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Trifluoromethylsulfinyl Esters of Fluorinated Alcohols

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Reactions of trifluoromethylsulfinyl fluoride, CF_3SOF, with fluoro alcohols in the presence of NaF(CsF) were used to prepare a series of new sulfinate esters of the general formula $R_fOS(O)CF_3$ ($R_f = CF_3(CH_3)CH$, $CF_3(CH_3)_2C$, $(CF_3)_2CH$, $(CF_3)_2C(CH_3)$, $CF_3(CF_2Cl)CH$). Perfluoro-*tert*-butyl trifluoromethylsulfinate, $(CF_3)_3COS(O)CF_3$, was prepared by the reaction of trifluoromethylsulfinyl chloride, CF_3SOCl, with the $(CF_3)_3COH \cdot Me_3N$ adduct. The reaction of ClF with $(CF_3)_2CHOS(O)CF_3$ resulted in the cleavage of the S–CF_3 bond to give $(CF_3)_2C(H)OS(O)F$. Because of a chiral sulfur center, the methyl groups in $CF_3(CH_3)_2COS(O)CF_3$ and the trifluoromethyl groups in $(CF_3)_2C(H)OS(O)CF_3$ and $(CF_3)_2C(H)OS(O)F$ are magnetically nonequivalent. The nmr spectra of $CF_3(CH_3)CHOS(O)CF_3$ and $CF_3(CF_2Cl)CHOS(O)CF_3$ showed the presence of two diastereoisomers. With the exception of $CF_3(CH_3)CHOS(O)CF_3$, all of the trifluoromethylsulfinates are decomposed by CsF in the 25–100° temperature range. Infrared, mass, and nmr spectra and elemental analysis data are reported.

Introduction

Magnetic nonequivalence of geminal hydrogen and fluorine atoms observed in nuclear magnetic resonance spectra of sulfur(IV) compounds has been a subject of discussion in many papers during recent years.[1-13] Recently King and Beatson[14] have reported that 1-chloroethylsulfinyl chloride, $CH_3C(Cl)HS(O)Cl$, at 25° shows an nmr spectrum typical of a mixture of two diastereoisomers due to the presence of two asymmetric centers at the carbon atom and at the sulfur atom. In our work, we observe magnetic nonequivalence of the trifluoromethyl groups in $(CF_3)_2C(H)OS(O)CF_3$ and $(CF_3)_2C(CH_3)OS(O)CF_3$ and methyl groups in $(CH_3)_2C(H)OS(O)CF_3$ and find that the sulfinates $CF_3(CH_3)C(H)OS(O)CF_3$ and $CF_3(CF_2Cl)C(H)OS(O)CF_3$ exhibit diastereoisomerism.

Because of the pyramidal (sp^3) geometry at the sulfur compared to the planar (sp^2) geometry at the carbon, the bonding and stereochemistry of the sulfinyl esters should differ from those of the analogous carboxylic esters.[15] In our previous studies,[16] we reported the high stability of fluorinated carboxylic esters with substituents other than fluorine on the alkoxy α-carbon atom toward fluoride ion attack. Comparison of the relative stabilities of the trifluoromethylsulfinates, $R_fOS(O)CF_3$, with those of the fluorinated carboxylic esters was of interest since the sulfur(IV) in these esters was expected to be a more reactive site than carbon in the carboxylic esters.

Although trifluoromethylsulfinates of primary alcohols have been prepared by the direct reaction of trifluoromethylsulfinyl fluoride, $CF_3S(O)F$, with alcohols at −78°,[2] in our present studies we found that this reaction did not proceed in the case of secondary and tertiary fluoro alcohols in the absence of a base.

Results and Discussion

Trifluoromethylsulfinyl fluoride reacts with fluoro alcohols in the presence of NaF(CsF) at 25° to give trifluoromethylsulfinates of the corresponding alcohols.

$$CF_3S(O)F + R_fOH \xrightarrow[25^\circ]{\text{base}} CF_3S(O)OR_f + \text{base}\cdot HF$$

Perfluoro-*tert*-butyl trifluoromethylsulfinate, $(CF_3)_3COS(O)CF_3$, could not be prepared by this method because of its instability to fluoride ion attack (see below). The latter was prepared by the reaction of trifluoromethylsulfinyl chloride with the trimethylamine–perfluoro-*tert*-butyl alcohol solid adduct at 25°.

$$(CF_3)_3COH \cdot Me_3N + CF_3S(O)Cl \xrightarrow{25^\circ} (CF_3)_3COS(O)CF_3 + Me_3N \cdot HCl$$

