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BIS(PERFLUOROALKYL)SULFUR DIFLUORIDES AND BIS(PERFLUOROALKYL) SULFOXIDES

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SUMMARY

Photolysis of $CF_3SOC(O)CF_2CF_3$ and $CF_3SOC(O)CF_2CF_2CF_3$ results in the previously unreported sulfides, $CF_3SCF_2CF_3$ and $CF_3SCF_2CF_2CF_3$. Fluorination of bis(perfluoroalkyl) sulfides with chlorine monofluoride leads to new derivatives of sulfur tetrafluoride, $CF_3SF_2CF_3$, $CF_3SF_2CF_2CF_3$ and $CF_3SF_2CF_2CF_2CF_3$. The cesium fluoride catalyzed reaction of SF_4 and C_2F_4 gives $CF_3CF_2SF_2CF_2CF_3$. Hydrolysis of the products resulting from reaction of the bis(perfluoroalkyl)sulfur difluorides with HCl yields bis(perfluoroalkyl) sulfoxides, $CF_3S(O)CF_3$, $CF_3S(O)CF_2CF_3$, $CF_3CF_2S(O)CF_2CF_3$ and $CF_3S(O)CF_2CF_2CF_3$. Infrared, NMR and mass spectra, as well as elemental analyses and vapor pressure data, are reported for these new compounds.

INTRODUCTION

Decarboxylation of the acid anhydrides, $CF_3SOC(O)CF_3$, $CF_3SOC(O)CF_2CF_3$ and $CF_3SOC(O)CF_2CF_2CF_3$, results in formation of the sulfides, CF_3SCF_3, $CF_3SCF_2CF_3$ and $CF_3SCF_2CF_2CF_3$. The sulfides, $Cl_nF_{3-n}SCF_3$, were previously prepared by this method[1], but no $CF_3SCF_2CF_2CF_3$ was isolated in this earlier work. As the R_f group of $CF_3SOC(O)R_f$ increases in complexity, smaller yields of the bis(perfluoroalkyl) sulfide are obtained. Earlier attempts to fluorinate bis(perfluoroalkyl) sulfides using metal fluorides, AgF_2 or CoF_3, did not yield bis(perfluoroalkyl)sulfur difluorides but rather cleaved the sulfur–carbon bond[2]. Elemental fluorine reacts vigorously with $(R_f)_2S$ at 25° to give degradation products only; however, fluorination at —119° is said to produce $(CF_3)_2SF_2$ (ref. 2). We find that direct synthesis of bis(perfluoroalkyl)sulfur difluorides in yields exceeding

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90% occurs when ClF is reacted with bis(perfluoroalkyl) sulfides. No carbon–sulfur bond cleavage is observed. The preparation of the bis(perfluoroalkyl)sulfur difluorides, $CF_3SF_2CF(CF_3)_2$ and $[(CF_3)_2CF]_2SF_2$ via the CsF-catalyzed reactions of CF_3SF_3 and SF_4 with $CF_3CF{=}CF_2$ has been demonstrated[3]. We have used this method to prepare $(CF_3CF_2)_2SF_2$. Pure bis(perfluoroalkyl)sulfur difluorides are remarkably stable to hydrolysis at 25°. However, this investigation shows that reaction of bis(perfluoroalkyl)sulfur difluorides with HCl followed by hydrolysis yields bis(perfluoroalkyl) sulfoxides[4], generally in high yields.

RESULTS AND DISCUSSION

Bis(perfluoroalkyl) sulfides, R_fSR_f'

Several bis(perfluoroalkyl) sulfides have been prepared recently by the photolysis of perfluoro(sulfenyl-carboxylic)acid anhydrides[1]. Photolysis of $CF_3SOC(O)CF_3$ is superior to other methods[2,5] for preparing CF_3SCF_3[1] because it invariably gives quantitative yields of product. In our work, decarboxylation of acid anhydrides was extended to form $CF_3SCF_2CF_3$ and $CF_3SCF_2CF_2CF_3$,

$$CF_3SCl + AgOC(O)R_f \longrightarrow CF_3SOC(O)R_f \xrightarrow{UV} CF_3SR_f + CO_2$$

In these cases, sulfide formation is accompanied by substantial amounts of $(R_fC(O))_2O$, $CF_3SSO_2CF_3$ and CF_3SSCF_3 which make gas chromatographic separations necessary in order to obtain the pure sulfides. These two new bis(perfluoroalkyl) sulfides are low-boiling colorless liquids which are stable toward glass and mercury, and are not hydrolyzed by aqueous base at 100°. Each of these compounds exhibits a molecular ion in its mass spectrum, and the fluorine NMR resonance for CF_3S– occurs at about φ 36 which is typical of trifluoromethyl groups bonded to sulfur(II).

