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Synthesis of Perhaloalkanesulfonyl Halides and Their Sulfonimide Derivatives

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Several perhalogenated alkanesulfonyl halides, R_fSO_2X (R_f = CF_3CF_2, $CF_3CF_2CF_2$, $ClCF_2CFClCF_2CF_2$, CF_3CCl_2, $CFCl_2$; X = Cl, F) and 1,6-bis(halosulfonyl)perfluorohexanes, $XO_2S(CF_2)_6SO_2X$ (X = Cl, F), have been prepared via the sodium sulfinates obtained from dehalogenosulfination reactions of the respective alkyl halides. Selected sulfonyl fluorides were further converted to the amides $R_xSO_2NH_2$ and imides $(R_xSO_2)_2NH$.

Introduction

Perhalogenated alkanesulfonyl halides are extremely useful intermediates in synthesis. Sulfonyl fluorides are used commercially in the preparation of ion-exchange resins, surfactants, and very strong acids, such as sulfonic acids and sulfonimides; their preparation and properties are summarized in a recent review.[1]

The most common method for synthesis of perfluoroalkanesulfonyl fluorides is electrochemical fluorination (ECF) of the corresponding alkanesulfonyl fluorides or chlorides.[2] A major disadvantage of this ECF method is that the yields of perfluoroalkanesulfonyl fluorides often decrease dramatically with the size of the alkyl group and, as a laboratory-scale synthesis, ECF is difficult and dangerous. Fluorinated sulfonyl fluorides have also been synthesized by the reaction of corresponding sulfonyl chlorides with CsF[3] and KF[4] and by the reaction of sulfonic acid anhydrides with NaF.[5] The latter reactions are historically a matter of convenience, since the sulfonic acids are the precursors and the acids are obtained via hydrolysis of the acid fluorides from ECF. Other methods include the reaction of fluorinated olefins with sulfuryl fluoride and CsF,[6] the rearrangement and decarboxylation of fluorinated sultones,[7] and the reaction of $ClSO_2F$ with tetrafluoroethylene.[8]

An attractive alternative route to a variety of perhaloalkanesulfonyl chlorides is dehalogenosulfination.[9,10] This method provides a route to many compounds that are difficult or inaccessible by other routes and is easily applied in the laboratory to readily available starting materials. Herein we report the extension of this method to several new alkanesulfonyl halides of interest as precursors to novel sulfonimides.[11,12]

Table I. Conversion of Perhaloalkyl Halides to Alkanesulfonyl Chlorides

R_fX	R_fSO_2Cl	yield, % (two steps)	bp (mp), °C	R_fX	R_fSO_2Cl	yield, % (two steps)	bp (mp), °C
1a	**3a**	81	56	**1d**	**3d**	70	(60)
1b	**3b**	80	75	**1e**	**3e**	53	(55)
1c	**3c**	84	150	**1f**	**3f**	70	(68)

Results and Discussion

The dehalogenosulfination reaction provides an excellent route to a number of perhaloalkanesulfonyl chlorides by chlorination of the corresponding intermediate perhaloalkanesulfinates as summarized in Table I.

$$\underset{\mathbf{1}}{R_fX} + Na_2S_2O_4 \xrightarrow[NaHCO_3 \text{ or } Na_2HPO_4]{CH_3CN\cdot H_2O} \underset{\mathbf{2}}{R_fSO_2Na}$$

$$\underset{\mathbf{2}}{R_fSO_2Na} + Cl_2 \xrightarrow{H_2O} \underset{\mathbf{3}}{R_fSO_2Cl}$$

$$R_fX = R_fCF_2I,^{13}\ R_fCF_2Br,^{14}\ R_fCCl_3,^{15}\ CF_3CF_2I\ (\mathbf{1a}),\ CF_3CF_2CF_2I\ (\mathbf{1b}),\ ClCF_2CFClCF_2CF_2I\ (\mathbf{1c}),\ CF_3CCl_3\ (\mathbf{1d}),\ CFCl_3\ (\mathbf{1e}),\ I(CF_2)_6I\ (\mathbf{1f})$$

The relative ease with which haloalkanes undergo the dehalogenosulfination reaction corresponds qualitatively with the energy of the bond to be broken, viz., $R_fCF_2I > R_fCF_2Br > R_fCCl_3$. The dehalogenosulfination reaction with compounds **1a–c** proceeded much more readily than with compounds **1d,e**. However, a single primary or even a secondary chlorine atom is always unreactive. As an excellent example of this, **1c** gave only the deiodosulfination product **2c**.

Halide exchange reactions of the mono- and bis(sulfonyl) chlorides with KF in CH_3CN at room temperature proceeded

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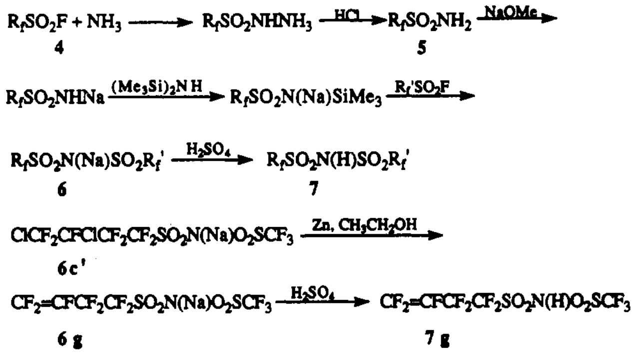
Table II. Conversion of Sulfonyl Chlorides to Fluorides by KF

