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Perhaloalkanesulfinyl Chlorides, $R_fS(O)Cl$, and Perhaloalkanesulfinate Esters, $R_fS(O)OR_f'$[1]

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Five halogenated methane- and ethanesulfinyl chlorides, $R_fS(O)Cl$ (R_f = CCl_3, $CFCl_2$, CF_2Cl, CF_3CCl_2, CF_3CBrCl) have been prepared by reacting the respective sulfinic acids, $R_fS(O)OH$, with $SOCl_2$. The sulfinyl chlorides have been converted to a series of new stable halogenated sulfinyl esters $R_fS(O)OR_f'$ (R_f' = CF_3CH_2, $CH_3(CF_3)CH$, $C(CF_3)_2CH_3$, C_6H_5) by treatment with fluoro alcohols or phenol in the presence of pyridine or triethylamine. The *tert*-butyl sulfinates (R_f = $CFCl_2$, CF_3CCl_2; R_f' = $C(CH_3)_3$) decompose upon distillation to give isobutylene and the parent sulfinic acid. Complex nuclear magnetic resonance spectra are observed for the esters with chiral centers at sulfur and carbon.

Introduction

Alkanesulfinic acids, alkanesulfinate salts, and alkanesulfinyl chlorides are extremely useful intermediates in the synthesis of organic and biologically active compounds. Perhalogenated analogues, especially perfluoroalkanesulfinyl compounds, have also received increasing attention, and their preparation and properties were summarized in recent reviews.[2] The methods described for the synthesis of fluorinated sulfinic acids are devoted primarily to perfluoroalkyl-containing compounds, e.g., addition of RSF_3[3] or $RNSF_2$[4] to perfluoro olefins followed by acid hydrolysis, reduction of perfluoroalkylsulfonyl fluorides with subsequent acidification,[5-7] treatment of perfluoroalkyl iodides with SO_2 in the presence of zinc,[8] and electrochemical fluorination of perfluoroalkyl and perfluoroaryl bromides[9] or iodides[10] in the presence of SO_2.

However, halogenated sulfinic acid derivatives which contain highly substituted chloro/bromo/fluoro alkyl groups have not been examined as extensively. This may be due in part to the lack of ready access to their precursors. Trichloromethanesulfinic acid, which has been known for over 100 years, is prepared by the reduction of CCl_3SO_2Cl with hydrogen sulfide followed by reaction with $SOCl_2$ to give $CCl_3S(O)Cl$.[11] 1-Chloro-1,2,2,2-tetrafluoroethanesulfinyl chloride and 1,1-dichloro-2,2,2-trifluoroethanesulfinyl chloride were obtained by multistep reactions.[12-15] The chlorination of perhalogenated sulfines results in sulfinyl chlorides, but sulfines are much less accessible compounds and, in fact, some sulfinyl chlorides are used as sulfine precursors.[15]

A straightforward route to a variety of halogenated alkanesulfinates which proceeds via sulfinatodehalogenation has been described.[16,17]

$$R_fX + Na_2S_2O_4 \xrightarrow[CH_3CN,H_2O]{NaHCO_3} R_fSO_2Na$$

R_fX = R_fCF_2I;[18,19] CCl_4, $CFCl_3$, R_fCCl_3;[20] CF_3CBr_3, CF_3CFBr_2, CF_3CBr_2Cl[21]

Because of the availability of a large selection of haloalkanes and the mild reaction conditions required, this is the method of choice for the preparation of halogenated alkanesulfinates. Since fluoroalkanesulfinates and their esters have been suggested as precursors to compounds with applications such as bactericides,[22] insecticides,[23] precursors to organic acids[24,25] and ketones,[25] fungicides,[26] and antiparasite agents,[27] we were interested in the preparation of several halogenated methane- and ethanesulfinates, sulfinic acids, and sulfinyl chlorides. The esterification of the last compounds by reaction with fluoro alcohols gives rise to new, stable compounds that exhibit interesting ^1H NMR spectra due to the presence of chiral centers at carbon and at sulfur.[28-30]

Table I. Preparation of Halogenated Alkanesulfinic Acids, R_fSO_2H

R_fX	R_fSO_2H	yield, %	bp, °C (*P*, mm)
$CBrCl_3$	CCl_3SO_2H	60	85 (0.5)
$CFCl_3$	$CFCl_2SO_2H$	70[a]	67 (1.0)
$CBrClF_2$	CF_2ClSO_2H	56	56 (0.25)
CF_3CCl_3	$CF_3CCl_2SO_2H$	78	78 (1.0)
CF_3CBr_2Cl	$CF_3CBrClSO_2H$	45	*b*

[a] 60% conversion. [b] Unstable during vacuum distillation over 40 °C.

