FLUORINATION OF PERFLUOROALKYLSULFENYL CHLORIDES, PERFLUORODIALKYL DISULFIDES AND PERFLUORODIALKYL SULFIDES WITH CHLORINE MONOFLUORIDE

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SUMMARY

In reactions with perfluoroalkylsulfenyl chlorides (R_fSCl; $R_f = CF_3$, C_2F_5, n-C_3F_7, n-C_4F_9) and perfluoroalkyl disulfides (R_fSSR_f'; $R_f = R_f' = CF_3$, $R_f = CF_3$, $R_f' = C_2F_5$) at 25°, chlorine monofluoride acts primarily as a chlorinating and fluorinating reagent to give the corresponding perfluoroalkylsulfur chloride tetrafluorides, R_fSF_4Cl, in good yields. However, small amounts of perfluoroalkylsulfur pentafluorides, R_fSF_5, are also obtained. A mixture of the *cis* and *trans* isomers of bis(trifluoromethyl)sulfur tetrafluoride and of trifluoromethyl pentafluoroethylsulfur tetrafluoride has been formed by the reaction of the corresponding bis(perfluoroalkyl) sulfides and chlorine monofluoride. The new perfluoroalkylsulfur chloride tetrafluorides are colorless, unpleasant smelling liquids. The infrared, mass and ^{19}F NMR spectral data, as well as thermodynamic and elementary analysis data, are given for the new compounds.

INTRODUCTION

In a recent study[1] in which the reaction of perfluorotetramethylene sulfide with chlorine monofluoride was investigated, the corresponding perfluorotetramethylenesulfur tetrafluoride as well as perfluorotetramethylenesulfur difluoride were formed depending upon the reaction conditions, showing the versatile oxidizing ability of chlorine monofluoride. Further syntheses of such perfluorocyclic derivatives of sulfur hexafluoride as perfluoro-1,3-dithietane octafluoride and perfluoro-1,4-dithiane octafluoride were similarly achieved by the oxidative

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fluorination of the respective perfluorocyclic sulfide. By using a reaction tempera-
ture of −78°, chlorine monofluoride fluorinated bis(perfluoroalkyl) sulfides to
bis(perfluoroalkyl)sulfur difluorides only (no tetrafluoride was formed) in high
yields[2]. It should be noted that no evidence was found for chlorination having
occurred with either the perfluorocyclic or bis(perfluoroalkyl) sulfides contrary
to our present report.

While trifluoromethylsulfur chloride tetrafluoride has been prepared by the
chlorination of trifluoromethylsulfur trifluoride with chlorine in the presence of
CsF at 25°, the percentage yield and full details of characterization have not been
published[3].

In this work, we wish to report the reaction of chlorine monofluoride as a
chlorinating and fluorinating or a fluorinating agent in synthesizing bis(perfluoro-
alkyl)sulfur chloride tetrafluorides from the corresponding perfluoroalkylsulfenyl
chlorides and bis(perfluoroalkyl) sulfides. Also, for the first time, it has been
possible to form both the *cis* and *trans* isomers of the bis(perfluoroalkyl)sulfur
tetrafluorides ($R_f SF_4 R_f'$; $R_f = R_f' = CF_3$, and $R_f = CF_3$, $R_f' = C_2F_5$) from the
respective bis(perfluoroalkyl) sulfides.

RESULTS AND DISCUSSION

At ambient temperature, the reaction of sulfur dichloride and chlorine
monofluoride resulted only in the formation of sulfur tetrafluoride, with no evi-
dence of compounds such as SF_4Cl_2. However, perfluoroalkylsulfenyl chloride,
$R_f SCl$, reacted easily with chlorine monofluoride to give stable perfluoroalkyl-
sulfur chloride tetrafluorides in yields ranging from 53–58%. Small amounts of
the corresponding perfluoroalkylsulfur pentafluorides were found among the
products. The reaction of bis(trifluoromethyl) disulfide with chlorine monofluoride
at 25° also resulted primarily in the formation of trifluoromethylsulfur chloride
tetrafluoride together with a trace of trifluoromethylsulfur pentafluoride. No
$CF_3SF_4SF_4CF_3$* was found which, considering the weak S–S bond (S–S stretch-
ing frequency assigned to a band at 536 cm^{-1} in the Raman spectrum) in
CF_3SSCF_3, is not surprising. When bis(pentafluoroethyl) disulfide was fluorinated,
an increase in the amount of the pentafluoroethylsulfur pentafluoride by-product
(17.1%) was accompanied by a concomitant decrease in the yield of pentafluoro-
ethylsulfur chloride tetrafluoride (25.4%). These new perfluoroalkylsulfur chloride
tetrafluorides, $R_f SF_4Cl$, ($R_f = C_2F_5$, n-C_3F_7, n-C_4F_9) are colorless liquids which
are stable at 25°, reactive towards mercury and which have boiling points 30–40°
higher than those of their $R_f SF_5$ analogues.