The reactions of trifluoromethylsulfinyl fluoride with secondary and tertiary alcohols are slow compared to its reactions with hydrogenated and partially fluorinated primary alcohols; *e.g.*, compare 5–7 days at 25° (Table I) with 24 hr at −78° in the absence of a base.[2] This can be accounted for by considering the decreasing basicity of the alcohols since, on the basis of pK_a values of the hydrogenated and fluoro alcohols, the secondary fluoro alcohols have the same order of acidity as phenol, and whereas the primary alcohols are less acidic, the tertiary alcohols compare with carboxylic acids.[17,18]

However, perfluoroisopropyl trifluoromethylsulfinate which would have been useful for comparison with the corresponding carboxylic ester could not be prepared by the reaction of $CF_3S(O)F$ with $(CF_3)_2C(F)O^-Cs^+$. In view of the ready decomposition of perfluoroisopropyl trifluoromethylcarboxylate above −78°[19] and of perfluoro-*tert*-butyl trifluoromethylsulfinate at 25° in the presence of fluoride ion (Table I), we believe that the fluoride ion generated during the preparation of the perfluoroisopropyl ester or the residual fluoride ion from $(CF_3)_2CO + CsF \rightleftarrows (CF_3)_2C(F)O^-Cs^+$ is responsible for its decomposition to $(CF_3)_2CO$ and $CF_3S(O)F$.

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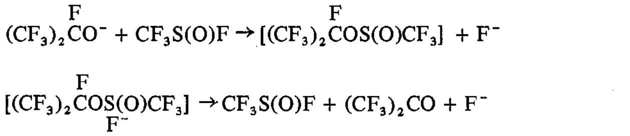
Table I. Preparative Conditions and Reactions of Trifluoromethylsulfinates, $R_fOS(O)CF_3$

Amt of CF_3SOF, mmol	Alcohol (mmol)	Ester (mmol)	Reactant, °C, hr	Products
7.9	$CF_3(CH_3)CHOH$ (2.1)	$CF_3(CH_3)CHOS(O)CF_3$ [a] (1.9)	CsF, 200, 24 H_2O, 200, 24 ClF, −78, 10	No reacn No reacn $CF_3(CH_3)C(F)OCl$,[b] HCl, $CF_3S_2CF_3$, CF_3SO_2F, CF_3SO_2Cl
9.3	$CF_3(CH_3)_2COH$ (3.0)	$CF_3(CH_3)_2COS(O)CF_3$ [a] (2.6)	CsF, 50, 10 H_2O, 200, 24	$CF_3(CH_3)_2CF$, CF_3SO_2Cs[c] No reacn
6.5	$(CF_3)_2CHOH$ (2.7)	$(CF_3)_2CHOS(O)CF_3$ [a] (2.6)	CsF, 40, 10 H_2O, 150, 10 ClF, −78, 6 Ag_2O, 150, 72	CHF_3, $(CF_3)_2CO$, CF_3SO_2Cs[c] $(CF_3)_2CHOH$, unidentified species CF_3Cl, $(CF_3)_2CHOS(O)F$[d] $(CF_3)_2CO$, CF_3SO_2Ag,[c] Ag, H_2O
5.3	$(CF_3)_2C(CH_3)OH$ (2.2)	$(CF_3)_2C(CH_3)OS(O)CF_3$ [e] (1.8)	CsF, 100, 10 H_2O, 200, 24 ClF, 25, 10 Ag_2O, 100, 24	$CF_3CF{=}CH_2$, CF_3H, CF_3SO_2Cs[c] No reacn CF_4, CF_3Cl, SO_2F_2, $CF_3SO_2SCF_3$, $(CF_3)_2C(CH_3)OCl$[f] No reacn
7.9	$CF_3(CF_2Cl)CHOH$ (2.1)	$CF_3(CF_2Cl)CHOS(O)CF_3$ [a] (2.0)	CsF, 60, 10 H_2O, 25[h] or 100, 4	CF_3SOF, $CF_3(CF_2Cl)C(H)OCs$[g] $CF_3(CF_2Cl)CHOH$, unidentified species
3.0[i]	$(CF_3)_3COH$ (1.0)	$(CF_3)_3COS(O)CF_3$ [j] (0.7)	CsF, 25, 1 H_2O + air, 25, 2	CF_3SOF, $(CF_3)_3COCs$[k] $(CF_3)_3COH$, COF_2, SO_2, SiF_4, H_2O
5.2[l]	$CF_3(CF_2Cl)CHOH$ (2.3)	$CF_3(CF_2Cl)CHOC(O)CF_3$ [m] (2.3)	CsF, 100, 10 H_2O, 100, 10 ClF, 25, 72	CF_3COF, $CF_3(CF_2Cl)C(H)OCs$[g] $CF_3(CF_2Cl)CHOH$, CF_3CO_2H No reacn

