ϕ^*_C −121.8 (m), ϕ^*_D −111.1 (m, t), δ_E 4.2 (s), J_{AC} = 10.0 Hz, J_{AD} = 2.0 Hz, J_{BD} = 14.0 Hz.

Reactions of $C_4F_9SO_2OBr$. *cis*-CHFCHF. Products were separated through −20 and −195 °C traps. Pure adduct stopped in the −20 °C trap. *erythro*-$C_4F_9SO_2CHFCHFBr$: colorless liquid; mp −45.1 °C; bp 55.2 °C (5 torr); IR 1480 (m), 1453 (m), 1354 (m), 1298 (w), 1250 (s), 1235 (sh, s), 1213 (s), 1190 (w), 1182 (w), 1150 (m), 1135 (sh, w), 1092 (m), 1075 (sh, m), 1036 (sh, m), 1015 (m), 925 (w), 900 (w), 875 (w), 850 (w), 832 (w), 800 (w), 790 (w), 745 (w), 725 (sh, w), 685 (w) cm^{-1}; ^{19}F NMR $(CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_3CHF^ECHF^FBr)$ ϕ^*_A −81.4 (2 t), ϕ^*_B −126.3 (m, t), ϕ^*_C −121.1 9 (m), ϕ^*_D −109.9 (m), ϕ^*_E −120.1 (m), ϕ^*_F −158.7 (m), J_{AC} = 9.6 Hz, J_{AD} = 2.2 Hz, J_{BD} = 14.0 Hz, $J_{H^EF^E}$ = 48.0 Hz, $J_{H^FF^F}$ = 53.0 Hz, J_{EF} = 19.5 Hz.

CF_2CH_2. Products were separated through −20 and −195 °C traps. Pure adduct stopped in the −20 °C trap. $C_4F_9SO_2OCF_2CH_2Br$: colorless liquid; mp −46.2 °C; bp 171.5 °C; ΔH = 12.3 kcal mol^{-1}; ΔS = 27.6 eu; log P (torr) = 8.9181 − 2684.788/T; IR 1484 (m), 1455 (m), 1440 (sh, m), 1405 (w), 1355 (m), 1300 (m), 1250 (s), 1240 (sh, s), 1220 (s), 1210 (sh, m), 1150 (s), 1135 (m), 1090 (w), 1080 (w), 1065 (w), 1035 (m), 1010 (m), 950 (sh, w), 930 (m), 915 (m), 902 (m), 872 (w), 840 (m), 812 (w), 802 (w), 788 (w), 750 (sh, w), 735 (w), 725 (w), 700 (w), 655 (w), 588 (w), 570 (w), 532 (w) cm^{-1}; ^{19}F NMR $(CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_2OCF_2{}^ECH_2{}^FBr)$ ϕ^*_A −81.4 (2 t), ϕ^*_B −126.3 (m, t), ϕ^*_C −121.1 (m), ϕ^*_D −110.1 (m), ϕ^*_E −67.4, J_{AB} = 10.0 Hz, J_{AD} = 2.2 Hz, J_{BD} = 14.0 Hz.

C_2F_3Cl. Products were separated through −20 and −195 °C traps. The adduct stopped in the −20 °C trap. $C_4F_9SO_2OCFClCF_2Br$: colorless liquid; mp −93.9 °C; bp 176.2 °C; ΔH = 10.8 kcal mol^{-1}; ΔS = 23.5 eu; log P (torr) = 8.1141 − 2351.6/T; IR 1505 (w), 1454 (m), 1352 (m), 1298 (m), 1250 (s), 1240 (sh, m), 1215 (s), 1185 (w), 1150 (m), 1135 (m), 1080 (m), 1065 (m), 1030 (w), 1005 (m), 998 (sh, m), 810 (m), 788 (w), 735 (w), 698 (w), 650 (w), 585 (m), 580 (w), 530 (w) cm^{-1}; ^{19}F NMR $(CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_2OCF^EClCF_2{}^FCl)$ ϕ^*_A −81.4 (2 t), ϕ^*_B −126.4 (m, t), ϕ^*_C −121.0 (br), ϕ^*_D −108.5 (br m) ϕ^*_E −72.0 (m), ϕ^*_F −65.2 (d), J_{AC} = 10.0 Hz, J_{AD} = 2.2 Hz, J_{BD} = 14.0 Hz, J_{EF} = 7.0 Hz, J_{DE} = 9.0 Hz.

