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Free-Radical Reactions of Fluoroalkanesulfenyl Halides. 3.[1a] Reactions of Fluoroalkane- and Chlorofluoroalkanesulfenyl Chlorides with Hydrocarbons

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Free-radical reactions of several fluoroalkane- and chlorofluoroalkanesulfenyl chlorides with toluene, cyclohexane, and butane have been studied. The organic products obtained from these reactions include thiols, disulfides, sulfides, and chlorohydrocarbons. The relative yields of these products depend upon the structure of both the sulfenyl chloride and the hydrocarbon. Steric arguments are proposed to account for the results.

Following a long period of concentration upon the ionic reactions of sulfenyl halides,[3] recent years have seen the beginnings of interest in the free-radical chemistry of these materials. Free-radical additions to olefins have been demonstrated,[4,5] and reactions with hydrocarbons yielding disulfides, sulfides, and/or chlorohydrocarbons have also been reported.[1,6–10] In the previous paper of this series, free-radical chain reactions of CF$_3$SCl with several hydrocarbons containing alkane C–H bonds were found to yield trifluoromethyl hydrocarbyl sulfides, bis(trifluoromethyl) disulfide, and chlorohydrocarbons, the relative proportions depending upon the structure of the hydrocarbon.[1a] This paper presents the results of a study of the free-radical reactions of several fluoroalkane- and chlorofluoroalkanesulfenyl chlorides with hydrocarbons aimed at assessing the influence of the structure of the sulfenyl chloride upon the course of the reaction.

Results and Discussion

The sulfenyl chlorides studied were **1–6**. Photoinitiated reactions of each of these with excess cyclohexane, toluene, and *n*-butane were examined. The results of the reactions are tabulated in Tables I–III and are discussed below.

$$\begin{array}{ccc} (CF_3)_3CSCl & (CF_3)_2CFSCl & n\text{-}C_3F_7SCl \\ \mathbf{1} & \mathbf{2} & \mathbf{3} \end{array}$$

$$\begin{array}{ccc} HCF_2CF_2SCl & ClCF_2SCl & Cl_2CFSCl \\ \mathbf{4} & \mathbf{5} & \mathbf{6} \end{array}$$

The reactions examined yielded four types of organic compounds as major products: thiols, disulfides, sulfides, and chlorohydrocarbons—one, two, or three of which may predominate in a particular reaction, depending upon the structure of the sulfenyl chloride and the hydrocarbon.

$$R_fSCl + RH \xrightarrow{h\nu} R_fSH + R_fSSR_f + R_fSR + RCl + HCl \qquad (1)$$

In no case were all four obtained as major products.

The reactions of perfluoro-*tert*-butanesulfenyl chloride (**1**) as a group were unique in that the only major products detected were the thiol and the chlorohydrocarbon (eq 2). Thus from cyclohexane, perfluoro-*tert*-butanethiol (**7**) and chlorocyclohexane were obtained.

$$\underset{\mathbf{1}}{(CF_3)_3CSCl} + RH \xrightarrow{h\nu} \underset{\mathbf{7}}{(CF_3)_3CSH} + RCl \qquad (2)$$

In all three cases at most traces of HCl were noted during the irradiation period, and one to several trace unknowns were detected by gas chromatography (GC). In the reaction with

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Table I. Photoreactions of Fluoroalkanesulfenyl Chlorides with Cyclohexane

sulfenyl chloride[f]	g (mol)	cyclohexane, mL, g (mol)	mol ratio of hydrocarbon–sulfenyl chloride	sunlamp irradiation time, min	disulfide and/or thiol[h] (yield, %)	sulfide (S)[g] (yield, %)	chlorocyclohexane[n] (Cl) yield, %	ratio of sulfide yield to chloride yield (S/Cl)	other products	gas chromatography conditions
$(CF_3)_3$-CSCl, **1**	6.16 (0.0214)	13, 10 (0.120)	5.6	17	$(CF_3)_3CSH$ (100), **7**	0	100	0	2 trace unknowns detected by GC	6 ft 20% SE 30 on 60–80 mesh WAWDMCS, *T* = 125 °C
$(CF_3)_2$-CFSCl, **2**	15.16 (0.0641)	60, 46.7 (0.555)	8.7	30	$[(CF_3)_2CF]_2S_2$ (65)[i] $(CF_3)_2$-CFSH (?), **9**	$(CF_3)_2CFS$-c-C_6H_{11} (0.5), **11**	37.7	0.013		6 ft 20% fluoroalkyl pyromellitate on 60–80 mesh gas chromosorb R, *T* = 100 °C
n-C_3F_7SCl, **3**	22.5 (0.095)	50, 39.0 (0.463)	4.9	11	$(n\text{-}C_3F_7)_2S_2$ (85.7)[j]	*n*-C_3F_7S-c-C_6H_{11}[a] (14.3), **14**	43.2	0.33	1 trace unknown detected by GC	6 ft 20% fluoroalkyl pyromellitate on 60–80 mesh (NAW) FB, *T* = 100 °C
HCF_2CF_2-SCl, **4**	27.6 (0.164)	80, 62.3 (0.741)	4.5	8	$(HCF_2CF_2)_2S_2$ (72.3)[k]	HCF_2CF_2S-c-C_6H_{11}[b] (27.7), **18**	31.5	0.88		6 ft, 20% fluoroalkyl pyromellitate on 60–80 mesh (NAW) FB, *T* = 100 °C
$ClCF_2SCl$, **5**	15.0 (0.0981)	50, 39.0 (0.463)	4.7	4	$(ClCF_2)_2S_2$ (88.4)[l]	$ClCF_2S$-c-C_6H_{11}[c] (11.6), **22**	39.4	0.29	2 trace unknowns detected by GC	6 ft 20% fluoroalkyl pyromellitate on 60–80 mesh (NAW), FB, *T* = 100 °C
Cl_2CFSCl, **6**	15.0 (0.0885)	45, 35.1 (0.417)	4.7	12	$(Cl_2CF)_2S_2$[d,e] (97)[m]	Cl_2CFS-c-C_6H_{11} (3), **26**	63.6	0.047	4 unknowns totalling <2% of total product yield	6 ft 20% SE 30 on 60–80 mesh WAWDMCS, *T* = 50 °C