[a] Agitated with NaF for 5-7 days at 25°. [b] Identified by mass spectrum. [c] Identified by reaction with ClF → CF_3SO_2Cl. [d] Decomposes at 25° in glass. [e] No reaction with NaF but with CsF at 25° for 8 days. [f] D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, *J. Amer. Chem. Soc.*, **92**, 2313 (1970). [g] Identified by reaction with ClF → HCl + $CF_3(CF_2Cl)CO$. [h] Reaction slow at 25°. [i] $CF_3S(O)Cl$. [j] In presence of $(CH_3)_3N$ (1.1 mmol) at 25°. [k] Identified by reaction with ClF → CF_3Cl + $(CF_3)_2CO$. [l] $CF_3C(O)F$. [m] Agitated with NaF for 2 days at 25°; mol wt 277.8 (calcd 280.0).



$$(CF_3)_2\overset{F}{C}O^- + CF_3S(O)F \rightarrow [(CF_3)_2\overset{F}{C}OS(O)CF_3] + F^-$$

$$[(CF_3)_2\overset{F}{C}O\underset{F^-}{S}(O)CF_3] \rightarrow CF_3S(O)F + (CF_3)_2CO + F^-$$

Decomposition occurred at −98° and below this temperature no reaction was observed. The preparation of this ester will require an alternate route that does not involve the presence of fluoride ion.

Except for $CF_3(CH_3)C(H)OS(O)CF_3$, all the other trifluoromethylsulfinates described in this paper are decomposed by CsF in the 25-100° range (Table I). On the other hand, the corresponding carboxylic esters, except for $CF_3(CF_2Cl)C(H)OC(O)CF_3$, were stable toward fluoride ion attack up to 200°.[16] The greater instability of trifluoromethylsulfinates toward fluoride ion in the majority of cases must arise from empty orbitals on the sulfur(IV) species which are available for attack.

Nucleophilic attack of fluoride ion at the positive carbon of the carbonyl group in the carboxylic esters with at least one fluorine atom bonded to the α-carbon atom has been demonstrated.[19] By analogy with the carboxylic esters, the trifluoromethylsulfinates would be expected to decompose *via* attack at the sulfur. It is, however, surprising to note that some of the trifluoromethylsulfinates decompose *via* attack at the alkoxy carbon atom. This suggests a greater positive character of the alkoxy carbon than of sulfur in these compounds.

$$R_fOS(O)CF_3 + F^- \rightarrow CF_3S(O)F + R_fO^- \quad (R_f = (CF_3)_3C,\ CF_3(CF_2Cl)CH) \tag{1}$$

$$CF_3(CH_3)_2COS(O)CF_3 + F^- \rightarrow CF_3SO_2^- + CF_3(CH_3)_2CF \tag{2}$$

$$(CF_3)_2C(CH_3)OS(O)CF_3 + F^- \rightarrow CF_3SO_2^- + (CF_3)_2CH_3CF \xrightarrow{100^\circ} CHF_3 + CF_3CF{=}CH_2 \tag{3}$$

More unexpected is the instability of the carboxylic ester $CF_3(CF_2Cl)CHOC(O)CF_3$ (which does not have a fluorine atom on the α-alkoxy carbon) toward fluoride ion attack compared with that of the previously reported carboxylic esters.[16]

$$CF_3(CF_2Cl)CHOC(O)CF_3 + F^- \xrightarrow{100^\circ} CF_3(CF_2Cl)CHO^- + CF_3C(O)F$$

The reaction of ClF with perfluoro alcohols is a well-known route to hypochlorites.[20] ClF also reacted with the esters $CF_3(CH_3)CHOS(O)CF_3$ at −78° and $(CF_3)_2C(CH_3)OS(O)CF_3$ at 25° to form the hypochlorites $CF_3(CH_3)CFOCl$ and $(CF_3)_2C(CH_3)OCl$, respectively (Table I). However, with $(CF_3)_2CHOS(O)CF_3$, the S-CF_3 bond was cleaved at −78°.

$$(CF_3)_2CHOS(O)CF_3 + ClF \xrightarrow{-78^\circ} (CF_3)_2CHOS(O)F + CF_3Cl$$

The sulfinyl fluoride is unstable, and, although the reaction was not tried at 25°, it is likely that the isopropyl hypochlorite would then result.