CF_2CCl_2. Products were separated through −20 and −195 °C traps. The adduct collected in the −20 °C trap. $C_4F_9SO_3CCl_2CF_2Br$: colorless liquid; mp −90.2 °C; IR 1500 (w), 1460 (m), 1355 (m), 1300 (w), 1250 (s), 1240 (sh, s), 1235 (sh), 1215 (s), 1185 (w), 1152 (m), 1135 (w), 1078 (m), 1062 (w), 1037 (w), 1008 (m), 910 (m), 901 (m), 810 (w), 735 (m), 700 (w), 685 (w); ^{19}F NMR $(CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_2OCCl_2CF_2{}^EBr)$ ϕ^*_A −81.4 (2 t), ϕ^*_B −126.4 (m, t), ϕ^*_C −121.0 (m), ϕ^*_D −108.5 (m, t), ϕ^*_E −61.8 (s), J_{AB} = 10.0 Hz, J_{AD} = 2.2 Hz, J_{BD} = 14.0 Hz.

Results and Discussion

The halogen derivatives of perfluoro-*n*-butanesulfonic acid are formed in essentially quantitative yields as shown in the eq 2 and 3.

$$C_4F_9SO_3H + ClF \xrightarrow{-78\text{ to }-30\ ^\circ C} C_4F_9SO_2OCl + HF \tag{2}$$

$$2C_4F_9SO_2OCl + Br_2 \xrightarrow{-78\text{ to }-10\ ^\circ C} 2C_4F_9SO_2OBr + Cl_2 \tag{3}$$

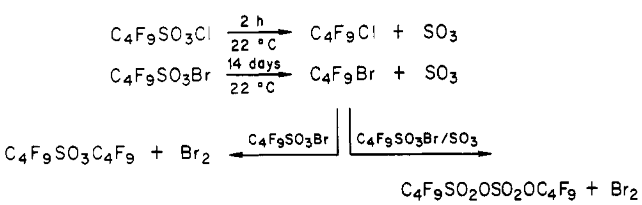
The acid can be prepared from commercially available $C_4F_9SO_2F$ by the following sequence[4] shown in eq 4. The

$$C_4F_9SO_2F \xrightarrow[22\ ^\circ C,\ 2\text{ days}]{KOH(aq)} C_4F_9SO_3K \xrightarrow{H_2SO_4} C_4F_9SO_3H \tag{4}$$

conversion of the sulfonyl fluoride to acid is somewhat difficult, and yields were only 50–70%. The saponification of the fluoride is slow, and recovery of the low volatile acid by vacuum distillation is inefficient. Intermediate conversion of the potassium salt to the barium salt might improve the yields, but this was not tried.

The new hypohalites are unstable at 22 °C, with $C_4F_9SO_3Br$ being more stable than $C_4F_9SO_3Cl$. Whereas the stability of $C_4F_9SO_3Cl$ is comparable to that of CF_3SO_3Cl, $C_4F_9SO_3Br$ is much more stable than CF_3SO_3Br. The decompositions proceed according to Scheme I. The difference in the decomposition products is due to the fact that C_4F_9Cl will not react with $C_4F_9SO_3Cl$ at 22 °C. In contrast, C_4F_9Br reacts slowly with $C_4F_9SO_3Br$ to form the ester. As in the decomposition of CF_3SO_3Br,[8] an additional product incorporating 1 mol of SO_3 is observed as a disulfonic acid ester. The latter clearly arises from the presence of SO_3 formed during the initial decomposition.

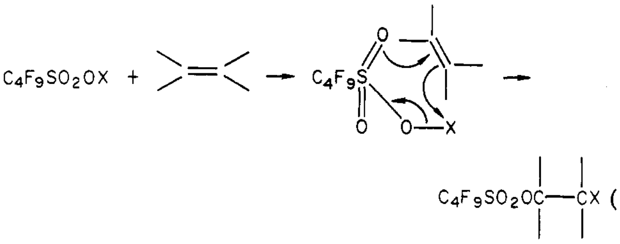
Scheme I



Reaction of pure $C_4F_9SO_3Br$ with C_4F_9Br gives only the monosulfonic acid ester. It is possible that the SO_3 first reacts with $C_4F_9SO_3Br$ to form $C_4F_9SO_2OSO_2OBr$ which then reacts with C_4F_9Br to give the observed ester.

