solution was cooled to −78 °C with magentic stirring, and a solution of $Mg(CH_2CMe_3)_2$·dioxane (0.048 g, 0.190 mmol) in 5 mL of ether was added slowly. The color of the solution changed from pink to yellow-brown. It was slowly warmed to room temperature and filtered and solvent removed from the filtrate in vacuo. The residue was recrystallized from toluene/pentane at 30 °C: yield 0.047 g (69%) yellow crystals; IR (Nujol mull) ν_{Os-N} 1110 cm^{-1}; ^1H NMR (C_6H_6, 200 MHz, 297 K) 3.456 (s, 2 H, CH_2CMe_3), 2.389 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.637 (s, 9 H, CMe_3), 0.977 (m), 0.779 ppm (m, 7 H, $NCH_2CH_2CH_2CH_3$); ^{13}C NMR (C_6D_6) 58.45 (t, $NCH_2CH_2CH_3$), 53.359 (t, J_{CH} = 116 Hz), CH_2CMe_3), 35.0 (s, CH_2CMe_3), 34.846 (q, J_{CH} = 123 Hz, CMe_3), 23.777 (t, $NCH_2CH_2CH_3$), 19.663 (t, $NCH_2CH_2CH_2CH_3$), 13.590 (q, $NCH_2CH_2CH_2CH_3$).

Preparation of $[NOsMe_4][NBu_4]$. $[NOs(OSiMe_3)_4][NBu_4]$ (0.564 g, 0.702 mmol) was dissolved in 20 mL of toluene. A toluene solution of $AlMe_3$ (2.40 mmol) was added slowly with magnetic stirring at 25 °C. The color of the solution changed from pink to yellow-brown, and a brown oil precipitated. Solvent was removed in vacuo, and the residual oil was extracted with several portions of diethyl ether. The yellow extract was filtered through diatomaceous earth. Pentane was added and the solution cooled to −30 °C. Yellow crystals were collected by filtration: yield of $[NOsMe_4][NBu_4]$ 0.246 g (69%); IR (Nujol mull) ν_{Os-N} 1105 cm^{-1}; ^1H NMR (C_6D_6, 200 MHz, 297 K) 2.62 (m, 2 H, NCH_3), 2.085 (s, 3 H, $OsCH_3$), 1.18 (m, 4 H, $NCH_2CH_2CH_2CH_3$), 0.89 ppm (t, 3 H, $NCH_2CH_2CH_2CH_3$); ^{13}C NMR (C_6D_6) 58.82 (NCH_2), 24.16 (OsMe), 24.13 ($NCH_2CH_2CH_2CH_3$), 20.02 ($NCH_2CH_2CH_2CH_3$), 13.84 ppm ($N(CH_2)_3CH_3$). Anal. Calcd for $OsN_2C_{20}H_{49}$: C, 47.40; H, 9.55; N, 5.53. Found: C, 47.21; H, 9.55; N, 5.46.

Preparation of $[NOsMe_4{\cdot}AlMe_3][NBu_4]$. $[NOs(OSiMe_3)_4][NBu_4]$ (0.339 g, 0.452 mmol) was dissolved in 15 mL of toluene. The solution was cooled to −78 °C. With magnetic stirring, a toluene solution of $AlMe_3$ (5.0 mmol in 10 mL) was added dropwise. The solution was slowly warmed to 25 °C. Solvent and excess $AlMe_3$ were removed in vacuo. The residue was crystallized from ether/pentane solution at −30 °C. Orange crystals of $[NOsMe_4{\cdot}AlMe_3][NBu_4]$ (0.225 g, 86%) were obtained: ^1H NMR (C_6D_6, 200 MHz, 298 K) 2.85 (br s, NCH_2 and $OsCH_3$, 17 H), 2.35 (br s, 3 H, CH_3), 1.6 (m, 16 H, $NCH_2CH_2CH_2CH_3$), 1.40 (m, 12 H, $NCH_2CH_2CH_2CH_3$), −0.05 ppm (br s, 9 H, $AlMe_3$).

Preparation of $[NOsMe_4][NBu_4]$ from $[NOsMe_4{\cdot}AlMe_3][NBu_4]$. In a vial, $[NOsMe_4{\cdot}AlMe_3][NBu_4]$ (0.10 g, 0.17 mmol) was dissolved in 3 mL of toluene. Excess TMEDA (0.5 mL) was added. The color of the solution immediately changed from orange to yellow. Yellow needles formed on standing. Additional yellow crystals were obtained by doubling the volume with pentane and cooling the mixture to −30 °C. Yield of pure $[NOsMe_4][NBu_4]$ was 0.075 g (87%).

Preparation of $NOsMe_3(THF)_2$. $[NOsCl_4][NBu_4]$ (1.70 g, 3.04 mmol) was dissolved in 75 mL of THF in a 200-mL flask equipped with a stir bar, dropping funnel, and N_2(g) inlet. The solution was cooled to −78 °C, and MeMgI (15.4 mmol) in 30 mL of ether was added slowly by means of the addition funnel. White precipitate formed, and the color of the solution changed from purple to yellow. The mixture was warmed to room temperature and filtered. Solvent was removed from the filtrate under vacuum. The residue was crystallized from toluene/pentane solution at −30 °C: yield, 1.10 g (92%) yellow solid; IR (Nujol mull) ν_{Os-N} 1025 cm^{-1}; ^1H NMR (C_6D_6, 200 MHz, 297 K) 3.55 (m, 2 H, THF), 2.167 (s, 3 H, OsMe), 1.36 ppm (m, 2 H, THF). Anal. Calcd for $OsNO_2C_{11}H_{25}$: C, 33.57; H, 6.40; N, 3.56. Found: C, 33.01; H, 6.75; N, 3.38.