Bis(perfluoroalkyl)sulfur difluorides, $R_fSF_2R_f'$

Nucleophilic attack of SF_4 on the pentafluoroethylcarbanion ($CsF + C_2F_4$) gives rise to bis(pentafluoroethyl)sulfur difluoride (I) in 40% yield

$$SF_4 + CF_2{=}CF_2 \xrightarrow[CsF]{150\text{–}200^\circ} CF_3CF_2SF_2CF_2CF_3\ (I)$$

Bis(pentafluoroethyl) disulfide, which is also observed as a product, arises from the pyrolysis of (I) to the unstable intermediate, CF_3CF_2SF, which subsequently undergoes disproportionation

$$CF_3CF_2SF_2CF_2CF_3 \xrightarrow{200^\circ} [CF_3CF_2SF] \longrightarrow CF_3CF_2SF_3 + (CF_3CF_2S)_2$$

This intermediate is reasonable when one considers the instability of the analogous compound CF_3SF, in glass, and its tendency to undergo disproportionation to

CF_3SF_3 and $(CF_3S)_2$[6]. Since $CF_3CF_2SF_3$ is an end product in its own right when the $CF_3CF_2^-$–SF_4 reaction proceeds in a 1:1 ratio, and also one which can be used up in further reaction with additional $CF_3CF_2^-$, it is not possible to establish the route of $(CF_3CF_2S)_2$ formation unequivocally. Formation of $CF_3CF_2SF_3$ by the former route can be minimized by using a 2–3-fold excess of C_2F_4.

Heretofore, attempts to fluorinate bis(perfluoroalkyl) sulfides to bis(perfluoroalkyl)sulfur difluorides with AgF_2 or CoF_3 resulted in bond cleavage and the sulfur was oxidized to sulfur(VI)[2]. The reaction of ClF with the bis(perfluoroalkyl) sulfides, CF_3SCF_3, $CF_3SCF_2CF_3$ and $CF_3SCF_2CF_2CF_3$ provides an effective route to the bis(perfluoroalkyl)sulfur difluorides in yields greater than 90%

$$CF_3SR_f + 2ClF \xrightarrow{-78^\circ \text{ to } 25^\circ} CF_3SF_2R_f + Cl_2$$

These new sulfur(IV) difluorides can be purified effectively using fractional condensation followed by gas chromatography. Pure samples are stable in glass at 25° for short periods of times, *e.g.*, pure gaseous $(CF_3)_2SF_2$ was stored in Pyrex for one week without decomposition occurring. Water vapor added to the vessel did not hydrolyze the difluoride after one week at 25°. The hydrolytic stability of these $(R_f)_2SF_2$ compounds is rather unexpected since such hydrolyses would be thermodynamically favored and SF_4[7], and the perfluoroalkylsulfur trifluorides[8–10], undergo rapid hydrolysis to SOF_2 and $R_fS(O)F$ respectively in the presence of trace amounts of water. On the other hand, $(CF_3)_2(CF)_2SF_2$ does not hydrolyze, apparently because of the shielding of the $-\overset{|}{S}F_2$ atoms by the bulky perfluoroisopropyl groups[3]. With the less complex perfluoroalkyl groups such shielding is not likely; therefore, the previous explanation for the hydrolytic stability of $(R_f)_2SF_2$ may not be the entire story.

These new bis(perfluoroalkyl) sulfur difluorides exist as colorless liquids which are unreactive towards mercury. All have a characteristic band at about 675 cm^{-1} in their infrared spectra. Previous workers[5] assigned bands in this region to an FCF mode; however, complete absence of this band in the corresponding sulfoxides suggests that assignment to an S–F stretching mode is more appropriate. Whilst molecular ions are not observed in the mass spectra, $(M-F)^+$ and $R_fSF_2^+$ are characteristically observed. The resonances in the ^{19}F NMR spectra integrate to the appropriate area ratios, further supporting the $(R_f)_2SF_2$ structure. The spectrum of the simplest molecule, $CF_3SF_2CF_3$, is easily interpreted with the CF_3 resonance occurring as a well-resolved triplet centered at φ 58.0, and the SF_2 resonance as a septet centered at φ 14.2 with a coupling constant of 19.5 cps. The higher members of the series, $CF_3SF_2CF_2CF_3$, $CF_3CF_2SF_2CF_2CF_3$ and $CF_3SF_2CF_2CF_2CF_3$, have much more complex spectra which seem to indicate AA'XX'-type interactions[11]. It appears as if the magnetic non-equivalence of the fluorine atoms bonded to the same sulfur atom or the α-methylene carbon atom can be explained on the basis of preferred rotamers existing within the molecule. Although the chemical shifts and evident coupling constants are given in Table 1, a complete analysis of these interactions is the subject of further investigation.