While the high stabilities of the trifluoromethylsulfinates $(CF_3)_2CHOS(O)CF_3$ and $(CF_3)_2C(CH_3)OS(O)CF_3$ toward hydrolysis by water or moist air are comparable with those of the corresponding carboxylic esters,[16] $CF_3(CH_3)_2COS(O)CF_3$ and $CF_3(CH_3)CHOS(O)CF_3$, whose carboxylic ester

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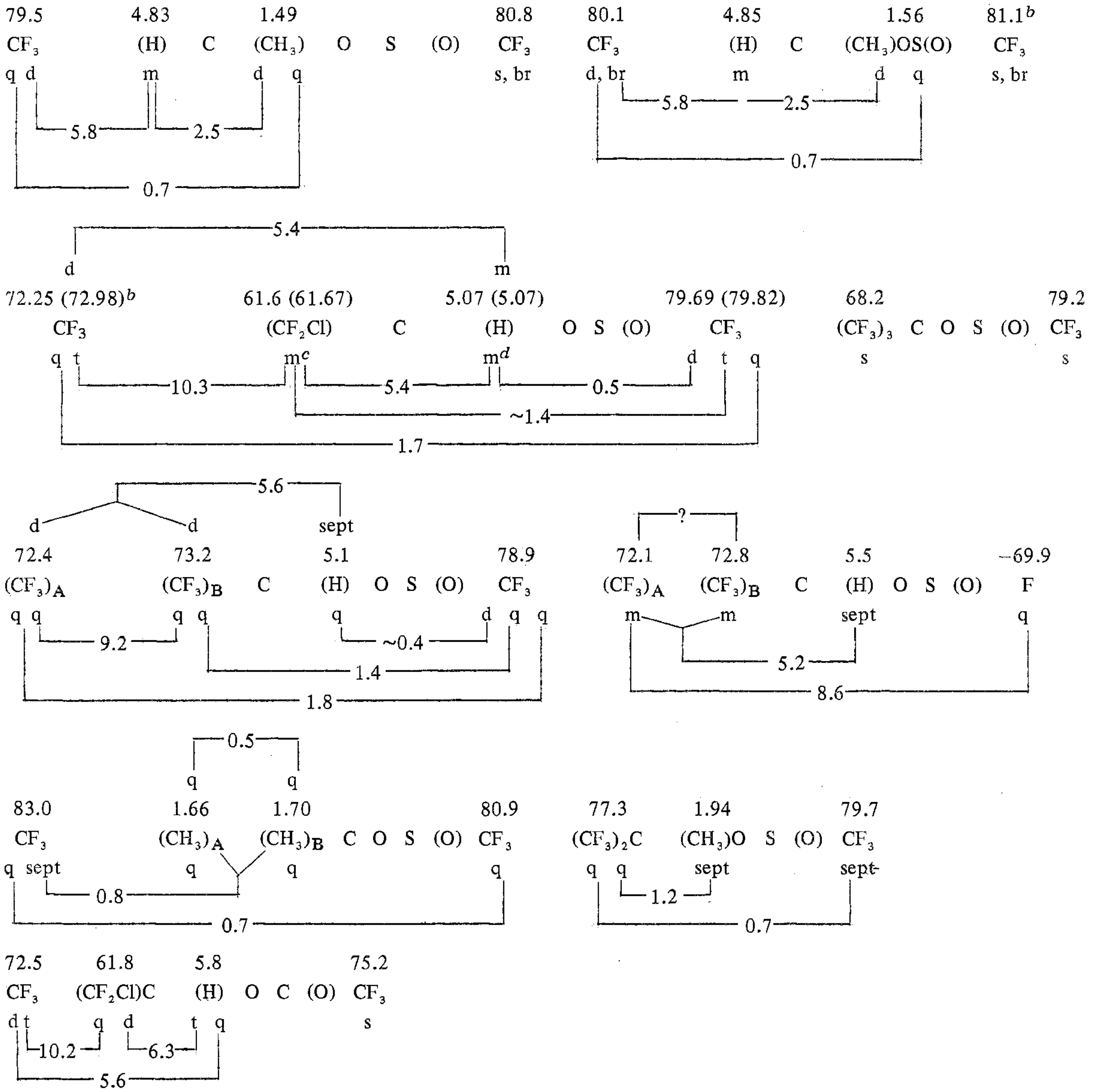
(20) D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, *J. Amer. Chem. Soc.*, **92**, 2313 (1970).