Preparation of $NOsMe_3$(TMEDA). $NOsMe_3(THF)_2$ (0.040 g, 0.10 mmol) was dissolved in 0.5 mL of acetonitrile. TMEDA (0.20 mL, 0.15 mmol) was added by microliter syringe. Yellow crystals formed on standing. Approximately 1.5 mL of diethyl ether was added, and the mixture was cooled. The solution was decanted, and the yellow crystals were washed with diether ether and dried under vacuum: yield 0.036 g (98%); IR (KBr) 1110 cm^{-1}; ^1H NMR (CD_3CN, 200 MHz, 297 K) 2.12 (s, 6 H, NMe), 2.09 (s, 6 H, NMe), 1.94 (s, 3 H, OsMe), 1.88 (s, 6 H, OsMe), 1.74, (s), 1.69, (s), 2.2 (m), 1.8 (m, NH_2). Anal. Calcd for $OsN_3C_9H_{25}$: C, 29.57; H, 6.89; N, 11.49. Found: C, 30.94; H, 7.18; N, 10.61.

Procedure for Thermal Decomposition Reactions of $[NOsR_4][NBu_4]$. A sample of $[NOsR_4][NBu_4]$ (10 mg) was added to a thick-walled NMR tube. The NMR tube was connected, through an adaptor, to the vacuum line. An appropriate NMR solvent, C_6D_6 or $CD_3C_6D_5$, was condensed into the tube, and the tube was sealed with a flame under vacuum. An initial NMR spectrum was obtained. The tube was heated in an oil bath to 90 °C. NMR spectra were obtained periodically.

Reaction of $[NOsR_4][NBu_4]$ with PMe_3, PBr_3, or TMEDA. The same procedure was followed as for the thermal decomposition reactions, except that a known quantity of ligand (PMe_3, PBr_3, or TMEDA) was condensed in along with the NMR solvent.

Reaction of $[NOsR_4][NBu_4]$ with CO and H_2. To a moderate pressure glass reaction vessel was added 20 mg of $[NOsR_4][NBu_4]$, a stir bar, and 5 mL of toluene. The vessel was pressurized to 30–40 psi with either CO or H_2. The solution was magnetically stirred for 2 days. Solution was analyzed by gas chromatography. NMR spectra were obtained of the osmium-containing products.

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Reactions of Polyfluoroalkyl Fluorosulfates with Nucleophiles: An Unusual Substitution at the Sulfur–Fluorine Bond

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Abstract: Polyfluoroalkyl fluorosulfates R_fOSO_2F [R_f = CF_3CH_2 and $(CF_3)_2CH$] react with amines and alcohols or alkoxides to yield new polyfluoroalkyl sulfamates and dialkyl sulfate esters, respectively. Unlike both perfluoroalkyl fluorosulfates and alkyl fluorosulfates, the sulfur–oxygen bond in these polyfluoroalkyl fluorosulfates remains intact in the presence of hard nucleophiles. With methanethiol, however, nucleophilic attack occurs primarily at the α-carbon of $CF_3CH_2OSO_2F$ to give methyl 2,2,2-trifluoroethyl sulfide.

In the past, the reaction chemistry of fluorosulfate esters has been limited to the formation of ketones and acyl derivatives due to the easy scission of the sulfur–oxygen bond, e.g.,[2] eq 1. Nucleophiles, such as F^-, predictably attack the hard sulfur(VI) atom,

$$CF_3CFBrCF(OSO_2F)CF_3 \xrightarrow[70\ °C,\ 12\ h]{CsF} CF_3CFBrC(O)CF_3 + SO_2F_2 \quad (1)$$

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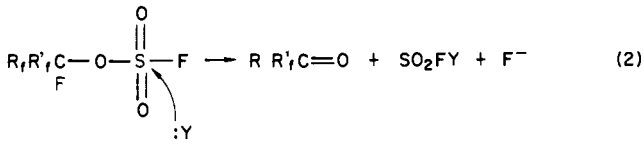
Table I. Yield of Sulfate Esters and Sulfamates from 2,2,2-Trifluoroethyl Fluorosulfate

nucleophile	yield, %	nucleophile	yield, %
$HN(CH_3)_2$	>96	$HOCH_2CF_3$	87
NH_2CH_3	58	$HOCH(CF_3)_2$	94
NH_3	50	$^-OCH_3$	56

cleave the S–O bond to eliminate SO_2FNu and fluoride ion to give the observed products (eq 2). Perfluoroalkyl chlorosulfates



often behave in an analogous fashion. For example, with ammonia, fluoroalkyl chlorosulfates react to give fluoroalkyl amides and sulfamide (eq 3 annd 4).[3]

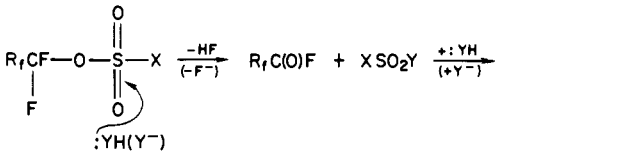
$$CF_3CF_2CF_2OSO_2Cl + 3NH_3 \rightarrow [CF_3CF_2CF_2OH] + (NH_2)_2SO_2 + NH_4Cl \quad (3)$$

$$[CF_3CF_2CF_2OH] \xrightarrow{-HF} CF_3CF_2C(O)F \xrightarrow[-HF]{NH_3} CF_3CF_2C(O)NH_2 \quad (4)$$

We recently reported the convenient syntheses of alkyl and polyfluoroalkyl fluorosulfates from sulfites, which provided us an opportunity to examine the reaction of fluorosulfates such as $CF_3CH_2OSO_2F$ with nucleophiles.[4] To our surprise and in sharp contrast with the reactions of alkyl or perfluoroalkyl fluorosulfates with nucleophiles described in the literature, we have discovered a facile synthesis of new sulfamates and dialkyl sulfate esters. In our studies of 2,2,2-trifluoroethyl fluorosulfate and hexafluoroisopropyl fluorosulfate with amines and alcohols, nucleophilic attack occurred at the sulfur–fluorine bond with fluorine as the leaving species to form new sulfur–nitrogen or new sulfur–oxygen bonds. Little or no attack occurred at the carbon of the polyfluoroalkyl group or at the sulfur that would have resulted in cleavage of the sulfur–oxygen bond. However, with sulfides or bromide ion attack occurred at the methylene carbon of $CF_3CH_2OSO_2F$ perhaps arising from the sensitivity of the carbon α to the fluorosulfate group to attack by soft nucleophiles. This latter reaction presumably involved the formation of unknown mono- or bis(thiosulfate) esters, R_fOSO_2SR or $RSSO_2SR$, which underwent decomposition to SO_2 and disulfanes, in addition to CF_3CH_2R. With Br^-, CF_3CH_2Br is formed quantitatively.