TABLE 1

NMR SPECTRA OF CF_3SR_f', $R_fSF_2R_f'$ AND $R_fS(O)R_f'$

Compound	CF_3S	CF_3C	αCF_2	βCF_2	CF	SF_2	Coupling Constants
$CF_3SCF_2CF_3$	36.2	84.6	90.4				$J(CF_3S\text{–}CF_2) = 9.9$ $J(CF_3C\text{–}CF_2) = 2.85$ $J(CF_3S\text{–}CF_3C) = 2.6$
$CF_3SCF_2CF_2CF_3$	35.5	80.8	86.3	124.9			$J(CF_3S\text{–}\alpha CF_2) = 9.9$ $J(CF_3C\text{–}\alpha CF_2) = 9.4$ $J(CF_3S\text{–}\beta CF_2) = 3.5$ $J(\alpha CF_2\text{–}\beta CF_2) = 2.25$
$CF_3SF_2CF_3$	58.0					14.2	$J(CF_3\text{–}SF_2) = 19.5$
$CF_3SF_2CF_2CF_3$*	55.8	80.2	100.7			13.0	$J(CF_3S\text{–}SF_2) = 19.5$ $J(CF_3S\text{–}CF_2) = 7.0$ $J(CF_3S\text{–}CF_3C) = 1.1$ $J(SF_2\text{–}CF_3C) = 9.4$ $J(CF_2\text{–}CF_3C) = 1.25$
$CF_3SF_2CF_2CF_2CF_3$*	55.6	81.2	97.1	123.1		11.2	$J(CF_3S\text{–}SF_2) = 20.1$ $J(CF_3S\text{–}\alpha CF_2) = 7.25$ $J(CF_3S\text{–}\beta CF_2) = 0.8$ $J(CF_3C\text{–}\alpha CF_2) = 9.15$ $J(SF_2\text{–}\beta CF_2) = 13.0$
$CF_3CF_2SF_2CF_2CF_3$*		80.5		98.9		11.2	$J(SF_2\text{–}CF_2) = 19.0$ $J(CF_3\text{–}CF_2) = 9.6$
$CF_3SF_2CF(CF_3)_2$**	61.7	75.4			170	16	$J(SF_2\text{–}CF_3) = 19$ $J(SF_2\text{–}CF) = 28$ $J(CF_3C\text{–}CF_3S) = 4.1$ $J(CF_3\text{–}CF) = 7.2$
$(CF_3)_2CFSF_2CF(CF_3)_2$**		75.0			146.4	13	$J(SF_2\text{–}CF_3) = 10$ $J(SF_2\text{–}CF) = 4.0$ $J(CF_3\text{–}CF) = 7.5$
$CF_3\overset{O}{S}CF_3$	64.5						
$CF_3\overset{O}{S}CF_2CF_3$	66.7	80.9	116.9				$J(F_a\text{–}F_b) = 242$ $J(CF_3S\text{–}F_a) = 14.0$ $J(CF_3S\text{–}F_b) = 10.0$ $J(CF_3S\text{–}CF_3C) = 2.6$ $J(F_a\text{–}CF_3C) = 1.25$ $J(F_b\text{–}CF_3C) = 1.75$

* Incomplete analysis, subject of further investigation.

** Previously reported[1], included for comparison (external standard).

TABLE 1 (Cont.)

Compound	CF_3S	CF_3C	αCF_2	βCF_2	CF	SF_2	Coupling Constants
 $CF_3CF_2\overset{O}{S}CF_2CF_3$		80.6	115.8				$J(F_a-F_b) = 228$ $J(F_a-CF_3) = 3.8$ $J(F_b-CF_3) = 2.2$
 $CF_3\overset{O}{S}CF_2CF_2CF_3$	66.4	80.1	114.6	125.5			$J(F_a-F_b) = 242$ $J(F_a-CF_3S) = 15.0$ $J(F_b-CF_3S) = 8.8$ $J(F_a-CF_3C) = 9.1$ $J(F_b-CF_3C) = 9.1$ $J(CF_3S-\beta CF_2) = 2.7$

Bis(perfluoroalkyl) sulfoxides, $(R_f)_2SO$

When the bis(perfluoroalkyl)sulfur difluorides were found to be stable to hydrolysis, other routes leading to bis(perfluoroalkyl) sulfoxides were sought. Yellow mercuric oxide slowly converts $CF_3SF_2CF_3$ to $CF_3S(O)CF_3$ in about 10% yield after one week at 25°. Higher temperatures were not tried since it was found that the reaction of anhydrous HCl with the bis(perfluoroalkyl)sulfur difluorides provides a good preparative route to bis(perfluoroalkyl) sulfoxides. For example, $CF_3SF_2CF_3$ reacts with HCl in Pyrex over a 12 h period to produce the sulfoxide quantitatively. The reaction is thought to proceed through a bis(perfluoroalkyl)sulfur dichloride intermediate, which is readily hydrolyzed by the water formed when HF attacks the glass vessel

$$\begin{aligned}
&(CF_3)_2SF_2 + 2HCl \longrightarrow (CF_3)_2SCl_2 + 2HF\\
&4HF + SiO_2 \longrightarrow 2H_2O + SiF_4\\
&(CF_3)_2SCl_2 + H_2O \longrightarrow (CF_3)_2SO + 2HCl
\end{aligned}$$