R_fSO_2Cl	R_fSO_2F	yield, %	bp, °C	R_fSO_2Cl	R_fSO_2F	yield, %	bp, °C
3a	**4a**	80	8	**3c**	**4c**	81	130
3b	**4b**	85	36	**3f**	**4f**	70	167

Scheme I



$$\underset{\textbf{4}}{R_fSO_2F + NH_3} \longrightarrow R_fSO_2NHNH_3 \xrightarrow{HCl} \underset{\textbf{5}}{R_fSO_2NH_2} \xrightarrow{NaOMe}$$

$$R_fSO_2NHNa \xrightarrow{(Me_3Si)_2NH} R_fSO_2N(Na)SiMe_3 \xrightarrow{R_f'SO_2F}$$

$$\underset{\textbf{6}}{R_fSO_2N(Na)SO_2R_f'} \xrightarrow{H_2SO_4} \underset{\textbf{7}}{R_fSO_2N(H)SO_2R_f'}$$

$$\underset{\textbf{6c'}}{ClCF_2CFClCF_2CF_2SO_2N(Na)O_2SCF_3} \xrightarrow{Zn,\ CH_3CH_2OH}$$

$$\underset{\textbf{6g}}{CF_2{=}CFCF_2CF_2SO_2N(Na)O_2SCF_3} \xrightarrow{H_2SO_4} \underset{\textbf{7g}}{CF_2{=}CFCF_2CF_2SO_2N(H)O_2SCF_3}$$

in high conversion and yield to the respective sulfonyl fluorides (Table II).

$$\underset{\textbf{3}}{R_fSO_2Cl} + KF \rightarrow \underset{\textbf{4}}{R_fSO_2F} + KCl$$

$$R_f = CF_3CF_2\ (\mathbf{a}),\ CF_3CF_2CF_2\ (\mathbf{b}),\ ClCF_2CFClCF_2CF_2\ (\mathbf{c}),\ \text{-}(CF_2)_6\text{-}\ (\mathbf{f})$$

We found that very dry and finely powdered KF and very dry solvent (CH_3CN) were critical for high conversions and yields of the sulfonyl fluorides. For example, fluorination of **3f** using reagent grade CH_3CN and KF, led to hydrolysis and a mixture of products.

$$ClO_2S(CF_2)_6SO_2Cl + H_2O \xrightarrow{CH_3CN,\ KF} KO_3S(CF_2)_6SO_3K,\ KO_3S(CF_2)_6SO_2F,\ \text{others}$$

In order to obtain pure compound **4c**, we used an alternative solvent sulfolane. After complete reaction, **4c** was easily separated from sulfolane by distillation, whereas it was very difficult to separate compound **4c** from CH_3CN.

Since bis(perfluoroalkysulfonyl)imides exhibit potentially useful electrochemical properties,[16] high Brønsted solution and gas-phase acidities,[17] and novel solid-state structures as metal salts,[18] these compounds are under extensive investigation in our laboratory. Extension of this research to several new sulfonyl fluorides in this work was therefore of interest. Using established methodology for the synthesis of sulfonimides from the respective sulfonyl fluorides,[17a,19] several new examples were prepared as summarized in Scheme I and Table III.

In an attempt to avoid the conversion of **3** to **4** for the preparation of the sulfonamides (**5**) reactions of **3** with NH_3 to give **5** were attempted.

Table III. New Bis(perfluoroalkylsulfonyl)imides

R_fSO_2F	$R_fSO_2NH_2$	$R_fSO_2N(Na)SO_2R_f'$ (R_f/R_f')	R_fSO_2N-(H)SO_2R_f'
4a	**5a**	(C_2F_5/C_2F_5) **6a**	**7a**
4a	**5a**	(C_2F_5/CF_3) **6a′**	**7a′**
4b	**5b**	(C_3F_7/C_3F_7) **6b**	**7b**
4b	**5b**	(C_3F_7/CF_3) **6b′**	**7b′**
CF_3SO_2F	$CF_3SO_2NH_2$	($CF_3/ClCF_2CFClCF_2CF_2$) **6c′**	**7c′**
		($CF_3/CF_2{=}CFCF_2CF_2$) **6g**[a]	**7g**

[a] From **6c′**; see Scheme I.

$$R_fSO_2Cl \xrightarrow{NH_3} R_fSO_2NHNH_4 + R_fSO_2NH_2 + \text{others}$$

$$R_f = CF_3CF_2,\ CF_3CCl_2$$

In addition to the desired **5**, this reaction resulted in several unidentified products. Pure **5** could be obtained from this mixture by acidification and recrystallization, but the yields of **5** from the sulfonyl fluorides (**4**) were much higher.

Unsuccessful attempts were made to convert **5d** to **6d** to prepare the sulfonimide $(CF_3CCl_2SO_2)_2NH$ (**7d**). However metalation of **5d** with NaOMe failed. Similarly **5e**, which is not included in this work due to incomplete characterization, could not be metalated by NaOMe.