Results and Discussion

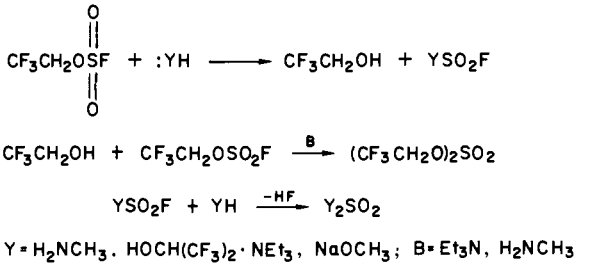
Usually the reactions of fluorosulfates and chlorosulfates with nucleophiles involved three types of products. First, and most predominantly, perfluoroalkyl fluorosulfates react with nucleophiles to give the products of sulfur–oxygen bond cleavage (eq 5).[3,5-8]



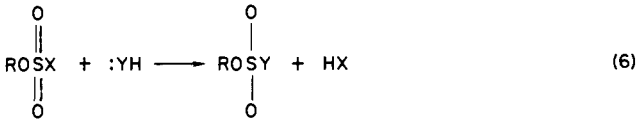
$$Y_2SO_2 + HX(X^-) \quad (5)$$

X = F, Cl; YH = H_2O, ROH, HNRR'; Y^- = F^-, OH^-

Scheme I

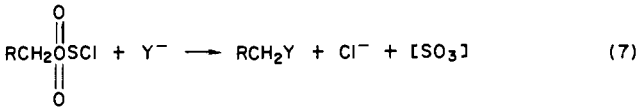


A much less prevalent reaction is the formation of sulfate ester derivatives ("in small yields") via rupture of the sulfur–fluorine or sulfur–chlorine bond (eq 6).[9,10]



X = Cl, F; Y = $N(CH_3)_2$, $N(C_2H_5)_2$; R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9

Finally, nucleophiles can attack chlorosulfates at the α-carbon to give ethers, alcohols, and alkyl halides (eq 7).[11,12] This reaction



R = H, CH_3; Y^- = m-$CH_3OC_6H_4O^-$, Cl^-, CH_3O^-, HO^-

may proceed either by direct displacement at carbon or first by dissociation of the S–Cl bond followed by attack at the carbon. In the latter case, pyridine reacts with n-alkyl chlorosulfates to give alkyl chlorides (eq 8).[13]

$$n\text{-}BuOSO_2Cl + C_5H_5N \xrightarrow{-80\ ^\circ C} Cl^- + [n\text{-}BuOSO_2{\cdot}NC_5H_5]^+ \rightarrow n\text{-}BuCl + C_5H_5NSO_3 \quad (8)$$

Buncel and others[14] have examined the relative occurrence of these three reactions to determine the factors governing selection of each mode of attack. In dealing with attack at the sulfur, the products formed appear to be the result of the better leaving group being cleaved from the sulfur. With perfluoroalkyl fluorosulfates, for example, the perfluoroalkoxy group is a better leaving group than F^-, while in alkyl chlorosulfates, Cl^- can be a better leaving group than RO^-. More subtle factors appear to be operating in the instance of attack at the α-carbon. Cohen[15] observed that long chain fluoroalkyl chlorosulfates apparently possess weaker fluoroalkyl–oxygen bonds than the corresponding p-toluenesulfonates because of the easy occurrence of reaction 9. The yields in this reaction were in the order Br > Cl > F, indicating that the α-carbon reacted more easily with "soft" nucleophiles such as Br^- (and presumably I^-).

$$R_fOSO_2Cl + MX \rightarrow R_fX + MOSO_2Cl \quad (9)$$

R_f = $H(CF_2CF_2)_2CH_2$, $HCF_2CF_2CH_2$; M = Li, K; X = F, Cl, Br

In our reactions of 2,2,2-trifluoroethyl fluorosulfate, hard nucleophiles such as HNRR' or HOR gave rise almost exclusively

(2) Earl, B. L.; Hill, B. K.; Shreeve, J. M. *Inorg. Chem.* **1966**, *5*, 2184.
(3) Hauptschein, M.; Braid, M. *J. Am. Chem. Soc.* **1961**, *83*, 2500.
(4) Kumar, R. C.; Kinkead, S. A.; Shreeve, J. M. *Inorg. Chem.* **1984**, *23*, 3112.
(5) Hauptschein, M.; Braid, M. *J. Am. Chem. Soc.* **1961**, *83*, 2505.
(6) Lustig, M.; Ruff, J. K. *Inorg. Chem.* **1964**, *3*, 287.
(7) Schack, C. J.; Christe, K. O *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 293.
(8) Ruff, J. K.; Merritt, R. F. *Inorg. Chem.* **1968**, *7*, 1219.
(9) Delepine, M.; Demars, R. *Bull. Sci. Pharmacol.* **1923**, *30*, 577.
(10) Binkley, W. W.; Degering, E. F. *J. Am. Chem. Soc.* **1939**, *61*, 3250.
(11) Guyot, J.; Simon, L.-J. *C. R. Hebd Seances Acad. Sci.* **1920**, *170*, 326.
(12) Hall, H. K. *J. Am. Chem. Soc.* **1956**, *78*, 1450.
(13) Charalambous, J.; Frazer, M. J.; Gerrard, W. *J. Chem. Soc.* **1964**, 5480.
(14) Buncel, E. *Chem. Rev.* **1970**, *70*, 323 and references therein.
(15) Cohen, W. V. *J. Org. Chem.* **1961**, *26*, 4021.

to sulfur–fluorine bond cleavage (eq 10 and 11). The yields in

$$CF_3CH_2OSO_2F + 2HNRR' \xrightarrow{25\ ^\circ C} CF_3CH_2OSO_2NRR' + [H_2NRR']^+F^- \quad (10)$$

$$R = H, CH_3;\ R' = H, CH_3$$

$$CF_3CH_2OSO_2F + ROH \xrightarrow{Et_3N} CF_3CH_2OSO_2OR + [Et_3NH]^+F^- \quad (11)$$

$$R = CF_3CH_2,\ (CF_3)_2CH,\ CH_3$$

each case (Table I) reflect the relative strength of the nucleophiles. Reactions of alcohols with fluorosulfates occurred in low yields or not at all unless the alcohol was first mixed with triethylamine which indicated that the anion is the actual attacking species. Yields of methyl 2,2,2-trifluoroethyl sulfate were low by this method, necessitating the use of sodium methoxide to effect reasonable yields.