Chart I. Nmr Spectra of the Trifluoromethylsulfinates, $R_fOS(O)CF_3$[a]



[a] Chemical shifts in ppm relative to internal CCl_3F or TMS; coupling constants in Hz. Legend: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; br, broad; m, multiplet. Relative areas of the signals correspond to the assignments in each case. [b] Second isomer. [c] Complex set of quartets. [d] Complex sextet.

analogs are not known, are even more stable toward hydrolysis. The new carboxylic ester $CF_3(CF_2Cl)CHOC(O)CF_3$ hydrolyzes at 100° according to

$$CF_3(CF_2Cl)CHOC(O)CF_3 + H_2O \xrightarrow{100^\circ} CF_3(CF_2Cl)CHOH + CF_3CO_2H$$

Since the proton on the alkoxy carbon of the ester is acidic, nucleophilic attack by water at this point should be very likely. The sulfur analog hydrolyzes slowly at 25° to give the same alcohol and an unidentified sulfur-containing species. In sharp contrast to the carboxylic ester $(CF_3)_3COC(O)CF_3$, $(CF_3)_3COS(O)CF_3$ hydrolyzes readily even in moist air at 25°.

$$(CF_3)_3COS(O)CF_3 + H_2O \xrightarrow{25^\circ} (CF_3)_3COH + COF_2 + SO_2 + SiF_4$$

The lower stabilities of the more highly fluorinated sulfur esters compared to those of the other sulfinates and the carboxylic esters can be attributed to the greater positive nature of the sulfur atom particularly where several strongly electron-withdrawing groups are present.

The nuclear magnetic resonance spectra of the new esters are given in Chart I. These spectra show clearly the magnetic nonequivalence of the trifluoromethyl groups of $(CF_3)_2CHOS(O)CF_3$ and $(CF_3)_2CHOS(O)F$ and methyl groups of $CF_3(CH_3)_2COS(O)CF_3$ due to the presence of an asymmetric center at the sulfur atom. Such magnetic nonequivalence in sulfur(IV) compounds is observed often; compare, *e.g.*, the methylene protons of $CH_3CH_2OS(O)CF_3$, $CF_3CH_2OS(O)CF_3$, $C_2H_5OS(O)C_6H_5$, and $C_6H_5CH_2S(O)CH_3$ as well as the fluorine atoms of the methylene group in $CF_3CF_2S(O)CF_3$ and methyl groups of $(CH_3)_2CHS(O)Cl$ and $(CH_3)_2CSO$.[2-4,12,21,22]

The suspected nonequivalence of the trifluoromethyl groups

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(21) J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961).

(22) W. A. Sheppard and J. Diekman, *J. Amer. Chem. Soc.*, **86**, 1891 (1964).

of $(CF_3)_2C(CH_3)OS(O)CF_3$ was not observed. In a related case,[5] while the equivalence of the methyl groups in $(CH_3)_2CHS(O)Cl$ and methylene protons of $CH_3CH_2S(O)Cl$ was detected, nonequivalence of methylene protons of $C_6H_5CH_2S(O)Cl$ was not. The apparent absence of nonequivalence in the methylene protons of benzylsulfinyl chloride was attributed to the conformational equilibria and a low intrinsic asymmetry. Similar factors could be responsible for the same phenomenon in the case of $(CF_3)_2CH_3COS(O)CF_3$.

Two sets of nmr signals for each of the CF_3S, CF_3C, CH_3, and H groups in $CF_3(CH_3)CHOS(O)CF_3$ and CF_3S, CF_3C, CF_2Cl, and H groups in $CF_3(CF_2Cl)CHOS(O)CF_3$ are observed. This is a clear indication of the presence of two diastereoisomers for each of these two trifluoromethylsulfinates. Although the optical isomerism in trihalomethylsulfur compounds which contain an asymmetric methyl carbon atom has been long predicted and sought for biological reasons,[23] it was only recently that King and Beatson[14] reported the existence of two diastereoisomers for $(CH_3)C(Cl)HS(O)Cl$.

The ^{19}F chemical shifts due to the CF_3S- group in the trifluoromethylsulfinate fall in the range 79–81 MHz which agrees very well with the previously reported chemical shifts for the CF_3S- group in compounds of the types $R_fS(O)CF_3$ and $(R_f)_2NS(O)CF_3$.[2] The assignment of the CF_3S- resonance in $CF_3(CH_3)_2COS(O)CF_3$ was made by considering both the electronegativity of the alkoxy group $CF_3(CH_3)CHO$ and the narrow range of chemical shifts for CF_3S- groups in these compounds.

The ^{19}F chemical shifts due to the trifluoromethyl moiety bonded to carbon in the R_f group reflect the inductive effect of the alkoxy substituents in the group in the order $(CF_3)_3CO > (CF_3)_2CHO \approx CF_3(CF_2Cl)CHO > (CF_3)_2CH_3CO > CF_3(CH_3)CHO > CF_3(CH_3)_2CO$. The ^{19}F chemical shift due to SF of $(CF_3)_2CHOS(O)F$ (-69.9 MHz) is the lowest compared with that of other related -S(O)F compounds (Table II). Significant F-S (p-d)π bonding in $(CF_3)_2CHOS(O)F$ could be another factor which contributes to deshielding of the sulfur nucleus.