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* This compound was reportedly synthesized by the electrochemical fluorination of *S*-methylthio-
glycolic acid chloride, but not of dimethyl disulfide; J. A. YOUNG AND R. D. DRESDNER, *J. Org.
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While the fluorination of bis(perfluoroalkyl) sulfides with ClF at low temperature[2] gave the corresponding bis(perfluoroalkyl)sulfur difluorides in good yield, when the reaction was carried out at 25° for 12 h with a four-fold molar excess of ClF, hexavalent sulfur was obtained in the respective bis(perfluoroalkyl)-sulfur tetrafluorides.

The mass spectra of the perfluoroalkylsulfur chloride tetrafluorides showed such characteristic ions as $R_fSF_2^+$, R_fSF^+, R_fSCl^+, R_fS^+, SF_4Cl^+, SF_4^+, SF_3^+, SF_2^+ and SF^+ (Table 2). The ^{19}F NMR spectra of the perfluoroalkylsulfur chloride tetrafluorides and perfluoroalkylsulfur pentafluorides are shown in Table 4. The spectra of the R_fSF_4Cl compounds contained resonances in the expected regions and the chemical shifts of the equatorial fluorines bonded to the hexavalent sulfur lie in the range -102 to -111 MHz. These are shifted down-field from the analogous fluorines in R_fSF_5 probably due to the availability of empty d orbitals on the chlorine. As already reported for CF_3SF_4Cl[3], the high-resolution ^{19}F NMR spectrum of the $-SF_4-$ group of R_fSF_4Cl showed only a single well-resolved multiplet expected for only the *trans* isomer. The coupling constants of $-SF_4-$ of R_fSF_4Cl with the difluoromethylene group $[J(SF_4-CF_2)]$ decrease as the number of bonds separating the groups increases and show essentially the same magnitude as that found for R_fSF_5.

While the *trans* forms of $CF_3SF_4CF_3$ and $CF_3SF_4C_2F_5$ have been obtained *via* the electrochemical fluorination of the appropriate dialkyl sulfides[4-6], it has not been possible to prepare the *cis*-bis(perfluoroalkyl)sulfur tetrafluorides previously. Although we have not separated the isomeric mixtures, the ^{19}F NMR spectra (CFCl$_3$ as internal reference) of both $CF_3SF_4CF_3$ and $CF_3SF_4C_2F_5$ clearly confirm the synthesis of the *cis* and *trans* isomers (Table 5). The $A_2B_2X_6$ and A_4X_6 systems are well resolved particularly for the less complicated $CF_3SF_4CF_3$ isomers. The CF_3 groups which are easily assigned to the *cis* or *trans* position are centered at φ 63.5 and φ 64.8. The former is close to a pentet arising from two partially overlapping triplets, $J(CF-SF_{eq.}) = 17.0$ Hz and $J(CF-SF_{ax.}) = 17.7$ Hz. While the latter is a pentet, $J(CF-SF) = 22.9$ Hz.

For the *cis* isomer, the sulfur–fluorine region with two sets of triplets of heptets centered at φ -12.3 and φ -49.6 arise from the chemically non-equivalent axial and equatorial S–F fluorines. The coupling interaction between $SF_{ax.}$ and $SF_{eq.}$ is 93.6 Hz which accounts for the two triplets and, because of this rather large value, it is possible to clearly resolve the heptets arising from CF–SF couplings, $J(CF-SF_{ax.}) = 17.7$ Hz and $J(CF-SF_{eq.}) = 17.0$ Hz.