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Table II. Preparation of Halogenated Sulfinate Esters, $R_fS(O)OR_f'$

R_f	R_f'	yield, %	bp, °C (*P*, mm)	anal., % C	H	F
CCl_3	CF_3CH_2	71	58–59 (10)	13.20 (13.56)[a]	0.70 (0.75)	21.1 (21.47)
	$CH_3(CF_3)CH$	75	35 (0.25)	17.11 (17.17)	1.39 (1.43)	22.3 (20.39)
	$CH_3(CF_3)_2C$	56	47 (1.5)	17.44 (17.27)	0.70 (0.86)	
	C_6H_5	65	83 (0.25)	32.03 (32.37)	1.89 (1.93)	40.72[b] (41.04)
$CFCl_2$	CF_3CH_2	78	65 (35)	14.68 (14.46)	0.81 (0.80)	31.1 (30.52)
	$CH_3(CF_3)CH$	67	36 (0.25)	18.64 (18.25)	1.52 (1.52)	28.8 (28.90)
	$CH_3(CF_3)_2C$	47	25 (0.75)	18.13 (18.13)	0.92 (0.91)	40.1 (40.18)
	C_6H_5	72	65 (0.25)	34.16 (34.57)	2.05 (2.06)	8.2 (7.82)
CF_3CCl_2	CF_3CH_2	72	55 (15)	16.27 (16.05)	0.72 (0.67)	38.2 (38.13)
	$CH_3(CF_3)CH$	81	43 (0.25)	19.21 (19.17)	1.19 (1.28)	36.2 (36.42)
	$CH_3(CF_3)_2C$	51	35 (1.0)	18.85 (18.90)	0.76 (0.79)	44.5 (44.88)
	C_6H_5	73	83 (1.0)	32.70 (32.76)	1.65 (1.71)	19.3 (19.45)

[a] Calculated values in parentheses. [b] Chlorine.

Table III. NMR Spectral Data for Halogenated Alkanesulfinate Esters

compd	chem shift,[a] ppm	coupling const, Hz
$CCl_3S(O)OCH_2CF_3$	4.77, 4.71, 4.36, 4.30, (4q, CH_2, AB), −74.27 (t, CF_3)	$J_{A-B} = 12$, $J_{A-F} = J_{B-F} = 8$
$CFCl_2S(O)OCH_2CF_3$	4.72, 4.66, 4.33, 4.27 (4q, CH_2, AB), −74.23 (t, CF_3), −66.61 (s, $CFCl_2$)	$J_{A-B} = 12$, $J_{A-F} = J_{B-F} = 8$
$CF_3CCl_2S(O)OCH_2CF_3$	4.77, 4.71, 4.34, 4.28 (4q, CH_2, AB), −74.33 (t, CF_3CH_2), −72.76 (s, CF_3CCl_2)	$J_{A-B} = 12$, $J_{A-F} = J_{B-F} = 8$
$CCl_3S(O)OCH(CH_3)CF_3$	4.96 (sept, CH), 1.57 (q/d, CH_3), 4.89 (sept, CH), 1.56 (q/d, CH_3), −78.77 (m, CF_3), −78.41 (m, CF_3)	$J_{H-CH_3} = 2$, $J_{H-F} = 6$
$CFCl_2S(O)OCH(CH_3)CF_3$	4.85 (m, CH), 1.56 (q/d, CH_3), 1.54 (q/d, CH_3), −78.77 (s, CF_3), −79.02 (s, CF_3), −66.86 (m, $CFCl_2$)	$J_{H-CH_3} = 2$, $J_{H-F} = 8$
$CF_3CCl_2S(O)OCH(CH_3)CF_3$	4.81 (m, CH), 1.58 (q/d, CH_3), 1.56 (q/d, CH_3), −78.69 (s, CF_3), −78.72 (s, CF_3), −72.27 (m, $CHCF_3$)	$J_{H-CH_3} = 2$, $J_{H-F} = 8$
$CCl_3S(O)OC(CF_3)_2CH_3$	1.98 (sept, CH_3), −77.90 (q, CF_3), −77.29 (q, CF_3)	$J_{F-F} = 7.5$, $J_{H-F} = 1$
$CFCl_2S(O)OC(CF_3)_2CH_3$	1.98 (sept, CH_3), −77.77 (q, CF_3), −77.36 (q, CF_3), −64.68 (s, $CFCl_2$)	$J_{H-F} = 1$, $J_{F-F} = 8$
$CF_3CCl_2S(O)OC(CF_3)_2CH_3$	1.97 (sept, CH_3), −77.20 (q, CF_3), −77.40 (q, CF_3), −72.12 (s, CF_3CCl_2)	$J_{H-F} = 1$, $J_{F-F} = 8$
$CCl_3S(O)OC_6H_5$	7.22–7.44 (m, C_6H_5)	
$CFCl_2S(O)OC_6H_5$	7.19–7.42 (m, C_6H_5), −65.36 (s, F)	
$CF_3CCl_2S(O)OC_6H_5$	7.19–7.45 (m, C_6H_5), −71.96 (s, F)	