[a] A pure sample of this sulfide was isolated by distilling the reaction mixture to obtain a fraction boiling at 78–80 °C (37 mm) (90% sulfide), followed by preparative scale GC (6 ft 20% fluoroalkyl pyromellitate on 60–80 mesh (NAW) FB; T = 100 °C). [b] This sulfide was isolated by distillation of the reaction mixture through a small spinning band still. [c] A pure sample of this sulfide was isolated by distilling the reaction mixture to remove the excess cyclohexane, followed by preparative scale GC (4 ft 25% TFAPM on 60–80 mesh Gas Chromosorb R; T = 100 °C). [d] A search was made for thiol in the reaction mixture, but none was found. [e] Distillation of the reaction mixture through a small spinning-band still yielded bis(dichlorofluoromethyl) disulfide (70% isolated) distilling at 70.5–75 °C (13 mm); $n^{25}{}_D$ 1.5136–1.5164.[25] [f] Registry no.—**1**, 32308-83-1; **2**, 51031-50-6; **3**, 662-42-0; **4**, 813-37-6; **5**, 993-38-4; **6**, 2712-93-8. [g] Registry no.—**11**, 68408-99-1; **14**, 68409-00-7; **18**, 4675-77-8; **22**, 68409-01-8; **26**, 68409-02-9. [h] Registry no.—**7**, 32308-82-0; **9**, 68408-97-9. [i] Registry no. 754-62-1. [j] Registry no. 356-63-8. [k] Registry no. 68408-98-0; [l] Registry no. 692-58-0. [m] Registry no. 675-63-8. [n] Registry no. 542-18-7.

Table II. Photoreactions of Fluoroalkanesulfenyl Chlorides with Toluene

sulfenyl chloride	g (mol)	toluene, mL, g (mol)	mole ratio of toluene-sulfenyl chloride	sunlamp irradiation time	disulfide and/or thiol (yield, %)	sulfide (S)[d] (yield, %)	α-chlorotoluene[e] (Cl) yield, %	ratio of sulfide yield to chloride yield (S/Cl)	other products	gas chromatography conditions
$(CF_3)_3CSCl$, **1**	10.0 (0.0349)	50, 43.3 (0.47)	13.5	34 min	$(CF_3)_3CSH$ (100), **7**		100	0	3 trace unknowns detected by GC	6 ft 20% SE 30 on 60–80 mesh WAWDMCS, $T = 100$ °C
$(CF_3)_2CFSCl$ **2**	14.52 (0.0614)	50, 43.3 (0.47)	7.7	45 min	$(CF_3)_2CFSH$ + $[(CF_3)_2CF]_2S_2$ (96)	$(CF_3)_2CFSCH_2Ph$[a] (~4), **12**	100	0.04		4 ft 20% silicone gum nitrile XE 60 on 60–80 mesh gas Chromosorb R, $T = 150$ °C
n-C_3F_7SCl, **3**	30.37 (0.129)	80, 69.4 (0.753)	5.8	1 h, 18 min	$(n\text{-}C_3F_7)_2S_2$ (45.6)	n-$C_3F_7SCH_2Ph$[b] (54.4), **15**	34.3	1.59	2 trace unknowns detected by GC	6 ft 20% fluoroalkyl pyromellitate on 60–80 mesh firebrick, $T = 100$ °C
HCF_2CF_2SCl, **4**	21.13 (0.125)	75, 65.0 (0.706)	5.6	1.75 h	$(HCF_2CF_2)_2S_2$ (13.1)	$HCF_2CF_2SCH_2Ph$[b] (86.9), **19**	4.6	18.9		6 ft 20% diglyceride of ω-trifluorohexanoic acid on 60–80 mesh gas Chromosorb R, $T = 125$ °C
$ClCF_2SCl$, **5**	17.0 (0.111)	60, 52.0 (0.565)	5.1	49 min	$(ClCF_2)_2S_2$[c] (35.0)	$ClCF_2SCH_2Ph$[b] (65.0), **23**	19.4	3.35		6 ft 20% fluoroalkyl pyromellitate on 60–80 mesh gas Chromosorb R, $T = 100$ °C
Cl_2CFSCl, **6**	12.99 (0.0766)	50, 43.3 (0.470)	6.1	1 h	$(Cl_2CF)_2S_2$[c] (75.8)	Cl_2CFSCH_2Ph[b] (24.2), **27**	58.4	0.41	2 trace unknowns detected by GC	4 ft 20% silicone gum nitrile XE 60 on 60–80 mesh gas Chromosorb R, $T = 180$ °C

[a] Distillation of the reaction mixture yielded a fraction distilling at 79 °C (26 mm) from which this compound was isolated by preparative scale GC. The structure was confirmed by mass spectra. [b] A pure sample of this material was isolated by distillation of the reaction mixture through a small spinning band still. [c] A search was made for thiol in the reaction mixture, but none was found. [d] Registry no.—**12**, 68409-03-0; **15**, 68409-04-1; **19**, 68409-05-2; **23**, 68409-06-3; **24**, 68409-07-4. [e] Registry no. 100-44-7.