In several syntheses of $CF_3CH_2OSO_2R$ (where R = OCH_3, $NHCH_3$, and $OCH(CF_3)_2$), trace amounts of the bis(trifluoroethyl) sulfate were identified by GC/MS. Presumably this sulfate must arise from rupture of the S–O single bond instead of the S–F bond (Scheme I). The small amounts of bis(trifluoroethyl) sulfate from these reactions (less than 1–2%) indicate the poor leaving ability of the trifluoroethoxy group compared to other perfluoroalkoxy groups.[3,5]

Because of the strong interaction between $(CF_3)_2CHOH$ and triethylamine, the yield of $CF_3CH_2OSO_2OCH(CF_3)_2$ was low unless the mixture was heated to 50–60 °C for several hours.

When hexafluoro-2-propanol–triethylamine mixtures were allowed to react with sulfuryl chlorofluoride (SO_2ClF), bis(hexafluoroisopropyl) sulfate [$[(CF_3)_2CHO]_2SO_2$] was isolated in 20% yield in addition to hexafluoroisopropyl fluorosulfate [$(CF_3)_2CHOSO_2F$].[4] Formation of the sulfate ester must result from the reaction of the alcohol–amine adduct with the fluorosulfate formed in situ (eq 12 and 13).

$$(CF_3)_2CHOH{\cdot}NEt_3 + SO_2ClF \rightarrow \underset{50\%}{(CF_3)_2CHOSO_2F} + [HNEt_3]^+Cl^- \quad (12)$$

$$(CF_3)_2CHOSO_2F + (CF_3)_2CHOH{\cdot}NEt_3 \rightarrow \underset{19\%}{[(CF_3)_2CHO]_2SO_2} + [HNEt_3]^+F^- \quad (13)$$

When trifluoroethyl fluorosulfate was allowed to react with methanethiol–triethylamine mixtures, none of the expected *S*-methyl 2,2,2-trifluoroethyl thiosulfate could be identified. Instead, approximately half of the fluorosulfate remained unreacted, while only a trace of the methanethiol could be found. Among the identified products were sulfur dioxide, dimethyldisulfane (CH_3SSCH_3), trifluoroethanol (as the triethylamine adduct), bis(trifluoroethyl) sulfate, and a large quantity of methyl trifluoroethyl sulfide ($CF_3CH_2SCH_3$). The sizable amount of sulfide found indicates a shift in the reaction pathway from substitution at sulfur to substitution at the carbon (eq 14). The sulfane, sulfur

$$CF_3CH_2OSO_2F + CH_3SH \xrightarrow{Et_3N} CF_3CH_2SCH_3 + [Et_3NH]^+[OSO_2F]^- \quad (14)$$

dioxide, trifluoroethanol, and sulfate can presumably arise from nucleophilic attack at sulfur followed by scission of the sulfur–oxygen bond (Scheme II). Since nucleophilic attack at sulfur(VI) by sulfur(–II) is apparently less favored than attack at the α-carbon, the amounts of these products will, of course, be less than the sulfide. Although appropriate fragments could be found in the GC/MS for the bis(methanethio)sulfate, its identity could not be confirmed.

Bromide ion is also a sufficiently soft nucleophile to attack the carbon preferentially.[15] While KF was observed to be unreactive with trifluoroethyl fluorosulfate at 60 °C, KBr converted the fluorosulfate into trifluoroethyl bromide quantitatively (eq 15). Because no evidence for sulfuryl bromofluoride (SO_2BrF) or its

Scheme II

$$CF_3CH_2OSO_2F + CH_3SH \longrightarrow CF_3CH_2OH + CH_3SSO_2F$$

$$CH_3SSO_2F + CH_3SH \xrightarrow{-HF} [(CH_3S)_2SO_2] \longrightarrow CH_3SSCH_3 + SO_2$$

$$CF_3CH_2OH + CF_3CH_2OSO_2F \xrightarrow[-HF]{Et\ N} (CF_3CH_2O)_2SO_2$$

decomposition products could be found, attack apparently does not occur at sulfur(VI).

$$CF_3CH_2O\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}F + KBr \xrightarrow{C_2H_4(OH)_2,\ 60\ ^\circ C,\ 12\ h} CF_3CH_2Br\ (>98\%) \quad (15)$$

A shift in the point of attack of nucleophiles within a molecule such as this, while unusual, is not without precedent. Burton and Shreeve[16] reported the reaction of *N*-trifluoromethanesulfenyl acetimidoyl chloride with amines and alcohols to give substitution products at carbon, while with thiols substitution products at sulfur predominate. In their work, the hardness of the nucleophile determined the point of attack. On the basis of existing tables that attempt to classify bases according to hardness and softness,[17] a four-coordinate carbon in the α-position is susceptible to attack by soft nucleophiles. These findings logically reflect the relative polarizability of the extremely electron-deficient sulfur atom relative to the α-carbon atom.

Unlike perfluoroalkyl fluoro- and chlorosulfates, trifluoroethyl fluorosulfate is remarkably stable to hydrolysis. The ^{19}F and ^1H NMR spectra were essentially unchanged even after 48 h at 125 °C in the presence of an excess of water. Although hydrolysis did eventually occur, even after 2 months at room temperature in an excess of water 78% of the fluorosulfate was unreacted, while the remainder had been converted to the alcohol CF_3CH_2OH. No evidence for the acid hydrogen sulfate $HOSO_2OCH_2CF_3$ was obtained.