No attempt was made to isolate the dichloride in this system. Although this reaction with HCl is essentially quantitative, reaction rates and yields tend to decrease as the R_f group becomes more complex. Impure bis(perfluoroalkyl)sulfur difluorides decompose in Pyrex to the corresponding sulfoxides. This decomposition is apparently catalyzed by HF which could arise from hydrolysis of, or glass attack by, small amounts of R_fSF_3 formed in the initial reaction of either SF_4 with fluoroolefin or ClF with bis(perfluoroalkyl) sulfides.

The characterization of the bis(perfluoroalkyl) sulfoxides is facilitated by the presence of molecular ions in the mass spectrum ranging in intensity from 1.5 to 3.3% base (Table 2). Typically, a peak at $m/e = 48$ (SO^+) is observed in the spectrum of each sulfoxide. The close proximity of the C–F asymmetric stretch and the S=O stretching frequency bands in the infrared spectra complicates the

TABLE 2

MASS SPECTRA OF R_fSR_f', $R_fSF_2R_f'$ AND $R_fS(O)R_f'$

$CF_3SCF_2CF_3$: 220 $CF_3SCF_2CF_3^+$ (8.9), 202 $C_2F_6S_2^+$ (2.0), 201 $CF_3SC_2F_4^+$ (1.53), 151 $CF_3SCF_2^+$ (9.2), 132 $C_2F_4S^+$ (1.53), 119 $CF_3CF_2^+$ (46.2), 113 $C_2F_3S^+$ (3.56), 101 CF_3S^+ (1.53), 100 $C_2F_4^+$ (2.0), 82 CF_2S^+ (8.2), 69 CF_3^+ (100), 63 SCF^+ (17.8), 50 CF_2^+ (3.56), 32 S^+, O_2^+ (7.65), 31 CF^+ (9.2).

$CF_3SCF_2CF_2CF_3$: 270 $CF_3SC_3F_7^+$ (3.9), 251 $CF_3SC_3F_6^+$ (0.8), 169 $CF_3CF_2CF_2^+$ (16.6), 163 $C_3F_5S^+$ (4.3), 151 $C_2F_5S^+$ (13.3), 119 $C_2F_5^+$ (3.7), 113 $C_2F_3S^+$ (1.4), 101 CF_3S^+ (0.8), 100 $C_2F_4^+$ (3.9), 82 CF_2S^+ (5.2), 69 CF_3^+ (100), 63 CFS^+ (12.7), 50 CF_2^+ (2.0), 31 CF^+ (5.9).

$CF_3SF_2CF_3$: 189 $CF_3SFCF_3^+$ (1.94), 139 $CF_3SF_2^+$ (1.14), 120 CF_3SF^+ (17.1), 101 CF_3S^+ (13.5), 82 CF_2S^+ (3.2), 69 CF_3^+ (100), 63 SCF^+ (2.4), 50 CF_2^+ (3.2), 51 SF^+ (4.8), 32 S^+, O_2^+ (4.8), 31 CF^+ (4.6).

$CF_3SF_2CF_2CF_3$: 239 $CF_3SFCF_2CF_3^+$ (2.76), 220 $CF_3SC_2F_5^+$ (0.8), 189 $CF_3SF_2CF_2^+$ (0.8), 170 $CF_3SFCF_2^+$ (8.0), 151 $CF_3SCF_2^+$ (12.7), 139 $CF_3SF_2^+$ (3.3), 120 CF_3SF^+, $CF_2SF_2^+$ (14.4), 119 $C_2F_5^+$ (65.2), 101 CF_3S^+, CF_2SF^+ (22.7), 100 $C_2F_4^+$ (3.3), 82 CF_2S^+ (3.3), 69 CF_3^+ (100), 63 SCF^+ (6.1), 51 SF^+ (6.1), 50 CF_2^+ (6.1), 32 S^+, O_2^+ (8.8), 31 CF^+ (14.9).

$CF_3SF_2CF_2CF_2CF_3$: 289 $CF_3CF_2CF_2SFCF_3^+$ (2.2), 270 $C_3F_7SCF_3^+$ (0.3), 239 $C_3F_7SF_2^+$ (0.3), 220 $C_3F_7SF^+$ (1.4), 201 $C_3F_7S^+$ (3.9), 169 $C_3F_7^+$ (30.5), 150 $C_3F_6^+$ (1.7), 139 $CF_3SF_2^+$ (2.8), 120 $CF_2SF_2^+$, CF_3SF^+ (12.2), 119 $C_2F_5^+$ (6.65), 113 $C_2F_3S^+$ (1.1), 101 CF_2SF^+, CF_3S^+ (12.8), 100 $C_2F_4^+$ (6.7), 82 CF_2S^+ (1.7), 69 CF_3^+ (100), 63 FCS^+ (3.32), 51 SF^+ (3.3), 50 CF_2^+ (2.8), 31 CF^+ (7.8).