[a] Relative to external TMS or CCl_3F.

Results and Discussion

The relative ease with which haloalkanes undergo sulfinatodehalogenation reactions is in keeping with the energy of the bond to be broken, viz., $R_fCF_2I > R_fCF_2Br$; $CBrCl_3 > CCl_4 > RCCl_3 > CFCl_3$; and $CF_3CBr_3 > CF_3CFBr_2 > RCF_2Br$. However, the preparative yields of the sulfinic acids resulting from conversion of the sodium sulfinates depend on the thermal stability of the products (Table I). In contrast to perfluoroalkanesulfinic acids,[2] which have limited thermal stability, the chlorinated analogues in which two chlorine atoms are bonded to the α-carbon, such as $CFCl_2SO_2H$ and $CF_3CCl_2SO_2H$, are sufficiently stable to survive vacuum distillation at ≤120 °C from concentrated H_2SO_4.

The sulfinic acids are converted readily to haloalkanesulfinyl chlorides on treatment with thionyl chloride.

$$R_fS(O)OH + SOCl_2 \longrightarrow R_fS(O)Cl + HCl + SO_2$$

R_f =	CCl_3	$CFCl_2$	CF_3CCl_2	CF_2Cl	CF_3CBrCl
Yield(%)	85	83	90	40	70
BP °C (Torr)	69(20)	45(35)	59(57)	60-65	50-55(20)
^{19}F NMR (δ)	--	-61.16	-71.07	-68.11	-68.98,-69.14 (AB)

While elemental analyses were not obtained for these new sulfinyl chlorides, they are confirmed by the excellent analytical data obtained for the ester derivatives as given in Table II. In an earlier report,[30] the anhydride $C_4F_9S(O)OS(O)C_4F_9$ was formed in addition to the sulfinyl chloride when $C_4F_9S(O)OH$ was reacted with $SOCl_2$. In our work, where diethyl ether was used as diluent, the anhydrides were not obtained. These new sulfinyl chlorides are considerably more stable than the analogous haloalkanecarboxylic acid chlorides and are hydrolyzed only slowly when mixed with cold water. For example, $CF_3CCl_2S(O)Cl$ does not react with fluoro alcohols, such as CF_3CH_2OH, at 80 °C or in refluxing diethyl ether. However, in the presence of triethylamine or pyridine, esterification occurs smoothly at −20 °C:

$$R_fS(O)Cl + R_f'OH \xrightarrow[\text{ether}]{\text{py}} R_fS(O)OR_f'$$

R_f = CCl_3, $CFCl_2$, CF_3CCl_2

R_f' = CF_3CH_2, $CH_3(CF_3)CH$, $C(CH_3)(CF_3)_2$, C_6H_5

The *tert*-butyl sulfinates were also prepared, but decomposed during distillation, i.e.

$$R_fS(O)OC(CH_3)_3 \rightarrow R_fS(O)OH + CH_2{=}C(CH_3)_2$$

R_f = $CFCl_2$, CF_3CCl_2

The new sulfinate esters are listed in Table II with yields, physical data, and elemental analyses. ^{19}F and ^1H nuclear magnetic

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resonance data are found in Table III.