Infrared spectra of the trifluoromethylsulfinates $R_fOS(O)CF_3$ are found in Table III. The close proximity of the C–F asymmetric stretch and the S=O stretching frequency bands in the infrared spectra complicates the definite assignments of either. The S=O stretching frequencies in structurally related compounds of the general formula $R_fS(O)CF_3$ (where R_f ranges from F to perfluoroalkyl and alkoxy groups) have been assigned in the range 1268–1209 cm^{-1}. Based on these results, the tentative values for $\nu_{S=O}$ in the trifluoromethylsulfinates under discussion are listed in Table IV. These values for $\nu_{S=O}$ are not strictly in the order of the inductive effects of the alkoxy substituent and therefore it is likely that steric effects of the alkoxy groups contribute.

In the mass spectra of these sulfinates, parent peaks were observed for $(CF_3)_2C(H)OS(O)CF_3$, $(CF_3)_2C(CH_3)OS(O)CF_3$, and $(CF_3)_3COS(O)CF_3$. $(M - CH_3)$ is the highest peak observed for $CF_3(CH_3)C(H)OS(O)CF_3$ and $(CF_3)(CH_3)_2COS(O)CF_3$. For all other compounds the highest peaks observed correspond to $M - X$ ($X = F$ or Cl). For the general trifluoromethylsulfinate esters, $R_fOS(O)CF_3$, a consistent cracking pattern was found. Fragments were observed for each ester corresponding to CF_3, CF_3SO, CF_3SO_2, $M - CF_3SO_2$ and $M - CF_3$. This is consistent with the mass spectra of the corresponding fluorinated carboxylic esters.[16]

Table II. ^{19}F Nmr Chemical Shifts[a] due to -SF in Some RS(O)F Compounds[b]

R	H_3CO	$H_3C\overset{H}{\underset{H}{C}}O-$	$C_2H_5\overset{H}{\underset{H}{C}}O-$	$n\text{-}C_3H_7\overset{H}{\underset{H}{C}}O-$	$(CH_3)_2CHO-$	$C_2H_5\overset{H}{\underset{CH_3}{C}}O-$
δ_{SF}	-54.7	-58.6	-58.8	-58.7	-62.4	-63.4

[a] From internal CCl_3F in ppm. [b] References 6, 7; C. T. Ratcliffe and J. M. Shreeve, *J. Amer. Chem. Soc.*, **90**, 5403 (1968).

Table III. Infrared Spectra of $R_fOS(O)CF_3$ (cm^{-1})

$CF_3(CH_3)CHOS(O)CF_3$	3015 w, 2970 w, 1465 m, 1395 sh, 1388 m, 1343 w, 1287 s, 1220 s, 1203 s, 1165 s, 1142 s, 1085 s, 1020 m, 918 s, 770 m, 760 sh, 668 w, 485 w
$CF_3(CH_3)_2COS(O)CF_3$	3015 w, 2965 w, 1482 mw, br, 1407 mw, 1390 w, 1335 m, 1235 sh, 1223 s, 1190 s, 1145 sh, 1133 s, 961 m, 885 s, 782 m, 732 m
$(CF_3)_2CHOS(O)CF_3$	2955 w, 1372 s, 1305 s, 1275 sh, 1245 s, 1218 s, 1140 s, 1123 m, 1078 s, 1060 sh, 910 m, 880 s, 780 s, 730 w, 695 m, 600 w, 570 w, 540 w, 450 w, 428 w
$(CF_3)_2C(CH_3)OS(O)CF_3$	2960 w, 1465 mw, 1400 w, 1312 s, 1245 s, 1232 s, 1210 w, 1130 s, 1093 m, 942 m, 880 w, 783 m, 742 mw, 707 w, 650 w, 543 w, 490 w, 458 mw
$CF_3(CF_2Cl)C(H)OS(O)CF_3$	2960 w, 1375 m, 1352 sh, 1288 s, 1249 sh, 1229 s, sh, 1217 s, 1142 s, 1079 s, 992 m, 895 sh, 882 mw, 865 sh, 840 mw, 770 s, 759 sh, 747 sh, 717 sh, 690 mw, 601 mw, 517 w, 490 mw, 460 w
$(CF_3)_3COS(O)CF_3$	1385 w, 1305 sh, 1290 s, 1270 sh, 1231 s, 1215 s, 1155 sh, 1140 s, 1102 s, 998 s, 988 s, 915 sh, 784 m, (738, 733) sd, 628 w, 570 w, 545 w, 495 w, 464 m
$(CF_3)_2CHOS(O)F$	2975 m, br, 1374 s, 1305 s, 1282 s, 1245 s, 1220 s, 1140 sh, 1122 s, 1078 sh, 1056 s, (910, 885) md, 809 s, 749 s, 735 sh, 695 w, 422 m
$CF_3(CF_2Cl)CHOC(O)CF_3$	2990 w, br, 1831 s, 1375 s, 1370 sh, 1332 m, 1285 s, 1250 s, 1215 s, 1200 s, 1177 sh, 1144 sh, 1124 s, 1065 w, 1001 m, 995 sh, 919 m, 892 w, 843 m, 824 w, 766 w, 735 m, 695 m, 640 w, br, 560 w, br, 540 w, br, 510 w, br