$CF_3CF_2SF_2CF_2CF_3$: 289 $C_2F_5SFC_2F_5^+$ (2.3), 201 $C_3F_5SCF_2^+$ (0.6), 189 $C_2F_5SF_2^+$ (2.3), 170 $C_2F_5SF^+$ (7.4), 151 $C_2F_5S^+$ (7.6), 119 $C_2F_5^+$ (100), 101 CF_2SF^+ (11.4), 100 $C_2F_4^+$ (2.9), 82 CF_2S^+ (1.7), 69 CF_3^+ (47.7), 63 CFS^+ (4.0), 51 SF^+ (2.0), 50 CF_2^+ (2.9), 32 S^+, O_2^+ (2.9), 31 CF^+ (9.1).

$CF_3S(O)CF_3$: 186 $CF_3S(O)CF_3^+$ (2.1), 119 $C_2F_5^+$ (6.7), 117 CF_3SO^+ (3.3), 101 CF_3S^+ (16.6), 100 $C_2F_4^+$ (1.2), 98 CF_2SO^+ (20.0), 82 CF_2S^+ (3.3), 69 CF_3^+ (100), 67 SOF^+ (11.7), 63 CFS^+ (3.3), 51 SF^+ (5.0), 50 CF_2^+ (6.6), 48 SO^+ (13.3), 32 S^+, O_2^+ (3.3), 31 CF^+ (9.15).

$CF_3S(O)CF_2CF_3$: 236 $CF_3CF_2S(O)CF_3^+$ (3.3), 169 $C_3F_7^+$ (2.8), 167 $C_2F_5SO^+$ (1.6), 151 $C_2F_5S^+$ (1.83), 148 $C_24_4SO^+$ (1.6), 119 $C_2F_5^+$ (27.2), 117 $CF_3S(O)^+$ (2.32), 101 CF_3S^+ (12.5), 100 $C_2F_4^+$ (6.1), 98 $CF_2S(O)^+$ (3.3), 82 CF_2S^+ (3.3), 69 CF_3^+ (100), 67 FSO^+ (6.3), 63 CFS^+ (3.9), 51 SF^+ (2.8), 50 CF_2^+ (6.0), 48 SO^+ (7.3), 32 S^+, O_2^+ (5.6), 31 CF^+ (11.6).

$CF_3CF_2S(O)CF_2CF_3$: 286 $C_2F_5S(O)C_2F_5^+$ (1.5), 170 $C_2F_6S^+$ (7.2), 151 $C_2F_5S^+$ (4.7), 148 $C_2F_4S(O)^+$ (0.7), 132 $C_2F_4S^+$ (1.4), 120 $C_2F_5^+$ (45.8), 101 CF_3S^+ (17.1), 100 $C_2F_4^+$ (4.4), 82 CF_2S^+ (4.2), 69 CF_3^+ (100), 67 SOF^+ (5.4), 63 CSF^+ (5.8), 51 SF^+ (1.9), 50 CF_2^+ (10.4), 48 SO^+ (5.5), 32 S^+, O_2^+ (9.4), 31 CF^+ (12.5).

$CF_3S(O)CF_2CF_2CF_3$: 286 $CF_3S(O)CF_2CF_2CF_3^+$ (2.56), 219 $C_4F_9^+$ (1.28), 217 $C_3F_7SO^+$ (0.6), 182 $C_3F_6S^+$ (1.9), 180 $C_2F_4S_2O^+$ (1.3), 169 $C_3F_7^+$ (28.9), 151 $C_2F_5S^+$ (1.3), 150 $C_3F_6^+$ (0.6), 149 $CF_3S_2O^+$ (1.3), 138 $C_2F_6^+$ (2.6), 136 CF_4SO^+ (5.8), 131 $C_3F_5^+$ (3.2), 119 $C_2F_5^+$ (33.9), 117 CF_3SO^+ (5.8), 101 CF_3S^+ (14.1), 100 $C_2F_4^+$ (11.5), 82 CF_2S^+ (8.3), 69 CF_3^+ (100), 63 CFS^+ (6.4), 51 SF^+ (4.5), 50 CF_2^+ (7.7), 48 SO^+ (11.5), 32 S^+, O_2^+ (12.2), 31 CF^+ (18.6).