Adequate characterization of all compounds is provided in the Experimental Section. The sulfonyl fluorides **4a,b** have been known for a long time,[2] but we could not find any spectroscopic data for these compounds. The ^{19}F NMR of compounds (**c**) containing the $ClCF_2CFClCF_2CF_2SO_2$ groups are interesting. The fluorines on the methylene carbon bound to sulfur are diastereotopic in every case except for $ClCF_2C^*FClCF_2CF_2SO_2$-Na (**2c**), where the observed spectrum is apparently first-order. For **3c**–**7c**, very typical AB patterns are observed for the $-CF_2$-SO_2- fluorines with $J/\delta \cong 0.5$. This situation is very similar to that for compounds of the type $RC^*FClOCF_2CF_2SO_2F$, where the $-OCF_2-$ methylene fluorines are similarly affected by the chiral carbons.[20]

The new sulfonimides **7** are very acidic, as indicated by the ^1H NMR. The infrared spectra for these compounds do not exhibit a typical sharp ν(N–H) as has been observed in favorable cases,[17a] due to the very hygroscopic/deliquescent nature of the compounds. In every case, our sampling techniques gave only a broad absorptions near 3500 and 1600 cm^{-1}, indicating the absorption of water by the very acidic sulfonimides.

Compounds **7a,a′** and **7b,b′** have provided useful new acidity values for superacids in the gas phase. The latter will be reported separately.[17b] Compound **6g** was prepared as a potential precursor to a functionalized polymer, but attempts at both homopolymerization and copolymerization with C_2F_4 were unsuccessful.[21] The use of **4f** for the synthesis of a novel difunctional sulfonimide and in other related applications is in progress.

Experimental Section

General Methods. IR spectra were recorded on a Perkin-Elmer 1430 spectrometer with a Model 7500 data station. A 10-cm gas cell fitted with KCl or AgCl windows was used for gas samples. Solids were sampled as Nujol mulls or thin films between AgCl or KCl windows. ^1H (200.13 MHz) and ^{19}F (188.31 MHz) NMR spectra were measured using solutions of 1–2 mmol/L concentrations in an appropriate deuterated solvent with $CFCl_3$ as an internal standard. The sensitivity of the ^{19}F NMR allows the detection of fluorine-containing impurities at a level of ca. 0.5%. Unless indicated otherwise, samples were a minimum of 99.5% pure by ^{19}F NMR. Compounds without hydrogen were checked by ^1H NMR for

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hydrogen-containing impurities and were found to be free of impurities by the procedures given.

Mass spectra were obtained with a Hewlett-Packard 5985-B spectrometer, at 70 eV, for EI and CI (CH_4) with the sample introduced by direct injection. Appropriate isotope ratios were observed for chlorine-containing compounds, and only the ^{35}Cl ions are given. The absence of mass spectra for certain volatile samples is due to the fact that our mass spectrometer has only operated sporadically over the last 1.5 years and is under replacement.

Reagents. The starting materials $Na_2S_2O_4$, $NaHCO_3$, KF, Zn, etc. were obtained from commercial sources. Active KF was prepared by fusion in a Pt dish followed by pulverization in a drybox. Acetonitrile was dried by distillation twice over CaH_2 and P_2O_5 and was stored over molecular sieves. Starting R_fX (**1**) were obtained from PCR, Inc.

Preparation of Sodium Perhaloalkanesulfinates 2. A typical procedure for the preparation of **2c** is described. In a 1000-mL three-necked flask provided with a dropping funnel, an efficient reflux condenser, and a magnetic stirrer, was placed 100 g of $Na_2S_2O_4$ (0.5 mol), 82 g of $NaHCO_3$ (1.0 mol), 250 mL of H_2O, and 150 mL of CH_3CN. With rapid magnetic stirring under a nitrogen atmosphere, 100 g of **1c** in a 100-mL dropping funnel was added dropwise to the reaction mixture over 1 h at 40 °C. The reaction was continued for 15 h at 40 °C. The reaction mixture was then distilled to remove CH_3CN and extracted with 300 mL of ethyl acetate, and the extract was washed with aqueous NaCl (saturated, 3 × 100 mL) to remove inorganic salts. Evaporation of ethyl acetate and water under vacuum gave dry solid product **2c** (82 g); yield 91.6%. All compounds **2** decompose near 300 °C without melting.

2c: IR (solid, KCl) 1465 (w), 1376 (m), 1356 (m), 1263 (vs), 1173 (vs), 1145 (vs), 1115 (vs), 1077 (vs), 1054 (s), 1030 (s), 956 (s), 904 (m), 842 (m), 797 (m), 778 (m), 726 (m), 683 (m), 646 (m), 613 (m) cm^{-1}; ^{19}F NMR (acetone-d_6, D_2O) $ClCF_2{}^{A}CF^{B}ClCF_2{}^{C}CF_2{}^{D}SO_2Na$, A −63.3 (2F, s), B −130.3 (1F, s), C −114.2 (2F, s), D −127.8 ppm (2F, s).

2a: IR (solid, KCl) 1343 (m), 1204 (vs), 1146 (vs), 1115 (vs), 1073 (vs), 955 (m), 743 (w), 646 (w) cm^{-1}; ^{19}F NMR (acetone-d_6) $CF_3{}^{A}CF_2{}^{B}SO_2Na$, A −79.1 (3F, s), B −132.2 ppm (2F, s).

2b: IR (solid, KCl) 1340 (s), 1288 (s), 1216 (vs), 1182 (vs), 1127 (vs), 1075 (vs), 1020 (vs), 833 (m), 737 (m), 677 (m), 603 (m), 532 (m) cm^{-1}; ^{19}F NMR ($CD_3CN + D_2O$) $CF_3{}^{A}CF_2{}^{B}CF_2{}^{C}SO_2Na$, A −80.8 (3F, t), B −126.4 (2F, s), C −131.6 ppm (2F, q), J_{AC} = 9.0 Hz.