In the case of the *trans* isomer, the sulfur–fluorines, now chemically equiv-alent, are centered at φ -18.6 and are split by the six equivalent carbon–fluorines into a heptet, $J(CF-SF) = 22.9$ Hz. Based on the relative areas of the S–F resonance peaks, the *cis*:*trans* ratio is about $1:1.6$.

Trifluoromethyl pentafluoroethylsulfur tetrafluoride showed much more complex spectra, and the equatorial fluorines of the $-SF_4-$ group in the *cis* form

could not be detected partly because of its low concentration. By the integration of the trifluoromethyl group attached to hexavalent sulfur, the ratio of the *cis* to *trans* form is 1:1.9. The ^{19}F NMR spectrum of this compound is being studied further. Although the aliphatic perfluoroalkylsulfur tetrafluorides which were obtained by the electrochemical fluorination of the corresponding dialkyl sulfide have been shown to have a *trans* configuration[6] which is considered to be more stable thermodynamically, the perfluorocyclic derivatives of SF_6, such as perfluorotetramethylenesulfur tetrafluoride[7], perfluorothioxane tetrafluoride[6], perfluoro-1,3-dithictane octafluoride and perfluoro-1,4-thiane octafluoride[1] have a *cis* configuration.

The fluorination mechanism of chlorine monofluoride towards perfluoroalkyl sulfur compounds is not understood and our studies are continuing.

EXPERIMENTAL

Reagents

Trifluoromethylsulfenyl chloride was prepared by the methods described in the literature[8]. Perfluoroethylsulfenyl chloride, perfluoro-n-propylsulfenyl chloride and perfluoro-n-butylsulfenyl chloride were obtained by heating the corresponding bis(perfluoroalkyl) disulfide with Cl_2 at about 100°. Bis(perfluoroethyl) disulfide and bis(perfluoro-n-propyl) disulfide were prepared according to the literature from perfluoroethyl iodide, perfluoro-n-propyl iodide and sulfur, respectively[9]. Bis(perfluoro-n-butyl) disulfide was synthesized by the thermolysis of perfluorotetramethylenesulfur difluoride at 300°[1].

Photolysis of sulfenyl-carboxylic anhydrides $CF_3C(O)OSCF_3$ and $CF_3SOC(O)C_2F_5$ afforded the monosulfides CF_3SCF_3 and $CF_3SC_2F_5$[2], respectively, in essentially quantitative yields. All compounds which were to be fluorinated were purified by gas chromatography.

Chlorine monofluoride was purchased from Ozark–Mahoning Co..

Apparatus

A Monel Hoke cylinder (75 ml) with a stainless-steel valve was used for the fluorination reactions. A standard Pyrex vacuum line which was equipped with a Heise–Bourdon tube pressure gauge was used for handling the volatile liquids and gaseous materials.

Infrared spectra were taken using a Perkin–Elmer Model 457 infrared spectrometer with a 5 cm gas cell equipped with KBr windows. Spectra were calibrated against the known absorption bands in a polystyrene film. ^{19}F NMR spectra were determined with a Varian Model HA-100 spectrometer operating at 94.1 MHz using Freon 11 as the internal standard. Mass spectra were obtained using a Hitachi Perkin–Elmer Model RMU 6E mass spectrometer. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Reaction of bis(perfluoro-n-butyl) disulfide with Cl_2

In a 200 ml Pyrex bulb fitted with a Teflon stopcock, bis(perfluoro-n-butyl) disulfide (0.85 g) and Cl_2 (6 mmole) were condensed, and the reaction took place at 100° over a period of 8 h. Separation of the reaction mixture by trap-to-trap condensation resulted in the collection of the clear yellow liquid perfluoro-n-butylsulfenyl chloride at −78°. Further purification by gas chromatography using a column composed of 15% Fluolube grease GR-90 on Chromosorb P afforded perfluoro-n-butylsulfenyl chloride in a yield of 64.8%. This compound was characterized by infrared, mass and NMR spectra and elementary analysis (Tables 2, 3, 4 and 6).