Similar to 1-chloroethanesulfinyl chloride,[31] 1-bromo-1-chloro-2,2,2-trifluoroethanesulfinyl chloride, which also possesses two asymmetric centers, shows an NMR spectrum typical of a mixture of two diastereoisomers (δ(F) singlet at −68.98 and −69.14 ppm). The NMR spectra of 2,2,2-trifluoroethanesulfinate esters, e.g., $CCl_3S(O)OCH_2CF_3$ and $CFCl_2S(O)OCH_2CF_3$, clearly show ABM_3 patterns.[28] Other sulfinate esters, e.g., $CCl_3S(O)OCH(CH_3)CF_3$ and $CFCl_2S(O)OCH(CH_3)CF_3$, led to more complicated spectra due to the presence of two asymmetric centers. Computer-generated spectra obtained by using the PMR program from Serena Software matched the experimental spectra. In the mass spectra of these sulfinate esters, peaks assigned to M^+ and $RS(O)O^+$ were observed.

We are continuing our studies on these interesting sulfur(IV) compounds, primarily via further derivatization of the acids and chlorides. The simple method of converting haloalkanes to alkali-metal sulfinates makes the further study of these materials much more attractive.

Experimental Section

General Procedures. Microanalyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. Infrared spectra were determined on liquids between KBr disks with a Perkin-Elmer Model 1700 FT IR spectrometer, nuclear magnetic resonance spectra were recorded with a Bruker NR200 Fourier transform spectrometer on $CDCl_3$ solutions with reference to $(CH_3)_4Si$ or CCl_3F, and mass spectra (CI) were obtained on a VG7070SH mass spectrometer.

Materials. The starting materials either were synthesized according to the literature methods (cited with the syntheses below) or methods described herein or were purchased and used as received from PCR.

Preparation of CCl_3SO_2Na, CCl_3SO_2H, and $CCl_3S(O)Cl$. To a mixture of 25 g (assay 85%, 0.12 mol) of sodium dithionite, 12.5 g (0.15 mol) of sodium bicarbonate, 50 mL of acetonitrile, and 50 mL of water was added dropwise 24 g of bromotrichloromethane at 25 °C with vigorous stirring. After completion of the addition, stirring was continued for 4 h. The acetonitrile layer was separated from the mixture, and the aqueous layer was extracted with 50 mL of acetonitrile. The acetonitrile aliquots were combined and evaporated under reduced pressure. The residue was treated with 50 mL of absolute methanol, and the insoluble substance was removed by filtration. The filtrate was evaporated under reduced pressure, and the resulting solid was dried in vacuum at 80 °C for 4 h to give 15 g (60.8%) of sodium trichloromethanesulfinate.

Twelve grams (0.055 mol) of sodium trichloromethanesulfinate was suspended in 30 mL of 98% sulfuric acid, and the suspension was stirred and warmed until the solid dissolved. Distillation under vacuum gave 8.6 g (85%) of trichloromethanesulfinic acid, boiling at 80–85 °C (0.5 mm) [lit.[11] bp 71–72 °C (0.04 mm)].

To a solution of 18.4 g (0.1 mol) of trichloromethanesulfinic acid in 40 mL of diethyl ether was added dropwise 25 g (0.21 mol) of thionyl chloride. The mixture was stirred at 25 °C for 6 h. After removal of ether and unreacted thionyl chloride, vacuum distillation gave 17.2 g (85%) of trichloromethanesulfinyl chloride, boiling at 69 °C (20 mm) [lit.[11] bp 36–38 °C (1 mm)].

Preparation of $CF_3CCl_2SO_2Na$, $CF_3CCl_2SO_2H$, and $CF_3CCl_2S(O)Cl$. According to literature method,[20] or the procedure described above, $CF_3CCl_2SO_2Na$ and $CF_3CCl_2SO_2H$ were prepared from CF_3CCl_3. In ether, 21.7 g (0.1 mol) of $CF_3CCl_2SO_2H$ was reacted with 18 g (0.15 mol) of $SOCl_2$ at 30–40 °C for 4 h to give 21 g (90%) of $CF_3CCl_2S(O)Cl$, boiling at 59 °C (57 mm).

Preparation of $CF_3CBrClSO_2Na$, $CF_3CBrClSO_2H$, and $CF_3CBrClS(O)Cl$. According to literature method,[21] or the procedure described above, $CF_3CBrClSO_2Na$ was prepared from CF_3CBr_2Cl. $CF_3CBrClSO_2H$ was not obtained by distillation with sulfuric acid, but rather as follows. A 14-g (0.05-mol) sample of $CF_3CBrClSO_2Na$ was dissolved in 20 mL of 15% hydrochloric acid. The solution was extracted with two portions of ether (2 × 50 mL). After removal of ether, the residue was dehydrated in vacuum at 40 °C. The crude product was used subsequently without purification. To a solution of $CF_3CBrClSO_2H$ (11 g, 0.042 mol) in ether (20 mL) was added thionyl chloride (10 g, 0.084 mol). After 4 h, the ether was evaporated and distillation under reduced pressure gave $CF_3CBrClS(O)Cl$ (8.2 g, 70%), which boils at 50–55 °C (20 mm).