2d: IR (solid, KCl) 1245 (vs), 1175 (vs), 1085 (vs), 1036 (s), 997 (s), 966 (s), 909 (m), 864 (m), 798 (w), 701 (w), 663 (m), 627 (w), 538 (m) cm^{-1}; ^{19}F NMR (D_2O/acetone-d_6) $CF_3CCl_2SO_2Na$, −71.4 ppm (s).

2e: IR (solid, KCl) 1348 (w), 1122 (vs), 1001 (vs), 827 (m), 673 (s), 664 (s), 603 (m), 581 (m), 538 (m), 484 (m) cm^{-1}; ^{19}F NMR (D_2O) $CFCl_2SO_2Na$, −68.9 ppm (s).

2f: IR (solid, KBr) 1209 (vs), 1199 (vs), 1139 (vs), 1103 (vs), 1080 (vs), 1030 (vs), 965 (m), 810 (w), 694 (m), 622 (s), 599 (m), 574 (m), 466 (s), 412 (m), 373 (w) cm^{-1}. ^{19}F NMR (acetone-d_6) $(CF_2{}^{C}CF_2{}^{B}CF_2{}^{A}SO_2Na)_2$, A −131.2 (4F, s), B −122.9 (4F, s), C −122.5 ppm (4F, s).

Preparation of 3 by Chlorination of 2. A typical procedure for preparation of **3c** is described. A 1000-mL three-necked flask, provided with a magnetic stirrer, a gas inlet tube, and a reflux condenser, was utilized. The upper end of the reflux condenser was connected with a washing bottle filled with concentrated NaOH(aq). A solution of compound **2c** (80 g) dissolved in 250 mL of H_2O was rapidly stirred while excess Cl_2(g) was bubbled into the reaction solution at ~0 °C over 0.15 h. The product **3c** is insoluble in water and forms a lower layer. Separation and washing with an aqueous solution of $NaHCO_3$, drying over molecule sieves, and distillation gave pure liquid product **3c** (76 g); 91.6% yield.

3c: bp = 150 °C; IR (liquid, KCl) 1417 (vs, SO_2Cl), 1279 (s), 1275 (vs), 1200 (vs), 1124 (vs), 1056 (vs), 960 (s), 912 (s), 867 (s), 807 (m), 756 (s), 708 (s), 686 (s), 619 (s) cm^{-1}; ^{19}F NMR ($CDCl_3$) $ClCF_2{}^{A}CF^{B}ClCF_2{}^{C}CF_2{}^{D,E}SO_2Cl$, A −64.1 (2F, s), B −131.5 (s), C −112.1 ppm (2F, s), D −103.9, E −100.7 ppm (2F, AB pattern), J_{DE} = 227 Hz ($J/\delta = 0.50$); major *m/z* [CI] 351 (3, M^+), 267 [66, $(M - SO_2F)^+$], 251 [100, $(M - SO_2Cl)^+$].

3a: bp = 56 °C; IR (liquid, KCl) 1425 (SO_2Cl, vs), 1321 (vs), 1235 (vs), 1212 (vs), 1134 (vs), 979 (vs), 762 (w), 653 (w), 619 (m), 594 (s), 553 (s), 527 (s) cm^{-1}; ^{19}F NMR ($CDCl_3$) $CF_3{}^{A}CF_2{}^{B}SO_2Cl$, A −77.9 (3F, s), B −109.9 ppm (2F, s).

3b: bp = 75 °C; IR (liquid, KCl) 1424 (vs, SO_2Cl), 1335 (vs), 1286 (vs), 1224 (vs), 1141 (vs), 1092 (vs), 1049 (vs), 932 (m), 861 (s), 814 (m), 747 (s), 685 (s), 656 (m), 628 (s), 612 (s), 603 (s), 525 (s) cm^{-1}; ^{19}F NMR ($CDCl_3$) $CF_3{}^{A}CF_2{}^{B}CF_2{}^{C}SO_2Cl$, A −81.1 (3F, t), B −124.1 (2F, t), C −105.8 ppm (2F, qt), J_{AC} = 9.5, $J_{BC} \leq 1.0$ Hz.

3d: mp = 60 °C; bp = 121 °C; IR (solid, KCl) 1403 (SO_2Cl, vs), 1210 (vs), 912 (m), 886 (m), 833 (m), 717 (m), 603 (m), 568 (s), 515 (s) cm^{-1}; ^{19}F NMR ($CDCl_3$) $CF_3CCl_2SO_2Cl$, −71.7 ppm (s); *m/z* [EI] 151 [100, $(M - SO_2Cl)^+$], 116 [8.0, $(M - SO_2Cl_2)^+$].

3e: mp = 55 °C; IR (solid, KCl) 1392 (vs, SO_2Cl), 1181 (vs), 1084 (vs), 879 (s) cm^{-1}; ^{19}F NMR ($CDCl_3$) $CFCl_2SO_2Cl$, −57.5 ppm (s); *m/z* [EI] 101 [100.0, $(M - SO_2Cl)^+$].

3f: mp = 68 °C; IR (solid, KBr) 1409 (vs, SO_2Cl), 1393 (w), 1218 (vs), 1177 (s), 1142 (vs), 1111 (m), 969 (w), 701 (w), 677 (w), 621 (w), 602 (w), 538 (s), 520 (s), 290 (w) cm^{-1}; ^{19}F NMR (CD_3CN) $(CF_2{}^{C}CF_2{}^{B}CF_2{}^{A}SO_2Cl)_2$, A −104.7 (4F, s), B −119.2 (4F, s), C −121.2 ppm (4F, s).