TABLE 1

SUMMARY OF THE REACTIONS OF PERFLUOROALKYLSULFENYL CHLORIDES, BIS(PERFLUOROALKYL) DISULFIDES AND BIS(PERFLUOROALKYL) SULFIDES WITH CHLORINE MONOFLUORIDE AT 25° FOR 10 h

Reactant (mmole)	ClF (mmole)	Products (% yield)
CF_3SCl (5.0)	25	CF_3SF_4Cl (56.5); CF_3SF_3 (trace)
C_2F_5SCl (3.5)	15	$C_2F_5SF_4Cl$ (52.7); $C_2F_5SF_5$ (trace)
$n\text{-}C_3F_7SCl$ (5.5)	25	$n\text{-}C_3F_7SF_4Cl$ (54.0); $n\text{-}C_3F_7SF_5$ (2.4)
$n\text{-}C_4F_9SCl$ (4.1)	19	$n\text{-}C_4F_9SF_4Cl$ (57.6); $n\text{-}C_4F_9SF_5$ (5.2)
CF_3SSCF_3 (5.2)	44	CF_3SF_4Cl (76.8); CF_3SF_5 (trace)
$C_2F_5SSC_2F_5$(7.5)	68	$C_2F_5SF_4Cl$ (25.4); $C_2F_5SF_5$ (17.1)
$CF_3SC_2F_5$ (4.9)	23	$CF_3SF_4C_2F_5$ (12.6); $CF_3SF_2C_2F_5$ (9.6); CF_3SF_4Cl (13.4); $C_2F_5SF_4Cl$ (31.1)
CF_3SCF_3 (4.7)	21	$CF_3SF_4CF_3$ (42.8); CF_3SF_4Cl (24.8)

TABLE 2

MASS SPECTRA OF PERFLUOROALKYLSULFUR CHLORIDE TETRAFLUORIDES [a]

CF_3SF_4Cl: 143 SF_4Cl^{35+} (6.9), 139 $CF_3SF_2^+$ (5.6), 120 CF_3SF^+ (2.8), 108 SF_4^+ (2.3), 105 SF_2Cl^{35+} (8.2), 89 SF_3^+ (45.8), 70 SF_2^+ (30.6), 69 CF_3^+, SCl^{37+} (100), 67 SCl^{35+} (5.1), 63 CFS^+ (2.3), 51 SF^+ (10.1), 50 CF_2^+ (4.5), 44 SC^+ (25.5), 35 Cl^{35+} (5.4) 32 S^+ (8.3), 31 CF^+ (6.0).

$C_2F_5SF_4Cl$: 189 $C_2F_5SF_2^+$ (8.1), 170 $C_2F_5SF^+$ (1.3), 151 $C_2F_5S^+$ (0.9), 143 SF_4Cl^{35+} (4.2), 120 CF_4S^+ (2.8), 119 $C_2F_5^+$ (100.0), 105 SF_2Cl^{35+} (9.2), 101 CF_3S^+ (5.7), 100 $C_2F_4^+$ (4.3), 89 SF_3^+ (60.6), 70 SF_2^+ (23.8), 69 CF_3^+, SCl^{37+} (96.0), 67 SCl^{35+} (5.6), 63 CFS^+ (5.1), 51 SF^+ (10.0), 50 CF_2^+ (9.1), 44 SC^+ (7.6), 35 Cl^{35+} (4.4), 32 S^+ (17.2), 31 CF^+ (29.4).

$n\text{-}C_3F_7SF_4Cl$: 239 $C_3F_7SF_2^+$ (2.9), 220 $C_3F_7SF^+$ (0.7), 201 $C_3F_7S^+$ (0.5), 169 $C_3F_7^+$ (40.3), 143 SF_4Cl^{35+} (4.2), 119 $C_2F_5^+$ (7.1), 105 SF_2Cl^{35+} (5.5), 101 CF_3S^+ (3.1), 100 $C_2F_4^+$ (7.1), 89 SF_3^+ (34.4), 70 SF_2^+ (11.3), 69 CF_3^+, SCl^{37+} (100.0), 67 SCl^{35+} (1.7), 63 CFS^+ (2.5), 51 SF^+ (4.0), 50 CF_2^+ (3.6), 44 SC^+ (2.1), 35 S^{35+} (1.5), 32 S^+ (4.3), 31 CF^+ (12.6).