Experimental Section

General Procedures. Standard vacuum-line techniques were used throughout and rigorous precautions were taken to exclude moisture from all systems. In particular, all glassware was flamed out before each experiment. All reactions were carried out in 200-ml Pyrex bulbs fitted with Teflon (Quickfit or Kontes Glass Co.) stopcocks. Pressures were measured with a Heise Bourdon tube gauge. Amounts of volatile materials were determined by *PVT* measurements assuming ideal gas behavior.

Infrared spectra were taken on a Perkin-Elmer 457 spectrometer using a 10-cm Pyrex-glass cell equipped with KBr windows and were calibrated against known absorption bands of a polystyrene film. The ^{19}F nmr spectra were obtained on a Varian HA-100 spectrometer operating at 94.1 MHz with Freon-11 as an internal standard. The ^1H nmr spectra were determined on a Varian A-60 or HA-100 spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained by using a Hitachi Perkin-Elmer Model RMU-6E mass spectrometer at 17 and 70 eV. Vapor pressures were determined by the method of Kellogg and Cady.[24] Elemental analyses were performed by Laboratorium Beller, Gottingen, Germany.

Reagents. Trifluoromethylsulfinyl fluoride was prepared by hydrolysis of CF_3SF_3 obtained from the reaction of $(CF_3S)_2$ (PCR,

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(24) K. B. Kellogg and G. H. Cady, *J. Amer. Chem. Soc.*, **70**, 3986 (1948).

Table IV. $\nu_{S=O}$ for $R_fOS(O)CF_3$ (cm^{-1})

R_f	$(CF_3)_2CH$	$(CF_3)_2CH_3C$	$(CF_3)_3C$	$CF_3(CH_3)_2C$	$CF_3(CH_3)CH$	$CF_3(CF_2Cl)CH$
$\nu_{S=O}$	1245[a]	1232	1231	1223	1220	1217

[a] $\nu_{S=O}$ for $(CF_3)_2CHOS(O)F$ is also assigned at 1245 cm^{-1}.

Table V. Elemental Analysis and Thermodynamic Data

Compd	Elemental analysis, %					Bp, °C	ΔH_v, kcal/mol	ΔS_v, eu	$\log P_{mm} = a - b/T$	
	C	H	Cl	F	S				a	b
$CF_3(CH_3)$-$CHOS(O)CF_3$	20.9 (20.9)[a]	1.8 (1.7)		49.1 (49.5)	14.0 (13.9)	101.5	8.8	23.5	8.01	1921
$CF_3(CH_3)_2$-$COS(O)CF_3$	24.5 (24.6)	2.5 (2.5)		46.5 (46.7)	13.2 (13.1)	114.5	8.5	21.9	7.66	1854
$(CF_3)_2$-$CHOS(O)CF_3$	17.0 (16.9)	0.4 (0.4)		60.2 (60.2)	11.3 (11.3)	88.5	9.4	26.0	8.58	2061
$(CF_3)_2C(CH_3)$-$OS(O)CF_3$	20.2 (20.1)	1.0 (1.0)		57.4 (57.4)	10.8 (10.7)	112	8.2	21.0	7.51	1784
$CF_3(CF_2Cl)$-$CHOS(O)CF_3$	16.0 (16.0)	0.3 (0.3)	11.9 (11.8)	50.8 (50.6)	10.7 (10.7)	7[b]				
$(CF_3)_3$-$COS(O)CF_3$	17.1 (17.0)			64.6 (64.8)	9.0 (9.1)	82	9.0	25.4	8.59	2025
$CF_3(CF_2Cl)$-$CHOC(O)CF_3$	21.4 (21.4)	0.5 (0.4)	12.8 (12.5)	54.0 (54.3)		64.5	8.9	26.0	8.57	1921

[a] Calculated values in parentheses. [b] Vapor pressure in mm at 23°.