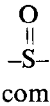
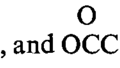
assignment of either. The S=O frequencies of SOF_2 and $SOCl_2$ occur at 1312 and 1229 cm^{-1} (ref. 12), while those of $CF_3S(O)F$, $CF_3S(O)Cl$ and $CF_3S(O)Br$ occur at 1268, 1238 and 1235 cm^{-1} (ref. 9). In addition, bands at 1260 and

TABLE 3

INFRARED SPECTRA

CF_3SCF_3	1226 (s–vs), 1202 (vs), 1165 (s–vs), 1082 (vs), 760 (w–m), 478 (w)
$CF_3SCF_2CF_3$	1342 (m), 1240 (vs), 1200 (vs), 1149 (s), 1102 (s), 970 (s–vs), 760 (m), 485 (w)
$CF_3SCF_2CF_2CF_3$	1344 (m), 1275 (m), 1250 (vs), 1198 (vs), 1145 (m–s), 1122 (s), 1082 (m), 1050 (w–m), 921 (w–m), 860 (m–s), 750 (m), 452 (w)
$CF_3SF_2CF_3$	1281 (vs), 1260 (s), 1215 (m–s), 1144 (m), 1081 (vs), 766 (m), 677 (s), 507 (m)
$CF_3SF_2CF_2CF_3$	1340 (m), 1278 (vs), 1235 (vs), 1151 (s), 1105 (s), 965 (m), 945 (s), 760 (m), 677 (s), 511 (w–m), 485 (m)
$CF_3CF_2SF_2CF_2CF_3$	1320 (m–s), 1262 (vs), 1236 (s–vs), 1160 (s), 1130 (m), 968 (m), 930 (s–vs), 758 (s), 675 (s), 511 (w), 469 (m)
$CF_3SF_2CF_2CF_2CF_3$	1343 (m), 1280 (vs), 1260 (s), 1230 (s–vs), 1158 (s), 1112 (s–vs), 1080 (w–m), 1045 (w), 905 (w–m), 842 (m), 760 (w–m), 697 (m), 675 (s), 505 (w), 482 (w–m)
 $CF_3\overset{O}{S}CF_3$	1244 (vs), 1191, 1187 (doublet, s), 1121 (m–s), 1105 (vs), 752 (w), 468 (w)
 $CF_3\overset{O}{S}CF_2CF_3$	1345 (m), 1242 (vs), 1222 (sh, s), 1178 (m–s), 1132 (m–s), 1113 (m–s), 948 (m), 755 (w–m), 490 (w), 458 (w–m)
 $CF_3CF_2\overset{O}{S}CF_2CF_3$	1320 (m–s), 1250, 1240 (doublet, vs), 1160 (m), 1145 (m–s), 1119 (m–s), 932 (m–s), 753 (m), 618 (w), 467 (w), 407 (w)
 $CF_3\overset{O}{S}CF_2CF_2CF_3$	1343 (m), 1296 (m), 1252 (vs), 1231 (s–vs), 1218 (s–vs), 1172 (m–s), 1140 (m–s), 1110 (s), 1045 (w–m), 901 (w–m), 833 (m), 743 (m), 678 (w–m), 448 (w–m)

1258 cm^{-1} in the spectra of $C_2F_5S(O)F$ and i–$C_3F_7S(O)F$ are attributed to the S=O stretch[9]. Based on these assignments, we have assigned bands at 1244, 1242, 1240 and 1231 to the S=O stretching frequencies in $CF_3S(O)CF_3$, $CF_3S(O)C_2F_5$, $C_2F_5S(O)C_2F_5$ and $CF_3S(O)CF_2CF_2CF_3$, respectively (Table 3).

The ^{19}F NMR spectra (Table 1) show resonances in the regions expected in all cases, although resonances assigned to fluorines of the trifluoromethyl groups bonded directly to  $-\overset{\overset{O}{\|}}{S}-$ appear at φ 64.5–66.7 which is considerably lower than values observed for compounds $CF_3S(O)X$, where X = OCH_2CF_3, NH_2, OCH_2CH_3, Cl, F, and  $O\overset{O}{C}CF_3$[9,13,14]. The α-methylene fluorine atoms of both the pentafluoroethyl and heptafluoropropyl groups are magnetically non-equivalent with $J(F_a–F_b)$ coupling constants of 242 Hz for $CF_3S(O)CF_2CF_3$ and $CF_3S(O)CF_2CF_2CF_3$,