$n\text{-}C_4F_9SF_4Cl$: 289 $C_4F_9SF_2^+$ (2.1), 286 $C_4F_9SCl^{35+}$ (0.5), 270 $C_4F_9SF^+$ (0.4), 251 $C_4F_9S^+$ (0.3), 219 $C_4F_9^+$ (10.1), 169 $C_3F_7^+$ (1.1), 143 SF_4Cl^{35+} (2.4), 131 $C_3F_5^+$ (12.3), 119 $C_2F_5^+$ (8.3), 105 SF_2Cl^{35+} (2.6), 101 CF_3S^+ (3.1), 100 $C_2F_4^+$ (7.2), 89 SF_3^+ (21.8), 82 CF_2S^+ (1.2), 70 SF_2^+ (10.9), 69 CF_3^+, SCl^{37+} (100.0), 67 SCl^{35+} (2.5), 63 CFS^+ (2.4), 51 SF^+ (3.6), 50 CF_2^+ (2.3), 44 SC^+ (2.2), 35 Cl^{35+} (1.3), 32 S^+ (1.6), 31 CF^+ (8.6).

[a] In addition to the fragments which contain ^{35}Cl, ions containing ^{37}Cl were observed essentially in a ratio of 3:1.

TABLE 3

INFRARED SPECTRA OF PERFLUOROALKYLSULFUR CHLORIDE TETRAFLUORIDES AND PERFLUORO-n-BUTYLSULFENYL CHLORIDE

CF_3SF_4Cl: 1260 (vs), 1223 (w), 1166 (s), 1140–1120 (w), 872 (vs), 801–797 (s), 751 (w), 720 (w), 691 (vs), 656 (m), 487 (w).

$C_2F_5SF_4Cl$: 1342 (m), 1258 (vs), 1234 (vs), 1162 (s), 998 (m), 872 (vs), 773 (m), 697 (vs), 652 (m), 541 (w).

$n\text{-}C_3F_7SF_4Cl$: 1334 (s), 1300–1290 (m), 1270–1260 (vs), 1235–1220 (vs–s), 1160 (vs), 1110 (s), 1069 (w), 943 (w), 868 (vs), 762 (w), 700–688 (vs), 655 (m), 592 (ms), 540 (w), 483 (w).

$n\text{-}C_4F_9SF_4Cl$: 1353 (m), 1288 (w), 1260–1253 (vs), 1232 (vs), 1200 (w), 1160 (s), 1133 (w), 1033 (w), 1017 (w), 872 (vs), 815 (w), 780 (w), 752 (w), 721–692 (w–vs), 652 (w), 628 (m), 538 (w), 482 (w).

$n\text{-}C_4F_9SCl$: 1352 (m), 1253 (vs), 1222–1200 (s–w), 1152 (s), 1115 (m), 1040–980 (w), 890–820 (w), 805 (w), 755 (w), 739 (m), 700 (w), 560–530 (w).

TABLE 5

^{19}F NMR SPECTRA OF *cis*- AND *trans*-BIS(TRIFLUOROMETHYL)SULFUR TETRAFLUORIDE AND *cis*- AND *trans*-TRIFLUOROMETHYL PENTAFLUOROETHYLSULFUR TETRAFLUORIDE. (INTERNAL CCl_3F REFERENCE)

Compound	Chemical shift (MHz)					Coupling constant (Hz)
	CF_3S	CF_3C	CF_2	$SF_{ax.}$	$SF_{eq.}$	
trans-$CF_3SF_4CF_3$	64.8				—18.6	$J(CF_3–SF_{eq.}) = 22.9$
cis-$CF_3SF_4CF_3$	63.5			—12.3	—49.6	$J(CF_3–SF_{ax.}) = 17.7$ $J(CF_3\ SF_{eq.}) = 17.0$ $J(SF_{ax.}–SF_{eq.}) = 93.6$
trans-$CF_3SF_4CF_2CF_3$	64.9	81.0	97.9		—21.7	$J(CF_3–SF_{eq.}) = 23.1$ $J(CF_3S–CF_2) = 0.6$ $J(CF_3C–SF_{eq.}) = 8.9$ $J(CF_3C–CF_2) = 0.4$ $J(CF_2–SF_{eq.}) = 15.2$
cis-$CF_3SF_4C_2F_5$[a]	61.3	80.7	99.4	—16.6	?	$J(SF_{ax.}–SF_{eq.}) = 93$

[a] Analysis of this spectrum is under way.