The reactivity of $C_4F_9SO_2OX$ is very high and similar to the previously reported CF_3SO_2OX[2,3,8] (X = Cl, Br) derivatives. Reactions of the perfluoro-*n*-butanesulfonyl hypohalites parallel those of trifluoromethanesulfonyl hypohalites in every case but are, in general, less exothermic and result in higher yields in many cases. The reactions of $C_4F_9SO_2OX$ are summarized in Table I. With olefins, addition takes place readily at low temperatures to form the esters in high yields.[10] Where structural isomers are possible, only one isomer is observed. This indicates that the additions are regiospecific, and we expect that this specificity would maintain with a wide variety of alkenes, although only a few illustrative examples have been examined in this work.

The stereochemistry of the addition was briefly investigated with *cis*-CFH═CFH. The addition of $C_4F_9SO_2OX$ gives rise to diastereomers which are easily differentiated by ^{19}F NMR. For both hypohalites, only one diastereomer is observed, and the additions are therefore stereospecific. By analogy with CF_3SO_2OX, the diastereomer appears to be the erythro isomer in each case, and the additions are then cis. The efficacy of these reactions for a variety of alkenes is of course not proven. We propose the concerted addition mechanism in eq 5 to account for the observed regio- and stereospecificity. This proposal is analogous to that suggested for CF_3SO_2OX additions.[2] The combined results for two examples of R_fSO_2OX (R_f = CF_3, C_4F_9) argue strongly for a concerted addition mechanism initiated by the pronounced electrophilic character of the halogen atom in R_fSO_2OX.

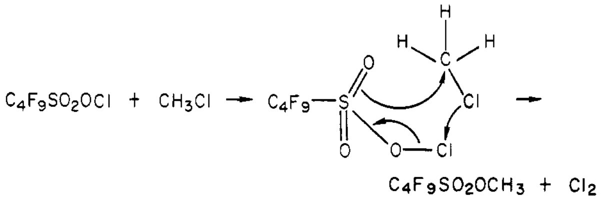


(5)

A second type of reaction investigated for $C_4F_9SO_2OX$ is with saturated halides of carbon, silicon, phosphorus, and sulfur. The reactions occur readily, leading to the substitution of the halogen by the perfluoro-*n*-butanesulfonate group (eq 6). This rather unusual transformation has been termed substitutive electrophilic dehalogenation (SED).[3b] Again, the reactions are initiated in some way by the electrophilic halogen atom of $C_4F_9SO_2OX$.

$$RX' + C_4F_9SO_2OX \rightarrow C_4F_9SO_2OR + XX' \quad (X, X' = Cl, Br) \quad (6)$$

Attempts to carry out similar substitution with other sources of $C_4F_9SO_3$ such as metal salts, the acid, or the anhydride cannot possibly succeed under the same conditions. Our interest is in the preparation of perfluoro compounds, and this reaction is very effective in this regard. While the synthesis of $C_4F_9SO_2OCH_3$ might be readily accomplished with CH_3I and $C_4F_9SO_3Ag$, a similar reaction involving CF_3I, for example, would be very difficult if not impossible. Only a limited number of SED reactions have been carried out with $C_4F_9SO_2OX$, but it is clear that these compounds can be used to prepare a wide variety of $C_4F_9SO_3$ derivatives from covalent chlorides and bromides as shown in Table I. The ability of $C_4F_9SO_2OCl$ to participate in the SED reaction with a given substrate depends on many factors. For example, CF_3Cl and SF_5Cl are unreactive below 20 °C, whereas CF_3Br and SF_5Br start reacting at temperatures as low as −50 °C. The reaction of CF_3Br is much faster than that of C_4F_9Br, and that of CH_3Cl is much faster than that of CF_3Br. These observations indicate that both the size and polarization of the halogen in the substrate are important and that there is a steric factor for a given halogen–element bond, i.e., C_4F_9Br vs. CF_3Br. The same considerations apply to SED reactions involving CF_3SO_2OX, and the larger number of examples investigated with the latter show these effects more clearly. A reaction scheme consistent with these observations is shown for CH_3Cl in eq 7. No reactions were carried out which would provide information on the stereochemistry of the SED reaction with $C_4F_9SO_2OX$. However, with CF_3SO_2OX two examples were obtained with erythro and threo isomers. The results indicated that the reactions were stereospecific. On the basis of NMR evidence, it was concluded that the reactions proceed with retention of configuration as required by the proposed scheme. It is very likely that the same considerations will hold for $C_4F_9SO_2OX$.