n-butane, 2-chlorobutane was the only chloroalkane obtained in substantial amount; just traces of 1-chlorobutane were detected. This suggests a very high selectivity for the hydrogen-abstracting species in this reaction, i.e., the perfluoro-*tert*-butanethiyl radical. Perfluoro-*tert*-butanethiol (**7**), which has been reported previously,[11] was converted to a sulfide **8** by UV irradiation with 1-butene.

$$\underset{\mathbf{7}}{(CF_3)_3CSH} + CH_2{=}CHC_2H_5 \xrightarrow{h\nu} \underset{\mathbf{8}}{(CF_3)_3CSC_4H_9\text{-}n} \quad (3)$$

The reactions of heptafluoro-2-propanesulfenyl chloride (**2**) gave high yields of chlorohydrocarbons, varying yields of thiol, i.e., heptafluoro-2-propanethiol (**9**) and disulfide, and low yields of heptafluoroisopropyl hydrocarbyl sulfides.

$$\underset{\mathbf{2}}{(CF_3)_2CFSCl} + RH \xrightarrow{h\nu} \underset{\mathbf{9}}{(CF_3)_2CFSH} + [(CF_3)_2CF]_2S_2 + RCl + (CF_3)_2CFSR + HCl \quad (4)$$

While the sums of the thiol and the disulfide yields in these reactions were high, the yield of the thiol alone varied from a few percent to probably over 90% depending upon the hydrocarbon:[13] n-butane < cyclohexane < toluene. A pure sample of the thiol **9** was not isolated, but its identity was established by IR and NMR spectra and by its photoinitiated addition to 1-butene which yielded heptafluoroisopropyl n-butyl sulfide (**10**).[14]

The results of the reactions of sulfenyl chlorides **3**, **4**, **5**, and **6** with the three hydrocarbons were similar to the results of the analogous reactions of CF_3SCl reported previously in that sulfides, disulfides, and chlorohydrocarbons were obtained as the organic products (eq 5).[1] The relative yields of these products varied appreciably from reaction to reaction (Tables I, II, and III).

$$R_fSCl + RH \xrightarrow{h\nu} R_fSR + R_fSSR_f + RCl + HCl \quad (5)$$

Several of the reaction mixtures were examined for thiol, but none was found. GC did, however, show the presence of trace unknowns in several cases. In the reactions of dichlorofluoromethanesulfenyl chloride (**6**) with cyclohexane and n-butane, the yields of sulfides were just a few percent; thus, as Kloosterziel has previously reported for the reaction of dichlorofluoromethanesulfenyl chloride (**6**) with cyclohexane, these reactions are essentially chlorination reactions.[7]

In general, these reactions appear to be chain reactions of long kinetic chain length. The variations in the yields of the products can be rationalized on a steric basis in terms of the steps of reaction Scheme I.[1,6,9] Step a is the photolysis of the sulfenyl chloride to a thiyl radical and a chlorine atom, both of which abstract aliphatic hydrogen from the hydrocarbon to produce alkyl radicals, HCl, and thiol (steps b and c). In step d, the thiol produced in c may react with sulfenyl chloride to give disulfide by an ionic process which does not interfere with the kinetic chain of the free-radical sequence. The sulfenyl chloride is attacked by the alkyl radical at chlorine (step e) to produce an alkyl

Scheme I

$$R_fSCl \xrightarrow{h\nu} R_fS\cdot + Cl\cdot \quad (a)$$

$$Cl\cdot + RH \rightarrow R\cdot + HCl \quad (b)$$

$$R_fS\cdot + RH \rightarrow R_fSH + R\cdot \quad (c)$$

$$R_fSCl + R_fSH \rightarrow R_fSSR_f + HCl \quad (d)$$

$$R\cdot + R_fSCl \rightarrow RCl + R_fS\cdot \quad (e)$$

$$R\cdot + R_fSCl \rightarrow R_fSR + Cl\cdot \quad (f)$$

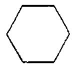
$$R\cdot + R_fSSR_f \rightarrow R_fSR + R_fS\cdot \quad (g)$$