Preparation of 4 by Reaction with KF. Method A. A typical procedure for the preparation of **4c** is described. In a 1000-mL vessel, as in the preparation of **3c**, was placed 250 mL of dried sulfolane, 100 g of activated KF, and 100 g of **3c**. The reaction mixture was stirred under dry nitrogen for 3 days at room temperature. After reaction was complete as monitored by ^{19}F NMR, the product was collected by pumping under vacuum through a trap at −196 °C. Distillation (740 mm) of the contents of the −196 °C trap gave pure **4c** (77 g, 81%) as a colorless liquid.

Method B. As above, 150 mL of dry CH_3CN, 11.6 g of activated KF, and 14.8 g of distilled **3c** were stirred under dry N_2 at 22 °C for 3 days. ^{19}F NMR indicated complete conversion to **4c**. Distillation gave a solution of **4c** in CH_3CN (150 mL), which could be used directly for the preparation **6c**.

4c: bp = 130 °C; IR (liquid, KCl) 1458 (vs, SO_2F), 1240 (s), 1193 (vs), 822 (s), 752 (s), 702 (s), 686 (s), 649 (m), 615 (s), 575 (s), cm^{-1}. ^{19}F NMR (CD_3CN) $ClCF_2{}^{A}CF^{B}ClCF_2{}^{C}CF_2{}^{D,E}SO_2F^{G}$, A −63.9 (2F, m), B −131.2 (1F, m), C −112.4 (2F, m), D −107.98, E −101.57 (2F, AB pattern), G 45.9 ppm (s), J_{DE} = 254 Hz ($J/\delta = 0.57$), other small coupling constants not readily determined; major *m/z* [CI] 315.0 [1.1, $(M - F)^+$], 251.0 [100, $(M - SO_2F)^+$].

4a: bp = 8 °C; IR (4 Torr, KCl) 1475.2 (vs, SO_2F), 1256.4 (vs), 1151.4 (s), 817.8 (s), 615.4 (s) cm^{-1}; ^{19}F NMR (CD_3CN) $CF_3{}^{A}CF_2{}^{B}SO_2F^{C}$, A −79.1 (3F, d), B −111.9 (2F, d), C 45.7 ppm (1F, tq (six lines)), J_{AC} = 7.1, J_{BC} = 6.3 Hz.

4b: bp = 36 °C; IR (5 Torr, KCl) 1475 (SO_2F, vs), 1345 (s), 1293 (s), 1252 (vs), 1150 (vs), 1111 (s), 1066 (m), 957 (w), 887 (s), 816 (s), 801 (s), 749 (s), 684 (m), 631 (s), 575 (s), 533 (s) cm^{-1}; ^{19}F NMR (CD_3CN) $CF_3{}^{A}CF_2{}^{B}CF_2{}^{C}SO_2F^{D}$, A −80.6 (3F, t), B −124.7 (2F, s), C −109.0 (2F, q), D 46.2 ppm (1F, s), J_{AC} = 4.3 Hz.

4f: bp = 167 °C; IR (liquid, KCl) 1461 (SO_2F, vs), 1216 (vs), 1151 (vs), 818 (s), 679 (m), 627 (s), 540 (s) cm^{-1}; ^{19}F NMR ($CDCl_3$) $(CF_2{}^{A}CF_2{}^{B}CF_2{}^{C}SO_2F^{D})_2$, A −121.9 (4F, s), B −120.7 (4F, s), C −108.5 (4F, s), D 46.2 ppm (2F, s).

Preparation of 5 by Reaction of 4 with NH_3. A typical procedure for the preparation of **5a** is described. Compound **4a**, 7.0 g (0.0346 mol), was bubbled into 200 mL of partially frozen NH_3 within 0.5 h. The reaction mixture was kept at −78 °C for 1 h in a 500-mL three-neck flask with magnetic stirrer and slow flow of dry N_2 to exclude moisture. The excess of ammonia was then removed by allowing the mixture to warm to room temperature under a flow of dry N_2, leaving a white solid, 8.0 g. The solid product ($CF_3CF_2SO_2NHNH_4$ and NH_4F) was acidified with 30 mL of H_2SO_4 (50%) followed by 50 mL of CH_3CN. Filtration gave a two-layered solution. The upper layer was separated from the mixture, and its volume was reduced to ~10 mL. Standing overnight gave a white crystalline product, which was collected by filtration and dried under vacuum, giving **5a**: 6.2 g (yield 90.0%); mp = 58 °C; IR (solid, KCl) 3300 (vs), 1394 (vs), 1385 (s), 1328 (vs), 1217 (vs), 1158 (vs), 1067 (vs), 1014 (vs), 880 (s), 851 (s), 760 (m), 616 (m) cm^{-1}; ^{19}F NMR (CD_3CN) $CF_3{}^{A}CF_2{}^{B}SO_2NH_2$, A −78.8 (3F, s), B −117.5 ppm (2F, s); ^1H NMR (CD_3CN) 7.0 (NH_2, s); major *m/z* [CI] 200 [100, $(M + 1)^+$], 80 [61.4, $(M - C_2F_3)^+$], 64 (25.8, SO_{2^+}).