(7)

All the new compounds given in Table I are stable, colorless liquids at 25 °C except $C_4F_9SO_2OPOF_2$. The latter compound decomposes to the symmetrical anhydrides $(C_4F_9SO_2)_2O$ and $(F_2P(O))_2O$ at 25 °C, and an equilibrium involving the three compounds may be established. The thermal stability of $C_4F_9SO_2OCF_3$ was checked at 210 °C in glass, and no decomposition was observed after 1 day.

The characterization of the new compounds by NMR, IR, and physical properties provide an unambiguous proof of structure in nearly every case. The IR spectra of $C_4F_9SO_2OCH_3$ provides the best opportunity to pick out the bands belonging mainly to the $C_4F_9SO_2O$ group, since only two bands of the CH_3O moiety are expected below 1500 cm^{-1}. One of these is clearly found at 1430 cm^{-1} [$\delta(CH_3)$], and the other is one of the three bands at 1040, 1015, or 1000 cm^{-1} [$\nu(CO)$]. All $C_4F_9SO_2O$ derivatives will have low overall molecular symmetry and for a given covalent derivative, only small variations in positions and intensity of absorptions due to the $C_4F_9SO_2O$ group are expected.

The ^{19}F NMR of the new compounds contain resonances assignable to each of the fluorine types in $CF_3{}^{A}CF_2{}^{B}CF_2{}^{C}CF_2{}^{D}SO_2OR$ as well as the expected pattern of ^1H and ^{19}F NMR signals of R. The chemical shifts of fluorines A–C are very consistent, and only D shows sig-

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(10) Accurate yields were difficult to measure because of uncertainties in the weight of $C_4F_9SO_3H$ and the low volatility of the final products. A rough estimate of the yield was made by measuring the amount of unreacted olefins or halogens liberated.

Table II. ^{19}F Chemical Shifts for $CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DSO_2OR$

R	$-\theta^*_A$	$-\theta^*_B$	$-\theta^*_C$	$-\theta^*_D$
Cl	81.4	126.6	121.3	106.4
Br	82.1	126.9	121.8	108.8
CF_2CH_2Cl	81.5	126.3	121.3	110.0
CCl_2CF_2Cl	81.4	126.4	121.0	108.5
$CFClCF_2Cl$	81.4	126.3	121.0	108.3
CF_2CF_2Cl	81.4	126.3	121.0	108.3
CHFCHFCl	81.4	126.3	121.1	110.0
CF_3	81.4	126.2	121.0	108.2
CH_3	81.5	126.4	121.8	111.1
SiF_3	81.4	126.2	121.1	109.6
$SiMe_3$	81.5	126.5	121.7	112.9
SF_5	81.4	126.3	121.0	107.6
POF_2	81.3	126.1	120.8	106.9
CF_2CH_2Br	81.4	126.3	121.1	110.1
CCl_2CF_2Br	81.4	126.4	121.0	108.5
$CFClCF_2Br$	81.4	126.4	121.0	108.5
CHFCHFBr	81.4	126.3	121.1	109.9

nificant variation depending on R. Homonuclear decoupling was used to establish the pattern of chemical shifts for fluorines A–D, although this technique does not allow evaluation of all couplings between fluorines A–D. The spectra of fluorines B and C show second-order effects which are presumed to be due to restricted internal rotation. In the C_4F_9 group, the $^3J_{FF}$ couplings are all near zero which may be due to an averaging of coupling constants of opposite sign in various rotomers. The significant couplings in terms of the observed spectra are then $^4J_{AC}$, $^5J_{AD}$, $^4J_{BD}$, and $^5J_{DF}$, where F is a fluorine in R. A similar $^5J_{DH}$ coupling was too small to be observed. The relevant values are given in the Experimental Section, and a summary of the chemical shifts of fluorines A–D are given in Table II. Two of the new compounds, $C_4F_9SO_2OC_4F_9$ and $C_4F_9SO_2OSO_2OC_4F_9$, are not listed in Table II since it was impossible to assign the observed resonances to the different C_4F_9 groups. On the other hand, eight different resonances in the appropriate areas were observed in each case, confirming the presence of the two different C_4F_9 groups. One additional important observation is the magnitude of $^1J_{PF}$ in $C_4F_9SO_2OP(O)F_2$. This value of 1090 Hz provides a measure of the group electronegativity of $C_4F_9SO_2O$. Within the experimental error, it is identical with CF_3SO_2O, where the same $^1J_{PF}$ value was 1089.2 Hz.[11]

In conclusion, the hypohalites $C_4F_9SO_2OX$ (X = Cl, Br) provide additional examples of the pronounced electrophilic character of the halogen in R_fSO_2OX. In addition, evidence has been found to support identical reaction mechanisms for the addition of R_fSO_2OX (R_f = CF_3, *n*-C_4F_9) to olefin and for the SED reaction with covalent halides. Finally, many new $C_4F_9SO_2O$ esters have been prepared, establishing the utility of $C_4F_9SO_2OX$ in synthesis.