Table III. Photoreactions of Fluoroalkanesulfenyl Chlorides with *n*-Butane

sulfenyl chloride	g (mol)	*n*-butane, mL/−76 °C, g (mol)	mole ratio of *n*-butane sulfenyl chloride	lamp (irradiation time)	disulfide and/or thiol (yield, %)	products from $CH_3CH_2CH_2CH_2$-		products from $CH_3CH_2CH(CH_3)$-		reactivity ratio secondary to primary H	other products	gas chromatography conditions
						structure[d] (yield, %)	ratio of sulfide to chloride	structure[f] (yield, %)	ratio of sulfide to chloride			
$(CF_3)_3CSCl$, **1**	3.51 (0.0122)	13, 10.4 (0.179)	14.7	sunlamp (27 min)	$(CF_3)_3CSH$ (100), **7**	$CH_3CH_2CH_2CH_2Cl$ (trace)		$CH_3CHClCH_2CH_3$[g] (100)		>100	several unknowns in trace or very low yields were detected by GC	6 ft 20% SE 30 on 60–80 mesh WAWDMCS, $T = 50$ °C
$(CF_3)_2CFSCl$ **2**	17.53 (0.0741)	30, 24.0 (0.413)	5.6	sunlamp (1.25 h)	$[(CF_3)_2CF]_2S_2$, (96)	$(CF_3)_2CFSC_4H_9$-*n* (0.5), **10**	0.09	$(CF_3)_2CFSCH(CH_3)C_2H_5$, (0.4), **13**	0.015	6.5		4 ft 20% silicone gum nitrile XE 60 on 60–80 mesh gas Chromosorb R, $T = 35$ °C
					$(CF_3)_2CFSH$ (4), **9**	*n*-C_4H_9Cl (5.9)[e]		$CH_3CHClC_2H_5$ (27.2)				6 ft 20% diglyceride of ω-trifluorohexanoic acid on 60–80 mesh gas Chromosorb R, $T = 73$ °C
n-C_3F_7SCl, **3**	35.15 (0.149)	65, 52.0 (0.895)	6.0	sunlamp (1.5 h)	$(n\text{-}C_3F_7)_2S_2$ (79.8)	*n*-$C_3F_7SC_4H_9$-*n*[a] (8.6), **16** *n*-C_4H_9Cl (5.3)	1.62	*n*-$C_3F_7SCH(CH_3)C_2H_5$[a] (11.6), **17** $CH_3CHClC_2H_5$ (30.8)	0.376	4.6	2 trace unknowns detected by GC	6 ft 20% fluoroalkyl pyromelittate on 60–80 mesh firebrick, $T =$ 75 °C
HCF_2CF_2SCl, **4**	30.5 (0.181)	55, 44.0 (0.76)	4.2	low pressure mercury resonance lamp (4.5 h)	$(HCF_2CF_2)_2S_2$ (54.1)	$HCF_2CF_2SC_4H_9$-*n*[b] (9.2), **20** *n*-C_4H_9Cl (2.1)	4.37	$HCF_2CF_2SCH(CH_3)C_2H_5$[b] (36.7), **21** $CH_3CHClC_2H_5$ (15.6)	2.35	7.0		6 ft 20% diglyceride of ω-trifluorohexanoic acid on 60–80 mesh gas Chromosorb R, $T = 74$ °C
$ClCF_2SCl$, **5**	27.0 (0.176)	60, 48.0 (0.826)	4.7	sunlamp (46 min)	$(ClCF_2)_2S_2$ (80.3)	$ClCF_2SC_4H_9$-*n*[c] (7.0), **24** *n*-C_4H_9Cl (2.8)	2.5	$ClCF_2SCH(CH_3)C_2H_5$[c] (12.7), **25** $CH_3CHClC_2H_5$ (21.8)	0.582	5.3		6 ft 20% diglyceride of ω-trifluorohexanoic acid on 6080 mesh gas Chromosorb R, $T = 74$ °C
Cl_2CFSCl, **6**	10.0 (0.059)	25, 20.0 (0.344)	5.8	sunlamp (15 min)	$(Cl_2CF)_2S_2$ (92.4)	$Cl_2CFSC_4H_9$-*n* (2.3), **28** *n*-C_4H_9Cl (8.5)	0.27	$Cl_2CFSCH(CH_3)C_2H_5$ (2.3), **29** $CH_3CHClC_2H_5$ (56.6)	0.041	8.2	3 trace unknowns detected by GC	6 ft 20% SE 30 on 60–80 mesh WAWDMCS, $T_1 = 50$ °C, $T_2 = 150$ °C (10 °C/min)

[a] Samples of the two sulfides were isolated by distillation of the reaction mixture to remove the excess *n*-butane and the chlorobutanes, followed by preparative scale GC on the residue (4 ft 25% diglyceride of ω-trifluorohexanoic acid on 60–80 mesh gas Chromosorb R; $T = 65$ °C). [b] Samples of the two sulfides were isolated by distillation of the reaction mixture to remove the excess *n*-butane followed by preparative scale GC on the residue as follows: a 4 ft 25% diglyceride of ω-trifluorohexanoic acid on 60–80 mesh gas Chromosorb R column ($T = 75$ °C) was used to separate the disulfide and **20** from **21**. Then a 4 ft 25% silicone-200 on "Distoport S" column ($T = 50$ °C) was used to separate **20** from the disulfide. [c] Exactly like footnote *a* except $T = 100$ °C. [d] Registry no.—**10**, 68409-08-5; **16**, 68409-09-6; **20**, 68409-10-9; **24**, 15520-08-8; **28**, 68409-11-0. [e] Registry no. 109-69-3. [f] Registry no.—**13**, 68409-12-1; **17**, 68409-13-2; **21**, 68409-14-3; **25**, 15520-09-9; **29**, 68409-15-4. [g] Registry no. 78-86-4.

Table IV. Ratio (S/Cl) of Attack by Radicals on the Sulfur vs. the Chlorine of Fluoroalkane- and Chlorofluoroalkanesulfenyl Chlorides

sulfenyl chloride	$C_6H_5CH_2\cdot$	n-$C_4H_9\cdot$	$CH_3\dot{C}HC_2H_5$	
CF_3SCl[1]	23.3	12	3.8	1.59
HCF_2CF_2SCl	18.9	4.37	2.35	0.88
n-C_3F_7SCl	1.58	1.62	0.38	0.33
$(CF_3)_2CFSCl$	0.04	0.09	0.015	0.013
$(CF_3)_3CSCl$	0	0	0	0
CF_3SCl	23.3	12	3.8	1.59
$ClCF_2SCl$	3.35	2.5	0.58	0.29
Cl_2CFSCl	0.42	0.27	0.041	0.047
Cl_3CSCl		0[a]	0[a]	

[a] Reactions of Cl_3CSCl were not examined in this study. However, Kloosterziel has reported that the radical reaction of this material with n-butane produces only butyl chlorides, disulfide, and HCl.[8]

chloride and a thiyl radical which re-enters the chain, and/or at the sulfur atom (step f) to give a molecule of sulfide and a chlorine atom which also re-enters the chain. As an alternative to step f for producing sulfide, step g, the reaction of the alkyl radical with disulfide, seems attractive, especially in those cases where disulfide is a major product. However, as a subsequent publication will show, this step is apparently not important, at least in reactions involving perfluoroalkanesulfenyl chlorides. Steps a–f thus afford a mechanism whereby the products detected in the reactions described in this paper are produced by a chain process.