The sulfamates prepared in this study are colorless, air- and water-stable liquids and solids with very low vapor pressures. While *N,N*-dimethyl-2,2,2-trifluoroethyl sulfamate [$CF_3CH_2OSO_2N(CH_3)_2$] is a liquid (vapor pressure at room temperature of ~1 mm) that is not miscible with water in any proportion, 2,2,2-trifluoroethyl sulfamate ($CF_3CH_2OSO_2NH_2$) is a solid (mp 50 °C) that is quite water soluble. The effect of intermolecular hydrogen bonding between the protons on the nitrogen atom and the oxygen atoms on sulfur in $CF_3CH_2OSO_2NH_2$ account for the increase in melting point and solubility in water.

All of the dialkyl sulfate esters are involatile liquids, insensitive to both air and water. Bis(2,2,2-trifluoroethyl) sulfate has been prepared previously in low yields from sodium trifluoroethoxide and SO_2Cl_2.[15] In these sulfamates and sulfate esters, all NMR spectra are first order. No long-range coupling between different groups attached to sulfur is observed. Although the CF_3 groups in bis(hexafluoroisopropyl) sulfite [$[(CF_3)_2CHO]_2SO$] are coupled to each other with $^4J_{CF_3\text{-}CF_3'} = 9.5$ Hz,[18] no such coupling could be observed in bis(hexafluoroisopropyl) sulfate [$[(CF_3)_2CHO]_2SO_2$].

While the value of $^3J_{HF}$ for the trifluoroethyl group varied only slightly from 7.3 to 8.1 Hz, for all the sulfamates and sulfates, the value of $^3J_{HF}$ for methyl trifluoroethyl sulfide has increased to approximately 10 Hz. Even though the mass spectra of all the sulfamates displayed molecular ions with electron-impact ionization, molecular ions were weak or absent for the sulfates. When chemical ionization was used, however, the quasi-molecular ions (M + 1) were intense and often the base peaks. Typically, major peaks were observed corresponding to $CF_3CH_2OSO_2^+$ (163), $ROSO_2^+$ (M – CF_3CH_2O), and $CF_3CH_2^+$ (83). The infrared spectra of these compounds showed strong absorption bands for

(16) Burton, C. A.; Shreeve, J. M. *Inorg. Chem.* **1977**, *16*, 1408.
(17) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827.
(18) De Marco, R. A.; Kovacina, T. A.; Fox, W. B. *J. Fluorine Chem.* **1975**, *5*, 221.

$\nu_{S=O_{asym}}$ at 1370–1410 cm^{-1} and $\nu_{S=O_{sym}}$ at about 1280 cm^{-1}.

Experimental Section

Materials. 2,2,2-Trifluoroethyl fluorosulfate,[4] $NaOCH_3$,[19] and SO_2ClF[20] were prepared according to the literature procedures. The other materials CF_3CH_2OH (Aldrich), $(CF_3)_2CHOH$ (PCR), NH_3 (Matheson), CH_3NH_2 (Matheson), $(CH_3)_2NH$ (Matheson), and CH_3SH (Eastman Organic) were used as received without further purification. Triethylamine (Baker) was distilled from KOH and stored over activated 3-Å molecular sieves for 18 h prior to use.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum apparatus equipped with a Heise Bourdon tube gauge. Most of the starting materials were measured quantitatively by using PVT techniques. Products were first separated from unreacted starting materials by fractional condensation (trap-to-trap distillation), followed, where necessary, by vacuum bulb-to-bulb distillation and by use of a Hewlett-Packard 5712 A gas chromatograph. For gas chromatographic separations, the columns were fashioned from 0.25-in. copper tubing packed with 30% QF-1 on Chromosorb P. Infrared spectra were recorded with a Perkin-Elmer 599B spectrometer using a 10-cm cell fitted with KBr windows for gases, a capillary film between AgCl windows for liquids, and a KBr pellet for solids. ^{19}F and ^1H NMR spectra were obtained on either a JEOL FX 90Q FT NMR or a Varian EM360L spectrometer using CCl_3F and tetramethylsilane as an external reference, respectively. $CDCl_3$ was used as a solvent. Signals upfield of CCl_3F in the ^{19}F NMR are assigned negative values. Mass spectra were recorded with a VG 7070 HS spectrometer operating either at 15 eV or in the chemical ionization mode. Elemental analyses were performed by Beller Mikronanalytisches Laboratorium, Göttingen, West Germany.

Reaction of 2,2,2-Trifluoroethyl Fluorosulfate with Dimethylamine [$(CH_3)_2NH$]. A 50-mL Pyrex flask fitted with a vacuum stopcock was charged with 2.0 mmol (0.36 g) of $CF_3CH_2OSO_2F$ and 4.0 mmol (0.18 g) of $(CH_3)_2NH$ at −196 °C, and then warmed slowly to room temperature over a period of several hours. The volatile products were distilled through traps held at −30 and −196 °C, while the reaction vessel was warmed from −196 to +40 °C. In addition to unreacted $(CH_3)_2NH$ (0.1 mmol) in the −196 °C, the trap at −30 °C contained 0.3960 g (96% yield) of a colorless liquid with a vapor pressure of 1 mm at 23 °C. Chromatographic analysis (0.25 in. × 50 cm QF-1 column at 90 °C) showed the liquid to be greater than 98% pure $CF_3CH_2OSO_2N(CH_3)_2$. The infrared spectrum of *N,N*-dimethyl-2,2,2-trifluoroethyl sulfamate, taken as a capillary film between AgCl plates, is as follows: 2927 (m-br), 1464 (m), 1423 (m), 1377 (s), 1287 (s), 1183 (vs), 1058 (s), 978 (s), 868 (m), 808 (s-br), 734 (m), 668 (w), 569 (s), 543 (m) cm^{-1}. The room temperature ^{19}F NMR spectrum shows a triplet at ϕ −74.7 with $^3J_{HF}$ = 8.1 Hz. In the ^1H NMR, two signals are observed, a quartet due to CH_2 at δ 4.66 (2 H), and a singlet at δ 3.06 (6 H) due to the two methyl groups on the nitrogen atom. The electron-impact mass spectrum shows an intense molecular ion at *m/e* 207 (52% of base peak), in addition to peaks at *m/e* 208 (M + 1, 5.5%), 209 (M + 2, 2.7%), and 206 (M − 1, 43.3%). Other fragments are found at *m/e* 163 (M − $N(CH_3)_2^+$, 1%), 124 (M − $CF_3CH_2^+$, 9.4%), 108 (M − $CF_3CH_2O^+$, base peak), and 83 ($CF_3CH_2^+$ 4.3%). This compound is a colorless, air-stable liquid which is soluble in CH_2Cl_2 and insoluble in water. The ^1H NMR of an equal volume mixture of sulfamate and water shows no change over a period of 2 weeks at room temperature. Anal. Calcd for $C_4H_8NF_3O_3S$: C, 23.18; H, 3.86; F, 27.53. Found: C, 24.09; H, 3.98; F, 28.30.