Compound **5b** was prepared in an identical manner in 92% yield: mp = 52 °C; IR (solid, KCl) 3392 (s), 3296 (s), 1393 (vs), 1370 (vs), 1340 (s), 1286 (s), 1210 (vs), 1136 (vs), 1066 (s), 856 (s), 746 (m) cm^{-1}; ^{19}F NMR ($CDCl_3$) $CF_3{}^{A}CF_2{}^{B}CF_2{}^{C}SO_2NH_2$, A −81.2 (t), B −125.0 (s), C −113.4 ppm (q), J_{AC} = 9 Hz; ^1H NMR ($CDCl_3$) 5.6 (NH_2, s); major *m/z* [CI] 250 [100, $(M + 1)^+$], 80 [60, $(M - C_3F_7)^+$], 64 (22, $SO_2{}^+$).

Preparation of 5a,d by Reaction of 3a,d with NH_3. In a 250-mL flask were placed 10.0 g of **3d** and 50 mL of $CHCl_3$. The stirred solution was cooled to −60 °C. Ammonia and N_2 were bubbled into the solution for 40 min, and the mixture was stirred at −60 °C for 2 h. After the mixture had warmed to 22 °C, the white solid was collected by filtration, (10.0 g) and was identified by ^{19}F NMR as a mixture of $CF_3CCl_2SO_2NHNH_4$

(−71.0 ppm), $CF_3CCl_2SO_2NH_2$ (−72.3 ppm), and one fluorine-containing byproduct (−75.5 ppm) (~20%).

A sample of this mixture (1.0 g) was dissolved in 5 mL of H_2O, and 2 mL of H_2SO_4 (98%) was added to the solution. After the mixture had cooled to room temperature, needle crystals formed, which were collected by filtration, dried, and identified as pure **5d** (0.5 g): mp = 130 °C; IR (solid, KCl) 3356 (s), 3259 (s), 1342 (s), 1234 (vs), 1200 (vs), 1170 (vs), 1062 (s), 716 (s), 612 (m), 558 (m), 489 (m) cm^{-1}; ^{19}F NMR (CD_3CN) −72.3 ppm (s); ^1H NMR (CD_3CN) 7.0 ppm (s); major *m/z* [CI] 231, (5.5, M^+), 151 [100, $(M - SO_2NH_2)^+$].

5a was also prepared by reaction of **3a** with NH_3 in a similar way. The **5a** isolated was identical to that prepared from **4a** above.

Preparation of $CF_3CF_2SO_2NHNa$ and $CF_3CF_2CF_2SO_2NHNa$. Compound **5a**, 6.2 g (30.0 mmol), was dissolved in 50 mL of CH_3OH in a 250-mL flask, NaOH, 1.21 g (30.0 mmol), was added to the solution, and the solution was stirred at 22 °C until clear. The solution was concentrated by heating to a volume of ca. 8 mL, and upon slow cooling, fine crystals were formed. Filtration and drying under vacuum gave the amide $CF_3CF_2SO_2NHNa$: 5.8 g (yield 87.0%); IR (solid, KCl) 3523 (m), 3273 (s), 1331 (s), 1262 (vs), 1225 (vs), 1201 (vs), 1173 (vs), 1151 (vs), 1131 (vs), 1085 (s), 1032 (vs), 985 (s), 756 (m), 651 (m), 622 (m) cm^{-1}; ^{19}F NMR (CD_3CN) $CF_3{}^ACF_2{}^BSO_2NHNa$, A −78.9 (3F, s), B −117.9 ppm (2F, s); ^1H NMR (CD_3CN) 2.68 ppm (s).

Using **5b**, $CF_3CF_2CF_2SO_2NHNa$ was similarly prepared in 90% yield: IR (solid, KCl) 3348 (w), 3280 (m), 1409 (m), 1336 (vs), 1295 (vs), 1256 (vs), 1223 (vs), 1176 (vs), 1134 (vs), 1112 (vs), 1068 (vs), 1016 (vs), 999 (s), 856 (m), 745 (w), 687 (w), 644 (m), 498 (w), 526 (w) cm^{-1}; ^{19}F NMR $CF_3{}^ACF_2{}^BCF_2{}^CSO_2NHNa$ A −80.4 (3F, t), B −123.7 (2F, s), C −114.5 ppm (2F, q), J_{AB} = 9.5 Hz; ^1H (CD_3CN) NMR 3.3 ppm (s).

Preparation of $R_fSO_2N(Na)Si(CH_3)_3$ ($R_f = C_2F_5, C_3F_7$). In a 500-mL three-necked flask, provided with a reflux condenser with a drying tube, were placed 4.0 g (18.1 mmol) of dry powdered $CF_3CF_2SO_2NHNa$, 80 mL of dry CH_3CN, and 100 mL of freshly distilled $HN[Si(Me)_3]_2$. The reaction mixture was refluxed at 110 °C for 12 h. The solvent and excess HMDS were then removed by vacuum distillation. The remaining solid was dried under high vacuum at 100 °C for 4 h to give 5.3 g of the very easily hydrolyzed product (yield 99.8%).

$CF_3CF_2SO_2NNaSi(CH_3)_3$: IR (solid, KCl) 2963 (w), 2814 (w), 2778 (w), 1282 (m), 1228 (s), 1136 (s), 1075 (s), 982 (s), 843 (s), 766 (s), 717 (m), 644 (w), 627 (m) cm^{-1}; ^{19}F NMR (CD_3CN) $CF_3{}^ACF_2{}^BSO_2NNaSi(CH_3)_3$, A −78.6 (3F, s), B −117.0 ppm (2F, s); ^1H NMR (CD_3CN) 0.03 ppm (CH_3, s).

$CF_3CF_2CF_2SO_2NNaSi(CH_3)_3$ was prepared in an identical manner and was used directly without further characterization for the preparation of **6b**.