Steps e and f represent options which a radical has in its reactions with an S–Cl function, and the work published to date offers examples in which each of these modes of attack occurs exclusively. For example, in the reaction of cyclohexyl radicals with SCl_2, it appears that attack occurs only on sulfur,[15] while in reactions with Cl_3CSCl, alkyl radical attack occurs only on the chlorine atom attached to sulfur.[8] In the group of reactions examined in this study, only the latter of these two extremes was encountered; in most cases attack appears to be occurring at both sites. From a strictly steric point of view, it should be easier for a radical to abstract the chlorine atom, i.e., a terminal atom of a sulfenyl chloride (step e), than to attack the sulfur atom (step f) which is more crowded. The operation of such a steric preference is evident when one compares the relative amounts of sulfide and chloride produced by the reactions of the same radical with a series of sulfenyl chlorides in which the crowding about the sulfur atom differs by virtue of the bulkiness of the R_f group. For example, in Table IV it is seen that the ratio of attack by the benzyl radical on the sulfur vs. the chlorine (S/Cl) decreases as the bulk of the R_f group in a series of fluoroalkanesulfenyl chlorides is increased: relative bulk, $CF_3 < HCF_2CF_2 < n\text{-}C_3F_7 < (CF_3)_2CF < (CF_3)_3C$. This same trend is obvious for all of the radicals tabulated in Table IV. The crowding is so severe in the reactions of perfluoro-*tert*-butanesulfenyl chloride (1) that no detectable attack on the sulfur atom by any of the hydrocarbon radicals examined in this study occurs. An analogous trend is evident in the series of halogenated methanesulfenyl chlorides examined; as the size of the group attached to sulfur increases by virtue of successive substitution of fluorine by chlorine, the S/Cl ratio decreases: relative bulk, $CF_3 < ClCF_2 < Cl_2CF < Cl_3C$.

Another steric trend is obvious by comparing the ratios in Table IV for all four radicals with a specific sulfenyl chloride. In all cases but two, the benzyl radical, a primary radical, shows the highest preference for attack on sulfur.[16,17] The next highest preference for the sulfur atom is exhibited by the n-butyl radical, also a primary radical. Of the two secondary radicals examined, the *sec*-butyl radical generally shows a higher order of preference for the sulfur atom than the cyclohexyl radical. Here again, a steric effect is evident: The less bulky primary radicals exhibit a greater preference for the less accessible sulfur atom than do the more bulky secondary radicals.

Steric effects may also be responsible for the absence of disulfide in the reactions of perfluoro-*tert*-butanesulfenyl chloride (1) and the low yield production of disulfide in some of the reactions of heptafluoro-2-propanesulfenyl chloride (2). In these cases, step c of Scheme I, the formation of thiol, obviously occurs, but the subsequent reaction of the thiol with the sulfenyl chloride to give disulfide (step d), which is ordinarly a rapid reaction, must be appreciably slower than the comparable reactions with the other sulfenyl chlorides investigated in this study. In all of the reactions of perfluoro-*tert*-butanesulfenyl chloride (1) examined, step d is so slow that all of the sulfenyl chloride is consumed before any detectable disulfide is made. This sluggishness in step d is no doubt due to the presence of the bulky perfluoro-*tert*-butyl group in both the sulfenyl chloride and thiol. Thus, the fact that in the reactions of perfluoro-*tert*-butanesulfenyl chloride (1) thiol and chloroalkane are obtained, but neither disulfide nor sulfide, can be understood entirely in steric terms. These steric effects are apparently also operating in the reactions of heptafluoro-2-propanesulfenyl chloride (2) but to a lesser degree.

Experimental Details

I. Irradiation Experiments. A stirred solution of the sulfenyl chloride dissolved in excess hydrocarbon contained in a quartz tube (9 in. × 1.5 in.) was irradiated under nitrogen with a sunlamp, or infrequently with a low pressure mercury resonance lamp, until the characteristic color of the sulfenyl chloride was gone or until there was no further color change and the evolution of gas ceased. The reaction mixture was then analyzed by GC, and principal products were identified by: (1) comparison of retention times with materials of known structure; (2) mass spectra examination of peaks in the gas chromatogram; or (3) isolation by distillation or preparative scale GC followed by elemental analysis and proton NMR analysis. In most cases, procedure (3) was used. The details of the experiments are tabulated in Tables I, II, and III. Characterization of the new sulfides which were isolated is given in Tables V and VI. Those sulfides which were not isolated in quantity were identified by mass spectra. Descriptions of experiments in which the procedure differed markedly from that just given follow.

A. Perfluoro-*tert*-butanesulfenyl Chloride (1) and Cyclohexane. A mixture of 6.13 g (0.0214 M) of perfluoro-*tert*-butanesulfenyl chloride (1) and 13 mL (9.9 g, 0.120 M) of "spectrograde" cyclohexane was irradiated with a sunlamp until colorless (17 min). During this period only trace HCl evolution was detected. A gas chromatogram contained two major product peaks (51 and 49% of the total product peak area), the later of which matched chlorocyclohexane in retention time. The other peak corresponded to perfluoro-*tert*-butanethiol (7). In addition, trace peaks for the starting sulfenyl chloride and two unknown materials were evident. Distillation of the reaction mixture through a small Vigreux still gave a fraction boiling at 49–50 °C which solidified on cooling to a soft, volatile crystalline solid. Elemental analysis showed that this fraction contained 69.2 mol % of thiol 7. A pure sample of the colorless, waxy, volatile, solid thiol was obtained by preparative scale GC (6 ft, 25% Fluorosilicone 1265 on 45–60 mesh Gas Chromasorb R, T = 60 °C):[11] IR 3.82 μm (SH), 7.85 (CF); ^{1}H NMR δ 2.81 (s).

Anal. Calcd for C_4HF_9S: F, 67.7; S, 12.7. Found: F, 67.3, 67.1; S, 13.4.