Inc.) and AgF_2 (Ozark-Mahoning).[25] Cesium fluoride (99%) was obtained from ROC/RIC Chemical Corp. and was dried as reported previously.[16] Trimethylamine was obtained from J. T. Baker and was used as such. Sodium fluoride was purchased from Mallinckrodt Chemical Co. and chlorine monofluoride from Ozark-Mahoning. All other chemicals were obtained from PCR, Inc., and were used without further purification.

Preparative Procedures. Except for the perfluoro-*tert*-butyl trifluoromethylsulfinate ester, $(CF_3)_3COS(O)CF_3$, all of the esters were prepared in essentially the same manner. In a typical reaction, a threefold excess of $CF_3S(O)F$ was condensed into a vessel containing 3 mmol of the appropriate alcohol and about 5 g of anhydrous NaF(CsF). The mixture was shaken at 25° for varying lengths of time. Progress of the reaction was monitored every 24 hr until the OH stretching frequency (~3600 cm^{-1}) disappeared from the infrared spectrum of the mixture. Additional quantities of CF_3SOF were occasionally distilled onto the reaction mixture in order to maintain a high pressure which enhanced the rate of the reaction. The volatilities of all of the esters were much less than that of the trifluoromethylsulfinyl fluoride (CF_3SOF), which facilitated the separation of the esters from the excess CF_3SOF by fractional condensation.

Preparation of Perfluoro-*tert*-butyl Trifluoromethylsulfinate ($(CF_3)_3COS(O)CF_3$). A 1.1-mmol sample of trimethylamine was distilled onto 1.0 mmol of perfluoro-*tert*-butyl alcohol. The mixture was allowed to warm to 25° where a white solid was obtained. The unreacted amine was pumped away and 3.0 mmol of trifluoromethylsulfinyl fluoride was distilled onto the white solid. The volatile compounds were separated by fractional condensation and the ester was retained in a trap at −78°.

Reaction conditions and yields of the products are given in Table I. Elemental analysis and thermodynamic data are found in Table V.

Reactions of Sulfinate Esters. Reaction with CsF. In a typical reaction 0.5 mmol of the appropriate ester was distilled onto ~0.5 g of dried CsF. The mixture was allowed to remain at 25° over a period of 10 days with occasional monitoring of the progress of the reaction by taking an infrared spectrum of a representative sample of the volatile components. If there was no reaction or if it was slow, the mixture was warmed stepwise from 40 to 200° after checking the progress of the reaction each time before the temperature was increased.

Reaction of ClF. After a 1.1–1.2-fold excess of ClF was condensed with the sulfinate ester at −183° in a glass vessel, the mixture was warmed to −78° and was allowed to remain for varying lengths of time (Table I). The contents of the vessel were then separated by fractional condensation and each fraction was characterized by infrared, mass, and/or nmr spectroscopy. If there was no indication of reaction at −78°, the contents of the vessel were allowed to warm slowly from −78 to +25° and in some cases left at 25° for varying lengths of time (Table I). *Caution!* Chlorine monofluoride is a strong oxidizing agent and should be handled with extreme care particularly in the presence of easily oxidized materials.

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Registry No. CF_3SOF, 812-12-4; $CF_3(CH_3)CHOH$, 374-01-6; $CF_3(CH_3)CHOS(O)CF_3$, 52225-48-6; $CF_3(CH_3)_2COH$, 507-52-8; $CF_3(CH_3)_2COS(O)CF_3$, 52225-49-7; $(CF_3)_2CHOH$, 920-66-1; $(CF_3)_2CHOS(O)CF_3$, 52225-50-0; $(CF_3)_2C(CH_3)OH$, 1515-14-6; $(CF_3)_2C(CH_3)OS(O)CF_3$, 52225-51-1; $CF_3(CF_2Cl)CHOH$, 24332-19-2; $CF_3(CF_2Cl)CHOS(O)CF_3$, 52225-52-2; $(CF_3)_3COH\cdot Me_3N$, 52225-53-3; $CF_3S(O)Cl$, 20621-29-8; $(CF_3)_3COS(O)CF_3$, 52225-54-4; $CF_3(CF_2Cl)CHOC(O)CF_3$, 52225-55-5; $CF_3C(O)F$, 354-34-7; ClF, 7790-89-8; $(CF_3)_2CHOS(O)F$, 52225-56-6; NaF, 7681-49-4; CsF, 13400-13-0.

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