Preparation of 6. A typical procedure for **6a** is described. In a 100-mL dried stainless steel bomb was placed 5.0 g of $CF_3CF_2SO_2N(Na)SiMe_3$ (17.0 mmol) in a drybox. Acetonitrile (30 mL) was added, and 4.0 g (19.8 mmol) of $CF_3CF_2SO_2F$ (**4a**) was transferred into the bomb through the vacuum line. The bomb was heated at 80 °C with shaking for 2 d. The bomb was then vented, and the solution was evaporated to dryness. The solid product was dried at 100 °C under vacuum for 5 h to give **6a**: 6.2 g (yield 90.2%); IR (solid, KCl) 1367 (vs), 1335 (vs), 1223 (vs), 1181 (vs), 1098 (s), 980 (s), 780 (m), 760 (m), 746 (s), 649 (m), 606 (s), 525 (s) cm^{-1}; ^{19}F NMR (CD_3CN) $(CF_3{}^ACF_2{}^BSO_2)_2NNa$, A −78.6 (6F, s), B −117.0 ppm (4F, s).

6a′ was prepared in a similar way in 95.4% yield by reacting $CF_3CF_2SO_2N(Na)SiMe_3$ with a 10% excess of CF_3SO_2F[22] in 95.4%: IR (solid, KCl) 1343 (vs), 1209 (vs), 1181 (vs), 1145 (vs), 1078 (s), 982 (s), 787 (m), 759 (m), 736 (m), 643 (m), 603 (m), 569 (m), 494 (m) cm^{-1}; ^{19}F NMR (CD_3CN) $CF_3{}^ACF_2{}^BSO_2N(Na)O_2SCF_3{}^C$, A −78.1 (3F, s), B −117.1 (2F, s), C −79.0 ppm (3F, s).

Compound **6b** was prepared from **4b** and $CF_3CF_2CF_2SO_2NNaSi(CH_3)_3$ identically to **6a** in ~95% yield. NMR showed that the product contained a few percent of $CF_3CF_2CF_2SO_2NHNa$, and purification was not carried out. The sample was used directly to prepare **7b**, from which **5b** formed from $CF_3CF_2CF_2SO_2NHNa$ and H_2SO_4 was easily removed during sublimation.

Compound **6b′** was prepared similarly to **6a′** in 94% yield: IR (solid, KCl) 1367 (vs), 1346 (vs), 1320 (vs), 1284 (m), 1204 (vs), 1152 (vs), 1131 (vs), 1111 (vs), 1062 (vs), 943 (w), 869 (vs), 745 (vs), 681(vs), 651 (s) cm^{-1}; ^{19}F NMR (CD_3CN) $CF_3{}^ASO_2N(Na)SO_2CF_2{}^BCF_2{}^CCF_3{}^D$, A −79.0 (3F, s), B −113.4 (2F, q), C -123.9 (2F, s), D −80.4 ppm (3F, t), J_{BD} = 9.6 Hz.

Compound **6c′** was prepared similarly to **6a** by allowing $CF_3SO_2N(Na)Si(CH_3)_3$[19b] (21.0 g) and to react with **4c** (29.0 g) in 100 mL of CH_3CN for 4 d at 80 °C. Crude **6c′** (40 g, 95.3% yield) was recrystallized from a minimum volume of water to give a white crystalline product after filtering and drying under vacuum at 100 °C: IR (solid, KCl) 1341 (vs), 1332 (vs), 1187 (vs), 1122 (vs), 1074 (s), 1054 (s), 961 (s), 915 (m), 877 (m), 790 (m), 751 (m), 707 (m), 684 (w), 643 (m), 609 (m), 561 (m), 512 (s) cm^{-1}; ^{19}F NMR (CD_3CN) $ClCF_2{}^ACF^BClCF_2{}^CCF_2{}^{D,E}SO_2N(Na)SO_2CF_3{}^F$, A −63.1 (2F, m), B −130.4 (1F, m), C −112.0 (2F, m), D −111.1, E −108.9 (2F, AB pattern), F −78.9 ppm (3F, s), J_{DB} = 22, J_{DC} = 6, J_{DE} = 257 Hz ($J/\delta = 0.64$), other coupling constants not readily determined.

Compound **6g** was prepared as follows. In a 500-mL three-necked flask, fitted with a reflux condenser and a magnetic stirrer, were placed 40 g of **6c′**, 150 mL of absolute ethanol, and 15 g of Zn powder. With stirring, the reaction mixture was heated at 80 °C under a N_2 atmosphere for 2.5 h. After filtration, the clear solution was evaporated to dryness under high vacuum to give a white solid **6g**: 34 g (yield 99.5%); IR (solid, KCl) 1778 (vs, sharp), 1340 (vs), 1203 (vs), 1175 (vs), 1145 (vs), 1077 (s), 1042 (s), 1011 (s), 909 (m), 843 (m), 784 (m), 748 (m), 651 (m), 555 (s), 514 (s) cm^{-1}; ^{19}F NMR (acetone-*d*$_6$) $F^AF^BC{=}CF^CCF_2{}^DCF_2{}^ESO_2N(Na)SO_2CF_3{}^G$, A −89.5 (1F, m), B −104.7 (1F, m), C −187.5 (1F, m), D = E −115.8 (4F, m), G −77.3 ppm (3F, s), J_{AC} = 38, J_{AB} = 55, J_{AD} = 6, J_{CD} = 31, J_{BC} = 115 Hz, other coupling constants not readily determined.