B. Perfluoro-*tert*-butanesulfenyl Chloride (1) and *n*-Butane. A mixture of 14.5 g (0.0506 M) of perfluoro-*tert*-butanesulfenyl chloride (1) and 36 mL (29 g, 0.49 M) of liquid (at −76 °C) n-butane was irradiated as described above for 5 h and 55 min.[18] The dry ice condenser was allowed to warm to room temperature as the excess n-butane distilled away. A GC analysis showed that the residue contained perfluoro-*tert*-butanethiol (7) and 2-chlorobutane as major products. The condenser was refilled with dry ice, 10 mL of liquid (at −76 °C) 1-butene was added to the reactor, and the mixture was then

Table V. Properties of Fluoroalkyl Sulfides

compd	bp, °C	n_D (°C)	molecular formula
$(CF_3)_3CSC_4H_9$-*n*,[a] **8**	78 (104 mm)	1.3538 (24)	$C_8H_9F_9S$
$(CF_3)_2CFSC_4H_9$-*n*,[b] **10**	128.5–130		$C_7H_9F_7S$
n-$C_3F_7SCH_2Ph$,[a] **15**	76–77 (13 mm)	1.4253–1.4270 (25)	$C_{10}H_7F_7S$
n-C_3F_7S-c-C_6H_{11},[a] **14**	66.5 (17 mm)	1.3863 (25)	$C_9H_{11}F_7S$
n-$C_3F_7SC_4H_9$-*n*,[a] **16**	127	1.3491 (25)	$C_7H_9F_7S$
n-$C_3F_7SCH(CH_3)C_2H_5$,[a] **17**	120	1.3481 (25)	$C_7H_9F_7S$
$HCF_2CF_2SCH_2Ph$,[a] **19**	86–88 (12 mm)	1.4741–1.4749 (24)	$C_9H_8F_4S$
HCF_2CF_2S-c-C_6H_{11},[a] **18**	64–65 (13 mm)	1.4243–1.4248 (24)	$C_8H_{12}F_4S$
$HCF_2CF_2SCH(CH_3)C_2H_5$,[a] **21**	127.5	1.3829 (24.5)	$C_6H_{10}F_4S$
$HCF_2CF_2SC_4H_9$-*n*,[a] **20**	135.5	1.3832 (24.5)	$C_6H_{10}F_4S$
$ClCF_2SCH_2Ph$,[a] **23**	87.5 (13 mm)	1.5088 (25)	$C_8H_7ClF_2S$
$ClCF_2S$-c-C_6H_{11},[a] **22**	100 (51 mm)	1.4578 (25)	$C_7H_{11}ClF_2S$
$ClCF_2SCH(CH_3)C_2H_5$,[a] **25**	128	1.4148 (25)	$C_5H_9ClF_2S$
$ClCF_2SC_4H_9$-*n*,[a] **24**	130	1.4160 (25)	$C_5H_9ClF_2S$
Cl_2CFSCH_2Ph,[a] **27**	64 (30 mm)	1.5459 (25)	$C_8H_7Cl_2FS$

[a] Satisfactory combustion analytical data (C, H, F, S ± 0.4%) were reported for these compounds. [b] Calcd: C, 32.6; H, 3.5; F, 51.4. Found: C, 33.6, 33.4; H, 3.8, 3.7; F, 50.5, 50.5.

Table VI. ^{1}H NMR Resonances for Fluoroalkyl Sulfides [a]

compd	chemical shift, δ (coupling constants Hz)
8	1.02 (3 H, m, CH_3), 1.57 (4 H, m, CH_2CH_2), 2.97 (2 H, m, CH_2S)
10	1.00 (3 H, m, CH_3), 1.57 (4 H, m, CH_2CH_2), 2.93 (2 H, m, CH_2S)
12	4.13 (2 H, s, CH_2), 7.37 (5 H, s, C_6H_5)
15	4.17 (2 H, s, CH_2), 7.32 (5 H, s, C_6H_5)
16	1.03 (3 H, m, CH_3), 1.58 (4 H, m, CH_2CH_2), 2.93 (2 H, m, CH_2S)
17	1.03 (3 H, t, J = 6.4, CH_3), 1.43 (3 H, d, J = 6.8, CH_3), 1.64 (2 H, q, J = 6.4, CH_2), 3.39 (1 H, q, J = 6.8, CH)
19	4.13 (2 H, s, CH_2), 5.74 (1 H, t, t, J_1 = 55, J_2 = 3, HCF_2CF_2), 7.38 (5 H, s, C_6H_5)
20	1.03 (3 H, m, CH_3), 1.60 (4 H, m, CH_2CH_2), 2.90 (2 H, m, CH_2S), 5.80 (1 H, t, t, J_1 = 54, J_2 = 3, HCF_2CF_2)
21	1.03 (3 H, t, J = 6.8, CH_3), 1.42 (3 H, d, J = 6.8, CH_3), 1.63 (2 H, q, J = 6.8, CH_2), 3.33 (1H, q, J = 6.8, CH), 5.68 (1 H, t, t, J_1 = 54, J_2 = 3, HCF_2CF_2)
23	4.11 (2 H, s, CH_2), 7.27 (5 H, s, C_6H_5)
24	1.02 (3 H, m, CH_3), 1.58 (4 H, m, CH_2CH_2), 2.94 (2 H, m, CH_2S)
25	1.03 (3 H, t, J = 6.5, CH_3), 1.41 (3 H, d, J = 6.5, CH_3), 1.62 (2 H, q, J = 6.5, CH_2), 3.29 (1 H, q, J = 6.5, CH)
27	4.22 (2 H, s, CH_2), 7.32 (5 H, s, C_6H_5)

[a] These spectra (60 M Hz) were obtained with an A-60 spectrometer manufactured by Varian Associates, Palo Alto, Calif., using 10% solutions in CCl_4 containing tetramethylsilane.

irradiated with a low pressure mercury resonance lamp for 2.75 h. GC now showed that the mixture no longer contained thiol 7. Distillation through a small spinning band still gave perfluoro-*tert*-butyl *n*-butyl sulfide (**8**) as a colorless liquid distilling at 78 °C (104 mm).