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Preparation of $CFCl_2SO_2Na$, $CFCl_2SO_2H$, and $CFCl_2S(O)Cl$. Into a mixture of $Na_2S_2O_4$ (50 g), $NaHCO_3$ (25 g), CH_3CN (100 mL), and water (100 mL) was passed 50 g (0.36 mol) of CCl_3F. The mixture was stirred at 20–30 °C for 48 h. After treatment as above, 25 g (37%) of $CFCl_2SO_2Na$ was obtained. $CFCl_2SO_2H$ and $CFCl_2S(O)Cl$ were prepared by using the same methods as for CCl_3SO_2H and $CCl_3S(O)Cl$.

Preparation of CF_2ClSO_2Na, CF_2ClSO_2H, and $CF_2ClS(O)Cl$. Into a flask which contained $Na_2S_2O_4$ (20 g), $NaHCO_3$ (10 g), CH_3CN (100 mL), and H_2O (60 mL) cooled in a water bath was passed 33 g (0.2 mol) of CF_2BrCl. The flask was fitted with a dry ice condenser. The mixture was stirred and warmed to 20–30 °C. After 4 h, the reaction was complete. After treatment, 21 g (61%) of CF_2ClSO_2Na was obtained. CF_2ClSO_2H and $CF_2ClS(O)Cl$ were prepared by the same procedure as $CF_3CBrClSO_2H$ and $CF_3CBrClS(O)Cl$.

Preparation of Sulfinate Esters. All of the sulfinate esters were prepared in the same manner. In a typical reaction, a solution of $CFCl_2S(O)Cl$ (4.04 g, 0.022 mol) in ether (10 mL) was added dropwise to a stirring solution of CF_3CH_2OH (3.20 g, 0.032 mol) and triethylamine (4.2 g, 0.042 mol) in ether (50 mL) at −20 to −10 °C. The stirring was continued for 1 h, and the mixture was then warmed to 25 °C. The mixture was poured into ice-cold water and stirred. The ether layer was isolated and dried over anhydrous sodium sulfate. Distillation in vacuum gave 4.3 g (78.2%) of product. Other sulfinate esters were prepared similarly. The preparative results and physical data are given in Tables II and III. Infrared spectral data are as follows (cm^{-1}). $CCl_3S(O)OCH_2CF_3$: 2973 m, 1446 w, 1407 m, 1280 s, 1171 s, 1013 s, 962 s, 829 s, 804 s, 737 s, 652 s, 560 s, 531 m, 512 m, 459 m. $CFCl_2S(O)OCH_2CF_3$: 2973 m, 1447 w, 1410 m, 1282 s, 1175 s, 1068 s, 1034 s, 1013 s, 963 s, 868 s, 750 s, 654 s, 588 m, 563 s. $CF_3CCl_2S(O)OCH_2CF_3$: 2976 w, 1449 w, 1408 m, 1283 s, 1250 s, 1186 s, 1035 s, 1013 s, 963 s, 925 s, 889 s, 847 s, 751 s, 706 s, 653 m, 560 m, 531 m, 513 m, 483 m, 457 m. $CCl_3S(O)OCH(CH_3)(CF_3)$: 3005 w, 2953 w, 1459 w, 1390 m, 1334 s, 1281 s, 1202 s, 1165 s, 1122 s, 1074 s, 1016 s, 921 s, 831 s, 809 s, 799 s, 765 s, 662 m, 556 m, 506 m, 472 s. $CFCl_2S(O)OCH(CH_3)(CF_3)$: 3006 m, 2954 m, 1416 w, 1392 m, 1336 s, 1283 s, 1197 s, 1077 s, 1014 s, 922 s, 873 s, 829 s, 759 s, 663 s, 598 m, 585 m, 556 s, 515 s, 467 s. $CF_3CCl_2S(O)OCH(CH_3)CF_3$: 3008 w, 2955 w, 1460 w, 1392 m, 1334 w, 1283 m, 1251 m, 1191 m, 1121 m, 1073 m, 1016 m, 930 m, 889 m, 807 w, 767 w, 707 w, 663 w, 586 w, 559 w, 506 w, 471 m. $CCl_3S(O)OC(CF_3)_2CH_3$: 3017 w, 2963 w, 1461 w, 1396 m, 1305 s, 1265 m, 1224 s, 1163 m, 1127 s, 1088 s, 937 s, 879 w, 834 m, 811 m, 777 m, 739 m, 702 m, 646 m, 594 w, 539 s. $CFCl_2S(O)OC(CF_3)_2CH_3$: 3020 w, 2962 w, 1462 w, 1396 m, 1306 s, 1235 s, 1164 m, 1132 s, 1089 s, 941 s, 900 m, 877 m, 818 w, 780 m, 740 m, 703 m, 648 m, 596 w, 515 w. $CF_3CCl_2SO(O)OC(CF_3)_2CH_3$: 3019 w, 2964 w, 1462 w, 1397 m, 1306 s, 1223 s, 1165 m, 1127 s, 1089 s, 941 s, 893 m, 878 m, 805 w, 781 s, 741 m, 723 w, 703 s, 646 m, 594 w, 560 m, 539 w. $CCl_3S(O)OC_6H_5$: 3063 w, 3041 w, 1586 s, 1489 s, 1483 s, 1456 m, 1201 s, 1176 s, 1153 s, 1072 m, 1024 m, 909 m, 844 s, 819 s, 795 s, 769 s, 717 s, 689 s, 585 m, 502 s, 462 s. $CFCl_2S(O)OC_6H_5$: 3065 w, 3042 w, 1587 s, 1488 s, 1457 m, 1407 m, 1289 m, 1201 s, 1177 s, 1156 s, 1070 s, 1024 m, 873 s, 848 s, 770 s, 718 s, 689 s, 606 m, 586 m, 501 s. $CF_3CCl_2S(O)OC_6H_5$: 3067 w, 3043 w, 1587 s, 1484 s, 1458 m, 1250 s, 1196 s, 1153 s, 1072 m, 1024 m, 918 m, 885 s, 835 s, 820 s, 771 s, 721 m, 704 m, 690 m, 612 w, 587 m, 559 m.