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Registry No. $C_4F_9SO_2OCl$, 79410-50-7; $C_4F_9SO_2OBr$, 79410-51-8; $C_4F_9SO_3H$, 375-73-5; ClF, 7790-89-8; Br_2, 7726-95-6; C_2F_4, 116-14-3; C_2F_3Cl, 79-38-9; CF_2CCl_2, 79-35-6; CF_2CH_2, 75-38-7; *cis*-CHFCHF, 1630-77-9; CF_3Br, 75-63-8; C_4F_9Br, 375-48-4; SiF_3Br, 14049-39-9; Me_3SiCl, 75-77-4; SF_5Br, 15607-89-3; POF_2Br, 14014-18-7; CH_3Cl, 74-87-3; $C_4F_9SO_2OCF_2CF_2Cl$, 79410-52-9; $C_4F_9SO_2OCFClCF_2Cl$, 79410-53-0; $C_4F_9SO_2OCCl_2CF_2Cl$, 79410-54-1; $C_4F_9SO_2OCF_2CH_2Cl$, 79410-55-2; *erythro*-$C_4F_9SO_2OCHFCHFCl$, 79410-56-3; $C_4F_9SO_2OCF_3$, 79410-57-4; $C_4F_9SO_2OC_4F_9$, 77945-21-2; $C_4F_9SO_2OSiF_3$, 79410-58-5; $C_4F_9SO_2OSF_5$, 79410-59-6; $C_4F_9SO_2OSiMe_3$, 68734-62-3; $C_4F_9SO_2OPOF_2$, 79410-60-9; $C_4F_9SO_2OCH_3$, 6401-03-2; *erythro*-$C_4F_9SO_2OCHFCHFBr$, 79410-61-0; $C_4F_9SO_2OCF_2CH_2Br$, 79410-62-1; $C_4F_9SO_2OCFClCF_2Br$, 79410-63-2; $C_4F_9SO_2OCCl_2CF_2Br$, 79420-97-6.

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Catalytic Asymmetric Hydrogenation of Methyl (*E*)- and (*Z*)-2-Acetamido-3-alkylacrylates†

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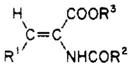
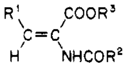
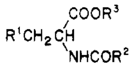
Rhodium–chiral phosphine complex catalyzed homogeneous hydrogenations of methyl (*Z*)- and (*E*)-2-acetamido-4-methoxybut-2-enoates ((*Z,E*)-**10**), methyl (*Z*)- and (*E*)-2-acetamidohex-2-enoates ((*Z,E*)-**16A**) and methyl (*Z*)- and (*E*)-2-acetamido-4-methylpent-2-enoates ((*Z,E*)-**16B**) are reported. With phosphines in which two achiral phosphorus atoms are connected by a chiral four-carbon unit, higher product enantiomeric excesses (ee's) are obtained from *E* than from *Z* substrates. With phosphines in which a two-carbon chiral unit separates two achiral phosphorus atoms, *Z* substrates are preferred. With dipamp (**28**), both *Z* and *E* substrates (particularly (*Z,E*)-**16A**) are reduced with high enantioselectivity. The additional oxygen atom in substrates (*Z,E*)-**10** has little effect on product ee with most phosphines.

Rhodium-chiral phosphine complex catalyzed enantioselective hydrogenations of 2-amido-3-arylacrylates **1** (R^1 = aryl) to give the corresponding chiral 2-amido-3-arylpropionates **2** (R^1 = aryl) have been widely studied.[2-4] Hydrogenations of (*Z*)-**1** (R^1 = aryl) are generally both fast and highly enantioselective and are useful synthetically since the pure *Z* isomers are readily prepared. The cor-


Z-1


E-1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†Dedicated to the memory of Dr. Willy Leimgruber, deceased July 8, 1981.

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