C. Heptafluoro-2-propanesulfenyl Chloride (2) and Toluene. A mixture of 50 mL (43 g, 0.47 M) of reagent grade toluene and 14.52 g (0.0614 M) of heptafluoro-2-propanesulfenyl chloride (**2**) was irradiated until colorless. Very little HCl evolution was detected during the irradiation period. A gas chromatogram contained a large peak (52.5% of the total product peak area) for *α*-chlorotoluene, a 5% unknown peak, and an early peak (42.5%) which was not reproducible in area and which apparently represented both bis(heptafluoroisopropyl) disulfide and heptafluoro-2-propanethiol (**9**). Further GC studies showed that the disulfide component of this peak was small.

About two-thirds of the reaction mixture was distilled through an 18 in. spinning band still connected via two dry-ice traps to a water pump. While the pressure was maintained at 100–200 mm, the flask was gently heated until the mixture began to reflux. There collected in the first dry-ice trap 1.5–2.0 mL of liquid, which on distillation through a microstill gave about 1 mL of colorless liquid boiling at 28 °C. The infrared and ^{1}H and ^{19}F NMR spectra indicated that it was largely heptafluoro-2-propanethiol (**9**): IR 3.85 *μ*m (SH), 7.73, 8.08 (CF); ^{1}H NMR δ 3.06 (d, q); ^{19}F NMR −77.03 (CF_3), −147.07 ppm (CF), J_{CF-H} = 5.3 Hz, J_{CF_3-H} = 1.5 Hz, J_{CF_3-F} = 9.5 Hz. The residue remaining after removal of the thiol was shown by GC to contain just a trace of bis(heptafluoroisopropyl) disulfide.

The remaining one-third of the reaction mixture was treated in the manner just described and the 1.5 mL of liquid which collected in the first dry-ice trap was transferred under vacuum to a quartz UV reactor (10 in. × $^{11}/_{16}$ in.) fitted with a dry-ice condenser. Four milliliters of liquid 1-butene was added and the resulting mixture was irradiated with a low pressure mercury resonance lamp for 1.5 h. After the excess 1-butene had been removed by warming, the residue (2.54 g) was shown by GC to contain about 90% of a single material. Distillation through a microstill yielded heptafluoroisopropyl *n*-butyl sulfide (**10**) (95% pure) distilling at 128.5–130 °C.

A mass spectrogram (C.E.C. 21-03 mass spectrometer, 70 eV) of a sample of the 5% unknown peak isolated by preparative scale GC showed that it was heptafluoroisopropyl benzyl sulfide (**12**). Thus the spectrum contains a parent ion (6%) at *m/e* 292 and a series of ions logically derived from it.

D. Heptafluoro-2-propanesulfenyl Chloride (2) and Cyclohexane. A solution of 15.16 g (0.0641 M) of freshly distilled heptafluoro-2-propanesulfenyl chloride (**2**) and 60 mL (0.555 M) of "Spectrograde" cyclohexane was irradiated as described above until the yellow color was gone (30 min). A gas chromatogram contained substantial peaks with the retention times of bis(heptafluoroisopropyl) disulfide [plus heptafluoro-2-propanethiol (**9**)], chlorocyclohexane, and a very small unknown peak. The thiol was removed as described in the preceding experiment. A GC on the residue contained major peaks for bis(heptafluoroisopropyl) disulfide and chlorocyclohexane and the small unknown peak whose size was about 3% of the size of the chlorocyclohexane peak. A mass spectrogram (Bendix TOF Model 12 mass spectrometer, 70 eV) of the small unknown peak contained a parent ion at *m/e* 284, an ion at *m/e* 215 (284 −CF_3), the most abundant ion at *m/e* 83 (cyclohexyl), and several other ions derived from fragmentation of the cyclohexyl group, thus confirming that the small yield product was heptafluoroisopropyl cyclohexyl sulfide (**11**).

E. Heptafluoro-2-propanesulfenyl Chloride (2) and *n*-Butane. A mixture of 21.8 g (0.092 M) of heptafluoro-2-propanesulfenyl chloride (**2**) and 32 mL (26 g, 0.44 M) of liquid (at −76 °C) *n*-butane was irradiated as described above for 1 h after which the mixture was colorless. The excess *n*-butane was removed from the reaction mixture by distillation through a low-temperature still. A GC analysis showed that the major products were the disulfide and the two chlorobutanes. In addition, two very small peaks were observed which mass spectra (Bendix TOF Model 12 spectrometer, 70 eV) showed were heptafluoroisopropyl butyl sulfides. Each mass spectrogram contained a parent ion at *m/e* 258. The GC retention time of one of the isomers matched that of heptafluoroisopropyl *n*-butyl sulfide (**10**), and the other was therefore heptafluoroisopropyl *sec*-butyl sulfide (**13**). These assignments were confirmed by comparison of the mass spectrograms with those of authentic samples of the corresponding trifluoromethyl sulfides, i.e., $CF_3SC_4H_9$-*n* and $CF_3SCH(CH_3)C_2H_5$.[1]

Distillation of the reaction mixture to isolate a thiol fraction, followed by addition of 1-butene to the distillate and UV irradiation as described in the two preceeding experiments, showed that little thiol remained at the end of the irradiation. GC analyses on appropriate fractions led to the estimates of thiol and disulfide yields given in Table III.