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Registry No. CCl_3Br, 75-62-7; CCl_3F, 75-69-4; $CBrClF_2$, 353-59-3; CCl_3CF_3, 354-58-5; CBr_2ClCF_3, 754-17-6; CCl_3SO_2H, 7430-24-2; CCl_2FSO_2H, 97966-19-3; $CClF_2SO_2H$, 97966-18-2; $CHCl_2CF_3$, 105507-21-9; $CF_3CBrClSO_2H$, 137822-76-5; $CCl_3S(O)OCH_2CF_3$, 137794-39-9; $CCl_3S(O)OCH(CF_3)CH_3$, 137794-40-2; $CCl_3S(O)OC(CF_3)_2CH_3$, 137794-41-3; $CCl_3S(O)OPh$, 137794-42-4; $CCl_2FS(O)OCH_2CF_3$, 137794-43-5; $CCl_2FS(O)OCH(CF_3)CH_3$, 137822-77-6; $CCl_2FS(O)OC(CF_3)_2CH_3$, 137794-44-6; $CCl_2FS(O)OPh$, 137794-45-7; $CF_3CCl_2S(O)OCH_2CF_3$, 137794-46-8; $CF_3CCl_2S(O)OCH(CF_3)CH_3$, 137794-47-9; $CF_3CCl_2S(O)OC(CF_3)_2CH_3$, 137794-48-0; $CF_3CCl_2S(O)OPh$, 137794-49-1; $CCl_3S(O)Cl$, 25004-95-9; $CF_3CCl_2S(O)Cl$, 103624-52-8; $CF_3CBrClS(O)Cl$, 137794-50-4; CF_3CH_2OH, 75-89-8; $CF_3CH(OH)CH_3$, 374-01-6; $CH(CF_3)_2(OH)CH_3$, 1515-14-6; PhOH, 108-95-2; sodium trichloromethanesulfinate, 42521-49-3; sodium 1,1-dichloro-2,2,2-trifluoroethanesulfinate, 94720-82-8; sodium 1-bromo-1-chloro-2,2,2-trifluoroethanesulfinate, 122536-06-5; sodium dichlorofluoromethanesulfinate, 94720-81-7; sodium chlorodifluoromethanesulfinate, 113900-37-1.