TABLE 4

^{19}F NMR SPECTRA OF PERFLUOROALKYLSULFUR CHLORIDE TETRAFLUORIDES AND PERFLUOROALKYLSULFUR PENTAFLUORIDES. (INTERNAL CCl_3F REFERENCE)

Compound	Chemical shift, (MHz)						Coupling constant (Hz)
	CF_3	α-CF_2	β-CF_2	γ-CF_2	$SF_{eq.}$	$SF_{ax.}$	
CF_3SF_4Cl	65.5 (67.3)[a]				−102.6 (−102.1)[a]		$J(CF_3\text{–}SF_{eq.})$ = 22.4 (24)[a]
$C_2F_5SF_4Cl$	81.1	98.8			−109.5		$J(CF_2\text{–}SF_{eq.})$ = 14.3 $J(CF_3\text{–}SF_{eq.})$ = 8.8 $J(CF_3\text{–}CF_2)$ = 0.6
$n\text{-}C_3F_7\text{-}SF_4Cl$	81.2	94.2	127.0		−110.5		$J(CF_3\text{–}\alpha\text{–}CF_2)$ = 12.0 $J(\alpha\text{–}CF_2\text{–}SF_{eq.})$ = 15.6 $J(\beta\text{–}CF_2\text{–}SF_{eq.})$ = 13.3 $J(CF_3\text{–}SF_{eq.})$ = 1.0
$n\text{-}C_4F_9SF_4Cl$	81.4	93.4	123.1	125.6	−110.7		$J(\gamma\text{–}CF_2\text{–}\alpha\text{–}CF_2)$ = 18.0 $J(\alpha\text{–}CF_2\text{–}SF_{eq.})$ = 16.0 $J(\beta\text{–}CF_2\text{–}SF_{eq.})$ = 13.6 $J(\gamma\text{–}CF_2\text{–}SF_{eq.})$ = 0.8
CF_3SF_5	66.2				−37.0	−61.3	$J(CF_3\text{–}SF_{ax.})$ = 6.2 $J(CF_3\text{–}SF_{eq.})$ = 21.8 $J(SF_{eq.}\text{–}SF_{ax.})$ = 146
$C_2F_5SF_5$	81.5	99.8			−43.1	−62.5	$J(CF_3\text{–}SF_{eq.})$ = 9.0 $J(\alpha\text{–}CF_2\text{–}SF_{eq.})$ = 14.0 $J(\alpha\text{–}CF_2\text{–}SF_{ax.})$ = 4.7 $J(SF_{eq.}\text{–}SF_{ax.})$ = 146
$n\text{-}C_3F_7SF_5$	81.2	94.1	127.4		−44.4	−61.8	$J(CF_3\text{–}\alpha\text{–}CF_2)$ = 23.6 $J(CF_3\text{–}SF_{eq.})$ = 2.0 $J(\beta\text{–}CF_2\text{–}SF_{eq.})$ = 13.4 $J(SF_{eq.}\text{–}SF_{ax.})$ = 145
$n\text{-}C_4F_9SF_5$	81.5	92.5	123.6	125.7	−44.4	−60.3	$J(CF_3\text{–}\beta\text{–}CF_2)$ = 10.7 $J(CF_3\text{–}\alpha\text{–}CF_2)$ = 2.6 $J(\gamma\text{–}CF_2\text{–}\alpha\text{–}CF_2)$ = 18.0 $J(SF_{eq.}\text{–}SF_{ax.})$ = 144

[a] Reported value in parentheses; see ref. 3.