II. Mass Spectra Identification of Dichlorofluoromethyl Sulfides (Du Pont Model 21-490 Mass Spectrometer (70 eV) Interfaced to a Varian Model 144 Gas Chromatograph). A. Dichlorofluoromethyl Butyl Sulfides (28 and 29). These structures were assigned to the low yield products seen by GC (~2% each) from the reaction of dichlorofluoromethanesulfenyl chloride (**6**) and *n*-butane. Each pattern contained parent ions at *m/e* 190 (most intense parent ion), 192, and 194.

B. *Dichlorofluoromethyl* Cyclohexyl Sulfide (26). This structure was assigned to the low yield product from the reaction of dichlorofluoromethanesulfenyl chloride (**6**) and cyclohexane on the basis of the mass spectrogram which contains parent ions at *m/e* 216 (2.15%), 218 (1.54%), and 220 (0.24%).

III. Preparation of Starting Materials. A. Perfluoro-*tert*-butanesulfenyl Chloride (1). This material was obtained from Dr. D. C. England of this laboratory, who prepared it by chlorination of bis(perfluoro-*tert*-butyl) trisulfide.[19] It has also been prepared by chlorination of the mercury salt of perfluoro-*tert*-butanethiol.[12]

B. Heptafluoro-2-propanesulfenyl Chloride (2). A mixture of 75 g (0.186 M) of bis(heptafluoroisopropyl) disulfide[20] and 30 g (0.424 M) of chlorine contained in a 1-L Hastelloy-C lined autoclave was heated at 125 °C for 4 h and then at 150 °C for 4 h. Distillation of the resulting reaction mixture through a small spinning band still gave 45.1 g (51%) of heptafluoro-2-propanesulfenyl chloride (**2**) distilling at 53.5 °C, $n^{25}{}_D$ = 1.3244 (previously reported bp 54–55 °C[21]).

C. Heptafluoro-1-propanesulfenyl Chloride (3). A mixture of 131 g (0.325 M) of bis(heptafluoro-*n*-propyl) disulfide and 75 g (1.06 M) of chlorine was treated as described in the previous experiment. There was thus obtained 114 g (74%) of heptafluoro-1-propanesulfenyl chloride (**3**) distilling at 57 °C, $n^{25}{}_D$ 1.3210 (previously reported constants: bp 51–51.5 °C; $n^{23}{}_D$ 1.3239[22]).

D. 1,1,2,2-Tetrafluoroethanesulfenyl Chloride (4). This sulfenyl chloride was prepared by the chlorination of 1,1,2,2-tetrafluoroethanethiol as described previously.[23]

E. Chlorodifluoromethanesulfenyl Chloride (5). A mixture of 25 mL of liquid (at −76 °C) thiocarbonyl difluoride and 39 mL of liquid (at −76 °C) chlorine was loaded into a dry-ice cooled trap at atmospheric pressure under nitrogen and maintained at −76 °C for 2 days. The mixture was then allowed to reflux from a dry-ice cooled condenser for 0.5 h. After distillation of the excess volatiles, the residue was distilled through an 18 in. spinning-band still. There was thus obtained 30.8 g of chlorodifluoromethanesulfenyl chloride (**5**) distilling at 52 °C, $n^{26}{}_D$ 1.4099 (previously reported constants: bp 52 °C; $n^{19}{}_D$ 1.4195[24]).

F. Dichlorofluoromethanesulfenyl Chloride (6). This sulfenyl chloride was prepared by the reaction of trichloromethanesulfenyl chloride with mercuric fluoride as described previously.[25]

IV. ^{19}F NMR and Infrared Spectra. ^{19}F NMR spectra (56.4 MHz) were obtained from 10% solutions of the compounds in CCl_4 with Cl_3CF as external standard using a Varian A-56/60 spectrometer. The resonances are reported in parts per million measured from the resonance of Cl_3CF. The IR spectra reported were obtained from solutions of the compounds in CCl_4 with a Perkin-Elmer 21 (prism) spectrometer.

Registry No.—**8**, 68409-16-5; cyclohexane, 110-82-7; butane, 106-97-8; toluene, 108-88-3; bis(heptafluoroisopropyl) disulfide, 754-62-1; bis(heptafluoro-*n*-propyl) disulfide, 356-07-0; thiocarbonyl difluoride, 420-32-6.

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(17) In a study of free-radical reactions of C_6F_5SCl with alkylbenzenes, overwhelming sulfide formation by the benzyl-type radicals was observed.[10]
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Synthesis of Alkyl Trithioperesters (Alkyl Thiocarbonyl Disulfides)[1]

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The first synthesis of alkyl trithioperesters (RC(S)SSR′, alkyl thiocarbonyl disulfides) is described. *tert*-Butyl trithiophenylperacetate (**4**) was synthesized starting with benzyl chloride. The Grignard of benzyl chloride is treated with carbon disulfide and hydrolyzed to give dithiophenylacetic acid (**1**). The dithio acid **1** was stabilized by formation of the metal salt **2**, which was reacted with *tert*-butylsulfenyl iodide (**3**) to form the trithioperester **4**. Other trithioperesters, *tert*-butyl trithiophenylperformate (**5**) and *tert*-butyl trithioanisylperformate (**6**), were synthesized by the same general reaction differing only in how the dithio acid was obtained. Preliminary observations concerning the thermal decomposition of *tert*-butyl trithiophenylperacetate (**4**) are discussed.

Several examples of the thermal homolytic cleavage of simple S–S bonds have been reported.[2] However, some of these do not involve the simple cleavage of the S–S bond,[3] and the homolytic reactions which may involve a simple homolytic cleavage do not take place at a reasonable rate below 100 °C. The only thorough kinetic study of a simple S–S bond was

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