with its chemical behavior, identified it as 4-chlorosulfinylbutanoyl chloride, $ClSOCH_2CH_2CH_2COCl$.

4-Benzylsulfonylbutanoic acid. The chlorination product just described was readily hydrolyzed by cold water and when its sodium bicarbonate solution was refluxed with benzyl chloride for 2–3 hr. and then acidified, 4-benzylsulfonylbutyric acid, $C_6H_5CH_2SO_2CH_2CH_2CH_2COOH$, separated. This acid, after recrystallization melted at 150–151° and unchanged when mixed with an authentic sample prepared by the method of Holmberg and Schjanberg.[17]

4-Anilinosulfinylbutananilide. The oil from the chlorination of another sample of 4,4′-dithiodibutanoic acid was added slowly to an ether solution of aniline at −20°. The resulting precipitate, after washing free of aniline hydrochloride and recrystallization from dilute methanol, weighed 2.6 g. and melted at 132–133°. The analysis corresponded to the dianilide, $C_6H_5NHSOCH_2CH_2CH_2CONHC_6H_5$.

Anal. Calcd. for $C_{16}H_{18}N_2O_2S$: C, 63.55; H, 6.00; N, 9.26; S, 10.60. Found: C, 63.53; H, 6.18; N, 9.06; S, 10.07.

ORONO, ME.

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(17) B. Holmberg and E. Schjanberg, *Arkiv. Kemi. Mineral. Geol.*, 14A, No. 8, (1940); *Chem. Abstr.*, 35, 2114 (1941).

[CONTRIBUTION NO. 592 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

The Reductive Thiolation of Fluorinated Carbonyl Compounds

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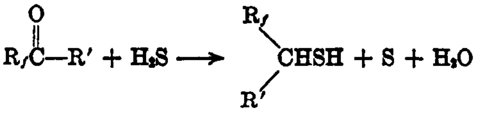
Reductive thiolation of highly fluorinated acids, acyl chlorides, aldehydes, and ketones provides a general method for the synthesis of α-hydrofluoroalkanethiols. The physical properties and some reactions of these thiols are described.

Although great advances have been made in recent years in the chemistry of organic fluorine compounds, highly fluorinated thiols are virtually unknown. Apparently, only four such compounds have been reported: trifluoromethanethiol,[1] perfluoro-1-propanethiol,[2] 2,2,2-trifluoroethanethiol,[3] and 1,1,7-trihydrododecafluoro-1-heptanethiol.[4] The methods used for their preparation were either narrow in scope or involved multistep low-yield routes.

It has now been found that the reductive thiolation of fluorinated acids, acid chlorides, ketones, and aldehydes (or their hydrates) provides a convenient route to a variety of highly fluorinated thiols:

$$R_fC(=O)\text{—}X + H_2S \longrightarrow R_fCH_2SH + S + HX + H_2O \qquad (5)$$

X = Cl, OH; R_f = fluoroalkyl



$$R_fC(=O)\text{—}R' + H_2S \longrightarrow (R_f)(R')CHSH + S + H_2O \qquad (6)$$

R′ = H, fluoroalkyl

The reactions were generally carried out at temperatures in the neighborhood of 200° in pressure autoclaves. Autogenous pressures were sufficient in the reactions of the aldehydes and their hydrates, but pressures of 2000–3000 atmospheres and temperatures of 200–250° were required with the ketones, acid chlorides, and acids.[5] The yields of the thiols ranged from 20–60%. In some of the reactions, the corresponding di- and trisulfides were obtained as byproducts. In the acid chloride reactions, there were also obtained considerable quantities of the corresponding acids, presumably resulting from hydrolysis of part of the starting material by water formed in the reaction.

It is interesting to note that fluorinated carbonyl compounds appear to undergo reductive thiolation much more readily than their hydrocarbon counterparts. Thus, the reductive thiolation of ordinary aldehydes and ketones has been effected only with the aid of sulfactive catalysts,[6] while alkanoic acids were resistant even to the catalytic process.

Physical properties. These fluorinated thiols are colorless liquids with characteristic odors similar to those of the corresponding hydrocarbon thiols. *p*Ka measurements in 50% aqueous ethanol indicate that they are considerably more acidic than their hydrocarbon analogs. For example, the *p*Ka of the primary thiol, 1,1-dihydroheptafluoro-1-butanethiol, was found to be 8.3, while that of 1-butanethiol has been reported to be 12.4[7] (also in 50% aqueous ethanol). The *p*Ka of 3-monohydrodecafluoro-3-pentanethiol was 4.6, indi-

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(1) E. L. Muetterties, U. S. Pat. 2,729,663 (1956).