Reaction of 2,2,2-Trifluoroethyl Fluorosulfate with Methylamine (CH_3NH_2). 2,2,2-Trifluoroethyl fluorosulfate (1 mmol, 0.18 g) and methylamine (2 mmol, 0.09 g) were condensed into a Pyrex reaction vessel at −196 °C. The contents were slowly warmed to room temperature and kept for 20 h. All the volatiles were removed under vacuum while the reaction mixture was kept at 0 °C. The product $CF_3CH_2OSO_2NHCH_3$ was separated from $CH_3NH_3^+F^-$ by vacuum distillation at 43 °C. *N*-Methyl-2,2,2-trifluoroethyl sulfamate is obtained as a colorless liquid in 58% yield and has a vapor pressure at room temperature of 1 mm. The infrared spectrum of $CF_3CH_2OSO_2NHCH_3$ is as follows: 3312 (m-br), 2980 (w), 1460 (sh), 1420 (m), 1360 (m-s), 1285 (s), 1170–1190 (s-br), 1050 (s), 970 (s), 860 (m), 815 (m), 680 (m), 565 and 580 (m), 520 (w) cm^{-1}. The ^{19}F NMR consists of a triplet at ϕ −73.8 with $^3J_{HF}$ = 8 Hz. The ^1H NMR is comprised of a broad singlet at δ 5.6 (1 H), a quartet at δ 4.34 (2 H), and a singlet at δ 2.8 (3 H). The EI mass spectrum contained a molecular ion, *m/e* 193 (11.5% of base peak), as well as fragments at *m/e* 124 (M − CF_3^+, 10.7%), 94 (M − $CF_3CH_2O^+$, base peak), and 83 ($CF_3CH_2^+$, 5.5%).

(19) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; John Wiley: New York, 1967; Vol. 1, p 1091.
(20) Tullock, C. W.; Coffman, D. D. *J. Org. Chem.* **1960**, *25*, 2016.

Anal. Calcd for $C_3H_6NF_3O_3S$: C, 18.65; H, 3.11; F, 29.5. Found: C, 18.81; H, 3.49; F, 28.6.

Reaction of 2,2,2-Trifluoroethyl Fluorosulfate with Ammonia. 2,2,2-Trifluoroethyl fluorosulfate (2 mmol, 0.36 g) and ammonia (8 mmol, 0.14 g) were condensed in a Pyrex reaction vessel at −196 °C and warmed slowly to room temperature, whereupon a white solid was observed to form. After the unreacted starting materials were removed under vacuum at 0 °C, the white solid was vacuum sublimed at 45 °C. The hygroscopic white platelets melt at 50–51 °C when dry and are insoluble in chloroform or methylene chloride but dissolve readily in water, methanol, or acetone. The infrared spectrum, taken as a KBr disk, is as follows: 3380 (m), 3170 (m), 3100 (w-br), 2980 (sh), 1605 (sh), 1525 (s), 1360 (s), 1304 (m), 1273 (m), 1174 (vs), 1049 (s), 966 (s), 939 (m), 855 (m), 819 (m-br), 670 (m), 583 (m), 549 (s), 505 (w) cm^{-1}. The ^{19}F NMR, taken in methanol, consists of a triplet at ϕ −75.2, with a value for $^3J_{HF}$ of 7.3 Hz. The ^1H NMR taken in 80:20 $CDCl_3/(CD_3)_2CO$ consists of a quartet at δ 4.47 (2 H) and a broad singlet at δ 2.12 (2 H), the latter chemical shift being strongly solvent dependent. The chemical ionization mass spectrum shows an intense quasi-molecular ion at *m/e* 180 (M + 1, base peak). Other fragments are observed at *m/e* 160 (M − F^+, 56.7%), 140 ($CFCH_2OSO_2NH^+$, 18.2%), 110 (M − CF_3^+, 29.9%), and 80 (M − $CF_3CH_2O^+$, 66.4%).

Anal. Calcd for $C_2H_4NF_3O_3S$: C, 13.40; H, 2.23; F, 31.83. Found: C, 12.82; H, 3.21; F, 32.8.

Reaction of 2,2,2-Trifluoroethyl Fluorosulfate with 2,2,2-Trifluoroethanol (CF_3CH_2OH). 2,2,2-Trifluoroethanol (2 mmol, 0.20 g) and triethylamine (2 mmol, 0.20 g) were condensed in a Pyrex reaction vessel and warmed to ambient temperature. After being stirred vigorously for 10 minutes, the mixture was cooled to −196 °C, 2,2,2-trifluoroethyl fluorosulfate (2 mmol, 0.36 g) was added, and the mixture was allowed to warm to room temperature over several hours. The volatile products and unreacted starting materials were removed under vacuum at −30 °C, and the product was vacuum distilled at 38 °C. Bis(2,2,2-trifluoroethyl)sulfate [$(CF_3CH_2O)_2SO_2$] is a colorless liquid with a vapor pressure of about 1 mm at room temperature. Yield of the sulfate ester by gas chromatography (50-cm QF-1 column at 120 °C, retention time = 7 min) was 87%. The infrared spectrum of the material is as follows: 2992 (w), 1412 (vs-br), 1288 (vs), 1178 (vs-br), 1028 (s), 973 (s), 883 (vs), 847 (s), 676 (m), 584 (s), 529 (w) cm^{-1}. The ^{19}F NMR consists of a triplet at ϕ −76.6 with $^3J_{HF}$ = 7.8 Hz. The ^1H NMR is comprised of a quartet at δ 4.5. The CI mass spectrum shows a quasi-molecular ion at *m/e* 263 (M + 1, base peak) with other prominent fragments at *m/e* 243 (M − F^+, 64.6%), 163 (M − $CF_3CH_2O^+$, 6.3%), 101 ($CF_3CH_2OH_2^+$, 20.8%), 83 ($CF_3CH_2^+$, 12.9%) and 81 (HSO_3^+ or CF_3C^+, 90.9%).