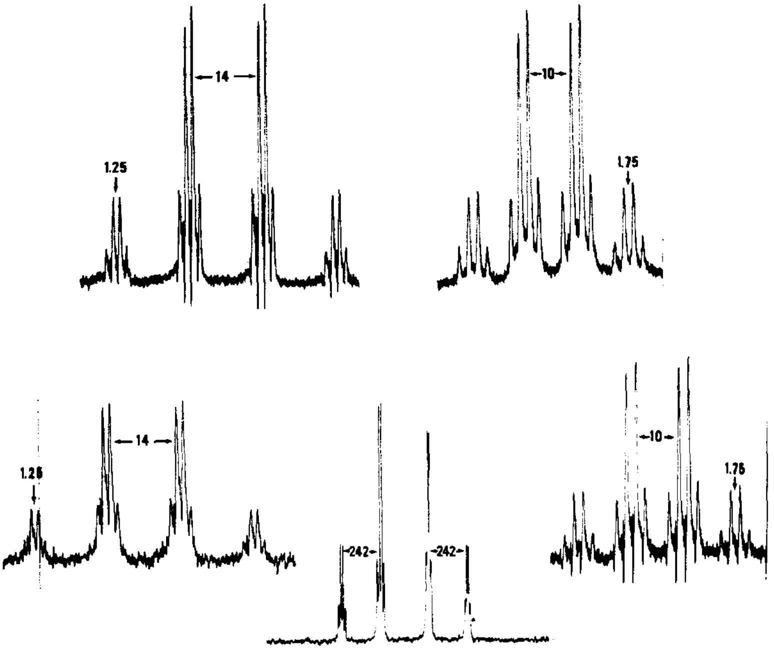


Fig. 1. Methylene ^{19}F NMR spectrum of $CF_3S(O)CF_2CF_3$.

and 228 Hz for $CF_3CF_2S(O)CF_2CF_3$ (Fig. 1). Such magnetic non-equivalence is not without precedent, for the fluorine atoms bonded to carbon in $ClCF_2NClF$ are also magnetically non-equivalent ($J = 128$ Hz)[15]. Also, as seen in Table 1, $J(F_a\text{–}CF_3S)$ differs from $J(F_b\text{–}CF_3S)$ indicating that the fluorine atoms are magnetically non-equivalent.

EXPERIMENTAL

Reagents: Silver trifluoroacetate, silver heptafluorobutyrate and trifluoromethylsulfenyl chloride were obtained from Peninsular ChemResearch Inc. Silver pentafluoropropionate was purchased from Columbia Organic Chemical Co., chlorine monofluoride from Ozark-Mahoning, and yellow mercuric oxide and anhydrous HCl from Matheson. Cesium fluoride was obtained from American Potash and sulfur tetrafluoride from K & K Laboratories. The monosulfides were prepared by photolyzing the appropriate sulfenyl-carboxylic anhydride with a 140 watt Hanovia UV lamp through Pyrex. Tetrafluoroethylene resulted from pyrolysis of Teflon at 600°C. All chemicals were used as received without further purification.

Apparatus: Infrared spectra were taken using a Perkin–Elmer Model 457 infrared spectrometer using a 10 cm gas cell fitted with KBr windows, and were calibrated against known absorption bands in polystyrene film. Fluorine NMR were determined with a Varian HA-100 NMR spectrometer using Freon 11 as an internal standard. Mass spectra were obtained using a Hitachi Perkin–Elmer Model RMU 6E mass spectrometer at 70 eV. Beller Mikroanalytisches Laboratorium performed the elemental analyses. Samples were purified by gas chromatography utilizing a column constructed of 0.25 in. copper tubing packed with 20% Kel-F 3 oil (3-M Co.) on Chromosorb P.

Preparation of CF_3SR_f

The monosulfides, CF_3SCF_3[3], $CF_3SCF_2CF_3$ and $CF_3SCF_2CF_2CF_3$, were all prepared in essentially the same manner. CF_3SCl reacted with the appropriate silver perfluorocarboxylate salt to form a sulfenyl-carboxylic anhydride ($CF_3SO\overset{O}{C}R_f$). Photolysis of the anhydride in a 2-liter Pyrex vessel gave the monosulfide. In a typical run 10 mmoles of CF_3SCl was condensed into a vessel containing excess $AgO\overset{O}{C}CF_3$ and allowed to warm slowly to room temperature. The $CF_3SO\overset{O}{C}CF_3$, produced in essentially quantitative yields, was then photolyzed for 1 h through Pyrex yielding CF_3SCF_3. Decarboxylation of $CF_3SO\overset{O}{C}CF_2CF_3$ and $CF_3SO\overset{O}{C}CF_2CF_2CF_3$ required photolysis times of 2 and 4 h yielding $CF_3SCF_2CF_3$ and $CF_3SCF_2CF_2CF_3$ in 70% and 50% yield, respectively. In all cases, these colorless compounds were purified by gas chromatography using a 17 ft, 20% Kel F on Chromosorb P, column.

Reactions of ClF with dialkylsulfides

A 2-fold excess of ClF with bis(perfluoroalkyl) sulfide produced a $> 90\%$ yield of the corresponding bis(perfluoroalkyl)sulfur difluoride when the reactants were allowed to warm slowly from —78 to 25°C over a period of 10 h. In a typical reaction, 3 mmoles of CF_3SCF_3 was condensed into a 75 ml Hoke bomb and 6 mmoles ClF added. The stainless steel bomb was placed in a —78°C bath and allowed to warm to room temperature overnight. Initial separation was performed by fractional condensation; however, gas-chromatographic purification is essential for obtaining pure $CF_3SF_2CF_3$, $CF_3SF_2CF_2CF_3$ and $CF_3SF_2CF_2CF_2CF_3$.