TABLE 6

ELEMENTAL ANALYSES AND THERMODYNAMIC DATA

	Elemental analysis (%)				B.p. (°C)	ΔH_v (kcal mole^{-1})	ΔS_v (e.u.)	$\log P \text{ (mmHg)} = X - Y/T(°K)$	
	C	S	F	Cl				X	Y
CF₃SF₄Cl[a]			60.8 (62.6)[b]		20.1	6.18	21.1	7.49	1352
C₂F₅SF₄Cl	8.99 (9.14)	12.22 (12.19)	65.6 (65.1)	13.52 (13.52)	50.7	6.85	21.2	7.50	1497
n-C₃F₇SF₄Cl	11.38 (11.52)	10.49 (10.24)	67.2 (66.9)	11.12 (11.36)	76.8	8.09	23.1	7.93	1768
n-C₄F₉SF₄Cl	13.14 (13.24)	8.85 (8.83)	68.4 (68.1)	9.73 (9.80)	100.0	8.88	23.8	8.08	1940
n-C₄F₉SCl	16.62 (16.75)	11.17 (11.17)	59.4 (59.7)	12.19 (12.39)	83.0	8.16	22.9	7.89	1783

[a] Molecular weight; Observed 211, Calcd. 212.5.
[b] Calculated values in parentheses.

General procedure of the fluorination of the perfluoroalkylsulfenyl chlorides with ClF

A typical example is the case of the fluorination of trifluoromethylsulfenyl chloride. Trifluoromethylsulfenyl chloride (0.68 g) and a four-fold excess of ClF (25 mmole) were condensed in a 75 ml Monel Hoke cylinder, and the reaction was carried out at 25° for 10 h.

Fractional condensation was used to remove the unreacted ClF, Cl_2 and the small amounts of low boiling by-products, such as CF_4, $CClF_3$, SF_4 and CF_3SF_5, using traps at -116, -131 and $-183°$. The trap at $-116°$ contained a clear liquid which was slightly contaminated with Cl_2. This was agitated in a small Pyrex tube which contained a small amount of 5A molecular sieves until the yellow color had disappeared. Further purification was conducted by gas chromatography using a column comprised of 20% Kel-F 3 oil on Chromosorb P. The yield of trifluoromethylsulfur chloride tetrafluoride was 56.5%.

The reaction conditions and yields used in the fluorinations of the other perfluoroalkylsulfenyl chlorides, including trifluoromethylsulfenyl chloride, are summarized in Table 1.

Fluorination of bis(perfluoroethyl) disulfide with ClF

Bis(perfluoroethyl) disulfide (1.5 g) was condensed in a Hoke cylinder followed by ClF in an excess of 1:8. After reacting at 25° for 10 h, the product mixture was condensed into a U-trap cooled at $-196°$, and trap-to-trap distillation was carried out using traps at -98, -116 and $-196°$. The first trap contained mainly $C_2F_5SF_4Cl$ and $C_2F_5SF_5$. In the second trap, mainly $C_2F_5SF_5$ and a trace of Cl_2 were found. The lowest boiling compounds which collected in the trap at $-196°$ were primarily Cl_2 and small amounts of C_2F_6, SF_4 and $C_2F_5SF_5$. The compounds in the first and second traps were subsequently separated by gas chromatography with a column of 15% Fluolube grease GR-90 on Chromosorb P. Thus, 1.0 g (25.4%) of $C_2F_5SF_4Cl$ and 0.63 g (17.1%) of $C_2F_5SF_5$ were obtained.

Fluorination of trifluoromethyl pentafluoroethyl sulfide with ClF

A reaction mixture of 1.1 g of trifluoromethyl pentafluoroethyl sulfide and 23 mmole of ClF in a 75 ml Monel Hoke cylinder was held at 25° for 10 h. The product was subjected to fractional condensation using consecutive U-traps immersed in baths at -116, -131 and $-183°$. Low boiling compounds in the traps at -131 and $-183°$ were CF_4, $CClF_3$, SF_6 and Cl_2. Gas chromatographic separation of the liquid product which was collected at $-116°$ employing a 6 mm × 5.1 m copper column packed with 20% Kel-F 3 oil on Chromosorb P yielded the following compounds: CF_3SF_4Cl (0.10 g), $CF_3SF_4C_2F_5$ (0.18 g), $CF_3SF_2C_2F_5$ (0.17 g), $C_2F_5SF_4Cl$ (0.40 g). The yield of $CF_3SF_4C_2F_5$ was 12.6%. Identification of these compounds was accomplished by infrared and ^{19}F NMR spectra. Further attempts were not made to separate the *cis* and *trans* isomers of $CF_3SF_4C_2F_5$.

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