Anal. Calcd for $C_4H_4F_6O_4S$: C, 18.32; H, 1.53; F, 43.5. Found: C, 18.69; H, 1.69; F, 43.4%.

Reaction of 2,2,2-Trifluoroethyl Fluorosulfate with Sodium Methoxide ($NaOCH_3$). A Pyrex reaction vessel was charged with sodium methoxide (3.0 mmol, 0.16 g), and at −196 °C, 2,2,2-trifluoroethyl fluorosulfate (2.6 mmol, 0.47 g) was used. After the reaction vessel had warmed at room temperature, the volatiles, which consisted of 0.5 mmol unreacted fluorosulfate, were removed under vacuum at −30 °C. The remainder of the material was vacuum distilled at 35 °C and consisted of 0.2289 g (56% yield) of methyl 2,2,2-trifluoroethyl sulfate. The material, which had a purity of >95% by gas chromatography (50 cm QF-1 at 90 °C, retention time = 7.5 min), has 2-mm vapor pressure at room temperature. The infrared spectrum of the material is as follows: 2978 (w), 1458 (m), 1420 (vs), 1292 (vs), 1197 (vs-br), 1062 (s), 1007 (s), 976 (m), 881 (s), 851 (s), 799 (m), 677 (m), 583 (s), 526 (w) cm^{-1}. The ^{19}F NMR of the liquid consists of a triplet at ϕ −73.2, with a value for $^3J_{HF}$ = 7.88 Hz. The ^1H NMR is comprised of a quartet at δ 4.46 (2 H) and a singlet at δ 3.99 (3 H) for the methoxy group. The CI mass spectrum shows a quasi-molecular ion at *m/e* 195 that is also the base peak. Other fragments of prominence are at *m/e* 175 (M − F^+, 37.3%), 125 (M − CF_3^+, 5.0%), and 95 (M − $CF_3CH_2O^+$, 8.7%).

Anal. Calcd for $C_3H_5F_3O_4S$: C, 18.55; H, 2.58; F, 29.4. Found: C, 19.43; H, 2.66; F, 29.2.

Reaction of 1,1,1,3,3,3-Hexafluoro-2-propanol [$(CF_3)_2CHOH$] with SO_2ClF. Hexafluoro-2-propanol (1 mmol, 0.17 g), and triethylamine (1 mmol, 0.10 g) were condensed into a 50-mL Pyrex reaction vessel equipped with a Teflon/glass stopcock at −196 °C and warmed to room temperature for 20 min. The mixture was cooled to −196 °C, and SO_2ClF (1 mmol, 0.12 g) was added to the reactor, whereupon the vessel was warmed to room temperature. After about 20 h, the mixture was distilled, and in addition to $(CF_3)_2CHOSO_2F$[4] found in the trap at −78 °C, the trap held at −20 °C contained a new sulfate, $[(CF_3)_2CHO]_2SO_2$, in about 20% yield. This new sulfate has infrared bands at 2990 (w), 1460 (s), 1372 (s), 1305 (s), 1255 (vs-br), 1123 (sh), 1065 (s), 896 (s), 882 (s), 700 (s), 615 (s), and 544 (m) cm^{-1}. The ^{19}F NMR shows a doublet centered at ϕ −76.2, with $^3J_{HF}$ = 6.1 Hz. The ^1H NMR shows

a heptet at δ 4.30. The highest fragment observed in the EI mass spectrum is M - F^+ at m/e 379.

Anal. Calcd for $[(CF_3)_2CHO]_2SO_2$: S, 8.05; F, 57.28. Found: S, 8.15; F, 58.0.

Reaction of 2,2,2-Trifluoroethyl Fluorosulfate with 1,1,1,3,3,3-Hexafluoro-2-propanol $[(CF_3)_2CHOH]$. 1,1,1,3,3,3-Hexafluoro-2-propanol (2 mmol, 0.34 g) and triethylamine (2 mmol, 0.20 g) were condensed in a Pyrex reaction vessel at -196 °C and warmed to room temperature for 20 min. The mixture was then frozen at -196 °C and 2,2,2-trifluoroethyl fluorosulfate (2 mmol, 0.36 g) added, whereupon the mixture was warmed slowly to room temperature with stirring. After the mixture was heated to 60 °C with stirring for 2-3 h, the volatiles were removed at -30 °C. The product, a colorless to pale yellow liquid, was analyzed by gas chromatography-mass spectroscopy and found to be 93.4% CF_3CH_2O-$SO_2OCH(CF_3)_2$, 4.0% unreacted $(CF_3)_2CHOH{\cdot}N(CH_2CH_3)_3$ (eluted at 120 °C as one component), and 2.6% $(CF_3CH_2O)_2SO_2$. The vapor pressure of 1,1,1,3,3,3-hexafluoroisopropyl 2,2,2-trifluoroethyl sulfate is approximately 5 mm at room temperature. The infrared spectrum for this new sulfate is as follows: 2980 (w), 1441 (s), 1370 (s), 1297 (vs), 1212 (vs-br), 1112 (m), 1069 (s), 1038 (vs), 970 (s), 911 (sh), 893 (s), 854 (s), 746 (w), 698 (s), 673 (w), 624 (m), 597 (m), 576 (m), 539 (m) cm^{-1}. The ^{19}F NMR shows a doublet centered at ϕ -75.2 ($^3J_{HF}$ = 5.4 Hz, 6 F), and a triplet at ϕ -76.0 (^3J = 7.3 Hz, 3 F). The ^1H NMR consists of a heptet at δ 5.23 (1 H) and a quartet at δ 4.62 (2 H). The CI mass spectrum shows a quasi-molecular ion at m/e 331 (base peak), as well as prominent fragments at m/e 311 (M - F^+, 88.6%), 231 (M - $CF_3CH_2^+$, 8.1%), 211 (M - $C_2H_2F_3^+$, 6.9%), 163 (M - $(CF_3)_2CHO^+$, 10.9%), 101 ($CF_3CH_2OH_2^+$, 12%), 81 (CF_3C^+, 36.9%), and 69 (CF_3^+, 16%).