Reaction of SF_4 with C_2F_4

A mixture of 22 mmoles C_2F_4, 10 mmoles SF_4 and 4 g anhydrous cesium fluoride was heated at 170°C for eight hours in a 75 ml Hoke bomb. Separation of the volatile components by gas chromatography gave $C_2F_5SF_2C_2F_5$ in 40% yield. Also isolated were $C_2F_5SF_3$ (7%) and $C_2F_5SSC_2F_5$ (15%).

Reaction of $CF_3SF_2CF_3$ with H_2O

Three mmoles of $CF_3SF_2CF_3$ was stored in a 250 ml Pyrex vessel for 7 days without any decomposition. Approximately 1 ml of water was added to the vessel and the mixture allowed to remain at 25° for one week where no hydrolysis of $CF_3SF_2CF_3$ occurred.

Reaction of $CF_3SF_2CF_3$ with HgO

Two mmoles of $CF_3SF_2CF_3$ was condensed into a 250 ml Pyrex bulb containing an excess of yellow HgO and warmed to 25°. Fractional condensation of the volatiles after one week produced 0.2 mmole $CF_3S(O)CF_3$. The remaining $(CF_3)_2SF_2$ was recovered unreacted.

Reactions of $R_fSF_2R_f$ with HCl

Reaction of the sulfur difluorides with HCl in Pyrex produced the corresponding sulfoxides in good yield. In a typical reaction, 2 mmoles $CF_3SF_2CF_3$ was reacted with 5 mmoles of HCl in a Pyrex vessel for 24 h. Fractional condensation of the volatiles enabled isolation of $CF_3S(O)CF_3$ in essentially quantitative yield. Yields decreased and longer reaction times were needed as the size of the R_f group increased. In the case of $CF_3SF_2CF_2CF_2CF_3$, some reduction occurred and $CF_3SCF_2CF_2CF_3$ was also isolated. The appropriate sulfoxides were isolated also when crude $R_fSF_2R_f$ (used without gas chromatographic purification) is allowed to remain at 25° in Pyrex for extended periods of time. In all cases, gas chromatography was essential for obtaining pure samples of the sulfoxides.

TABLE 4

ELEMENTAL ANALYSES AND THERMODYNAMIC DATA

	Elemental analysis (%)			B.p.	$\triangle H_v$ (kcal/ mole)	$\triangle S_v$ (cal/ mole · °K)	log P_{mm} = $X-Y/T$ [°K]	
	C	S	F	(°C)			X	Y
$CF_3SCF_2CF_3$ (nc)	—	15.45(15.54)*	69.8(69.1)	6.3	6.88	23.4	7.28	1228
$CF_3SCF_2CF_2CF_3$ (nc)	17.71(17.78)	11.98(11.85)	70.0(70.4)	38.6	6.61	22.9	7.50	1439
$CF_3SF_2CF_3$ (nc)	—	15.56(15.38)	—	21.0	6.88	23.4	8.00	1507
$CF_3SF_2CF_2CF_3$ (nc)	—	12.58(12.40)	73.6(73.6)	44.1	6.98	22.0	7.69	1525
$CF_3SF_2CF_2CF_2CF_3$ (nc)	15.16(15.57)	10.24(10.38)	73.8(74.0)	69.3	7.83	22.9	7.88	1712
$CF_3CF_2SF_2CF_2CF_3$ (nc)	15.37(15.57)	10.23(10.39)	73.8(74.0)	69.5	7.70	22.5	7.80	1685
$CF_3S(O)CF_3$ (nc)	12.65(12.85)	17.38(17.20)	60.5(61.3)	37.3	6.78	21.9	7.66	1483
$CF_3S(O)CF_2CF_3$ (nc)	15.16(15.25)	13.66(13.56)	64.6(64.4)	58.2	7.76	23.4	7.28	1228
$CF_3S(O)CF_2CF_2CF_3$ (nc)	16.90(16.78)	11.37(11.19)	67.2(66.4)	64.0	8.04	23.8	8.24	1790
$CF_3CF_2S(O)CF_2CF_3$ (nc)	16.72(16.78)	11.16(11.19)	65.3(66.4)	62.7	8.39	24.9	8.35	1836

* ( ) Calculated value.

Properties of R_fSR_f', $R_fSF_2R_f'$ and $R_fS(O)R_f'$

These compounds are colorless liquids at room temperature (except $CF_3SF_2CF_3$ and $CF_3SCF_2CF_3$ which boil at 21° and 6°) and solidify to colorless solids. Elemental analyses and thermodynamic data are presented in Table 4.

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