Preparation of 7. Compound **7a** was prepared as follows. In a sublimator, 5.0 g of dry **6a** was dissolved in 43 g of H_2SO_4 (100%). At 60 °C under high vacuum, 4.2 g of white solid **7a** was collected (yield 91%): mp = 42 °C; IR (solid, AgCl) 1345 (vs), 1226 (vs), 1189 (vs), 1146 (vs), 1099 (m), 984 (s), 783 (w), 746 (w), 650 (m), 621 (m), 532 (m) cm^{-1}; ^{19}F NMR (CD_3CN) $(CF_3{}^ACF_2{}^BSO_2)_2NH$, A −78.6 (6F, s), B −116.9 ppm (4F, s); ^1H NMR (CD_3CN) 8.2 ppm (NH, s).

Compound **7a′** was prepared in the same manner as **7a** (93.3% yield): mp = 39 °C; IR (solid, AgCl), 3300 (m, br), 1345 (vs), 1247 (vs), 1178 (s), 1145 (s), 1074 (s), 990 (s), 790 (m), 744 (m), 619 (s), 591 (w), 518 (m) cm^{-1}; ^{19}F NMR (CD_3CN) $CF_3{}^ACF_2{}^BSO_2N(H)O_2SCF_3{}^C$, A −78.2 (3F, s), B −116.1 (2F, s), C −78.5 ppm (3F, s); ^1H NMR (CD_3CN) 7.4 ppm (s).

Compound **7b** was prepared as above from **6b** (85% yield): mp = 45 °C; IR (solid, AgCl), 1345 (vs), 1294 (vs), 1225 (vs), 1157 (vs), 1078 (s), 946 (m), 870 (m), 685 (m), 634 (m), 598 (w) cm^{-1}; ^{19}F NMR (CD_3CN) $(CF_3{}^ACF_2{}^BCF_2{}^CSO_2)_2NH$, A −80.3 (6F, t), B −123.9 (4F, s), C −113.3 ppm (4F, q), J_{AC} = 9.5 Hz; ^1H NMR ($CDCl_3/CD_3CN$, 10:1) 7.86 ppm (s).

Compound **7b′** was prepared as above from **6b′** (80% yield): mp = 38 °C; IR 3526 (s, br), 1341 (vs), 1214 (vs), 1148 (vs), 1132 (vs), 1109 (vs), 1066 (vs), 946 (m), 881 (s), 785 (s), 745 (s), 681 (s), 628 (vs), 569 (vs) 517 (s) cm^{-1}; ^{19}F NMR (CD_3CN) $CF_3{}^ASO_2N(H)SO_2CF_2{}^BCF_2{}^CCF_3{}^D$, A −79.0 (3F, s), B −113.4 (2F, q), C −123.9 (2F, s), D −80.3 ppm (3F, t), J_{BD} = 9.5 Hz; ^1H NMR ($CDCl_3$) 7.20 ppm (s).

Compound **7c′** was prepared as follows. In a sublimator, 0.5 g of **6c′** was dissolved in 4 mL of H_2SO_4 (98%), and the mixture was sublimed at 120 °C, under high vacuum, giving pure white liquid **7c′**: 0.4 g (83.8% yield); IR (liquid, AgCl) 3509 (m), 1371 (s), 1342 (vs), 1321 (vs), 1185 (vs), 1148 (vs), 1122 (vs), 1075 (s), 1053 (s), 961 (s), 915 (m), 789 (m), 750 (m), 610 (s), 560 (s), 510 (s) cm^{-1}; ^{19}F NMR ($CDCl_3$) $ClCF_2{}^ACF^BClCF_2{}^CCF_2{}^{D,E}SO_2N(H)SO_2CF_3{}^F$, A −64.2 (2F, m), B −131.5 (1F, m), C −112.6 (2F, m), D −107.8, E −105.4 (2F, AB pattern), F −76.3 ppm (1F, s), J_{AD} = 16, J_{CD} = 5, J_{DE} = 269 Hz ($J/\delta = 0.54$), other coupling constants not readily determined; ^1H NMR ($CDCl_3$) 8.5 ppm (s); major *m/z* [CI] 463 (17.2, M^+), 251 [100, $(M - SO_2NHSO_2CF_3)^+$].

Compound **7g** was prepared as follows. In a 250-mL flask, 37 g of **6g** was dissolved in 70 mL of HCl (36%). A white solid NaCl deposited and was removed by filtration. On standing at 22 °C, the filtrate separated into two layers. The lower oily layer was distilled under reduced pressure to give **7g** as a clear liquid: 30 g (yield 92.7%); bp = 65 °C/3 mmHg; IR (liquid, AgCl) 1778 (s), 1431 (m), 1362 (vs), 1343 (vs), 1313 (vs), 1206 (vs), 1174 (vs), 1137 (vs), 1073 (s), 1011 (m), 904 (m), 843 (m), 783 (w), 747 (w), 629 (s), 561 (w), 514 (m) cm^{-1}; ^{19}F NMR ($CDCl_3$) $F^AF^BC{=}CF^CCF_2{}^DCF_2{}^ESO_2N(H)SO_2CF_3{}^G$, A −86.8 (1F, m), B −103.6 (1F, m), C −189.4 (1F, m), D −116.2 (2F, m), E −112.1 (2F, m), G −77.1 ppm (3F, s), J_{AD} = 6.0, J_{AC} = 40, J_{AB} = 47, J_{BC} = 116, J_{BD} = 15, J_{CE} = 5, J_{CD} = 36 Hz; ^1H NMR ($CDCl_3$) 9.0 ppm (s).

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