Anal. Calcd for $C_5H_3F_9O_4S$: C, 18.18; H, 0.91; F, 51.8. Found: C, 19.19; H, 1.19; F, 53.7.

Reaction of 2,2,2-Trifluoroethyl Fluorosulfate with Methanethiol (CH_3SH). A Pyrex reaction vessel was charged with CH_3SH (4 mmol, 0.20 g), triethylamine (2 mmol, 0.20 g), and 2,2,2-trifluoroethyl fluorosulfate (2 mmol, 0.36 g), at -196 °C, and warmed slowly with stirring, to room temperature. Immediately, the volatile products were removed at 0 °C, and the volatile and involatile products were analyzed by GC/MS. In addition to unreacted fluorosulfate (46.6%), trifluoroethanol (as triethylamine adduct, 1.8%), bis(2,2,2--trifluoroethyl) sulfate (trace), SO_2 (6.3%), dimethyldisulfane (14.0%), and methyl 2,2,2-trifluoroethyl sulfide (31.4%) were found. Spectral data for $CF_3CH_2SCH_3$: ^{19}F NMR ϕ -68.5 (t, ^3J = 9.7 Hz); ^1H NMR δ 3.03 (q, ^3J = 9.9 Hz, 2 H), 2.24 (s, 3 H); mass spectrum (CI), m/e 131 (M + 1, 57.6%), 111 (M - F^+, 100%), 61 (M - CF_3^+, 10.6%); infrared spectrum 3005 (w, 2950 (w), 1423 (w), 1321 (s), 1288 (s), 1265 (s), 1188 (w), 1142 (vs), 1100 (sh), 992 (w), 861 (w), 752 (m), 658 (m), 497 (w) cm^{-1}. The molecular weight of $CF_3CH_2SCH_3$ was found to be 132 (calcd 130). When the mixture was allowed to react for approximately 2 days prior to analysis, the amount of bis(2,2,2-trifluoroethyl) sulfate increased to about 10% and the sulfide to about 45% of the mixture with an accompanying decrease in the amount of unreacted fluorosulfate and triethylamine. Trace amounts of a substance of molecular weight 158 were also found in the mass spectrum; however, no compound was isolated.

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Registry No. $CF_3CH_2OSO_2F$, 66950-71-8; Me_2NH, 124-40-3; $CF_3CH_2OSO_2NMe_2$, 66950-70-7; $MeNH_2$, 74-89-5; $CF_3CH_2OSO_2NHMe$, 92720-78-0; NH_3, 7664-41-7; $CF_3CH_2OSO_2NH_2$, 92720-79-1; CF_3CH_2OH, 75-89-8; $(CF_3CH_2O)_2SO_2$, 665-97-4; MeONa, 124-41-4; $CF_3CH_2OSO_2OMe$, 92720-80-4; $(CF_3)_2CHOSO_2F$, 38252-04-9; $[(CF_3)_2CHO]_2SO_2$, 92720-81-5; $CF_3CH(OH)CF_3$, 920-66-1; $(CF_3)_2CHOSO_2OCH_2CF_3$, 92720-82-6; MeSH, 74-93-1; CF_3CH_2SMe, 5187-55-3.

Palladium-Catalyzed Carbonylative Coupling of Vinyl Triflates with Organostannanes. A Total Synthesis of (±)$\Delta^{9(12)}$-Capnellene

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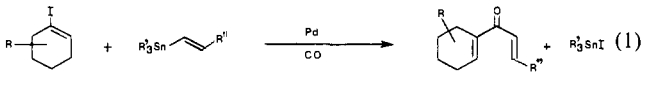
Abstract: The palladium-catalyzed carbonylative coupling of vinyl triflates with alkyl-, vinyl-, allyl-, and arylstannanes gives good yields of the cross-coupled ketone products. Regioselectively formed vinyl triflates can be used to produce divinyl ketones as regioisomerically pure compounds. The *E* and *Z* geometry of the vinylstannane is maintained during the coupling reaction. This methodology was applied to a total synthesis of the marine natural product $\Delta^{9(12)}$-capnellene.

Divinyl ketones are important intermediates in organic synthesis since they can act as Michael acceptors for a diverse range of nucleophiles[1] or participate in Nazarov reactions to give cyclopentenones.[2] We reported recently that the palladium-catalyzed carbonylative coupling of vinyl ioides with vinylstannanes afforded unsymmetrical divinyl ketones in good yields (eq 1).[3]



(1)

However, an expeditious route for the regioselective generation of a cyclic vinyl iodide is not currently available. For example, cyclic vinyl iodides have traditionally been prepared from the corresponding cycloalkanone via a two-step sequence involving hydrazone formation and subsequent oxidation with iodine in the presence of triethylamine.[4] This procedure gives only moderate yields of the desired vinyl iodide, the major side product being the geminal diiodide. More recently, a modification of this procedure which significantly increases the yield of the vinyl iodide has been reported.[5] The regioselective generation of a cyclic vinyl iodide from a hydrazone precursor utilizing this methodology was

(1) Bergman, E. D.; Ginsburg, D.; Pappo, R. *Org. React.* **1959**, *10*, 179-555.
(2) Santelli-Rouvier, C.; Santelli, M. *Synthesis* **1983**, 429-442.
(3) Goure, W. F.; Wright, M. E.; Davis, P. D.; Labadie, S. S.; Stille, J. K. *J. Am. Chem. Soc.*, in press.
(4) Pross, A.; Sternhell, S. *Aust. J. Chem.* **1970**, *23*, 989-1003.
(5) Barton, D. H. R.; Bashiardes, G.; Fourrey, J.-L. *Tetrahedron Lett.* **1983**, *24*, 1605-1608.

0002-7863/84/1506-7500$01.50/0 © 1984 American Chemical Society