(2) R. N. Haszeldine and J. H. Kidd, *J. Chem. Soc.*, 3871 (1955).

(3) J. T. Barr and F. E. Lawler, U. S. Pat. 2,894,991 (1959).

(4) P. D. Faroute and J. A. O'Rear, *J. Am. Chem. Soc.*, 78, 4999 (1956).

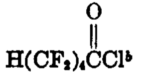
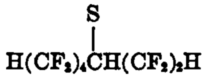
(5) In one example, an acid chloride was reductively thiolated at autogenous pressures in the presence of cobalt polysulfide. At autogenous pressures without a catalyst, the acid or acid chloride yielded the corresponding thiolacid [W. A. Sheppard and E. L. Muetterties, *J. Org. Chem.*, 25, 180 (1960).]

(6) M. W. Farlow, W. A. Lazier, and F. K. Signaigo, *Ind. Eng. Chem.*, 42, 2547 (1950).

(7) J. Maurin and R. A. Paris, *Compt. rend.*, 232, 2428 (1951).

TABLE I

PREPARATION OF FLUOROALKANETHIOLS

Starting Material	Moles of H_2S	Temp.	Time, Hr.	Pressure, Atm.	Products Isolated	Yield, %
ACIDS						
 $CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}OH$ 21.7 g., 0.10 mole	1.7	160 180 200	2 2 6	3000	$C_3F_7CH_2SH$ $C_3F_7CO_2H$	28[a] 30
ACID CHLORIDES						
 $CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}Cl$ 23.2 g., 0.10 mole	2.0	150 170 190	2 2 6	3000	$C_3F_7CH_2SH$ $C_3F_7CO_2H$	39 23
 $CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}Cl$ 23.2 g., 0.10 mole (CoS_x, 2.5 g.)	1.0	200 225 250	2 2 4	Autogenous	$C_3F_7CH_2SH$ $C_3F_7CO_2H$	23 26
 $H(CF_2)_4\overset{O}{\overset{\|}{C}}Cl$[b] 26.3 g., 0.10 mole	1.8	200	6	3000	$H(CF_2)_4CH_2SH$ $[H(CF_2)_4CH_2S]_2$ $H(CF_2)_4CO_2H$	21 9 12
 $Cl\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}Cl$ 27.7 g., 0.10 mole	1.7	250	6	3000	$HSCH_2(CF_2)_3CH_2SH$	18
ALDEHYDES						
$CF_3CH(OH)_2$ 100 g., 0.86 mole	3.76	200	5	Autogenous	CF_3CH_2SH	51
C_2F_5CHO 55 g., 0.372 mole	1.77	200	5	Autogenous	$C_2F_5CH_2SH$ $(C_2F_5CH_2S)_2$	54 2
$CF_3CF_2CF_2CHO$ 25 g., 0.125 mole	1.8	200	6	2000	$C_3F_7CH_2SH$	21
$CF_3CF_2CF_2CH(OH)_2$ 123.5 g., 0.571 mole	2.65	200	5	Autogenous	$C_3F_7CH_2SH$	50
$H(CF_2)_4CHO$[c] 115 g., 0.50 mole	2.0	200	5	Autogenous	$H(CF_2)_4CH_2SH$ $[H(CF_2)_4CH_2S]_2$ $[H(CF_2)_4CH_2S]_2S$	45 21 12
$H(CF_2)_4CHO$ 25 g., 0.11 mole	1.8	190	6	3000	$H(CF_2)_4CH_2SH$	62
KETONES						
$(ClCF_2)_2C(OH)_2$[d] 54 g., 0.25 mole	1.8	130	3	2000	$(ClCF_2)_2CHSH$	61
$(C_2F_5)_2C{=}O$[e] 28 g., 0.105 mole	1.8	200	5	2000	$(C_2F_5)_2CHSH$	25[f]
$(CF_3CF_2CF_2)_2C{=}O$ 25 g., 0.067 mole	1.8	200	5	3000	$(C_3F_7)_2CHSH$	51
 $H(CF_2)_4\overset{O}{\overset{\|}{C}}(CF_2)_2H$[g] 10 g., 0.030 mole	1.8	200	5	2000	 $H(CF_2)_4\overset{S}{\overset{\vert}{C}}H(CF_2)_2H$	42

[a] A reaction using similar amounts of reactants at 150° and 3000 atm. yielded less than 10% of the thiol. [b] Prepared from the corresponding acid (U. S. Pat. 2,559,629) by reaction with benzotrichloride. [c] Prepared by oxidation of the corresponding alcohol with chlorine (U. S. Pat. 2,842,601). [d] We are indebted to Dr. W. J. Middleton of this laboratory for this experiment. [e] A sample of decafluoro-3-pentanone was kindly supplied by Dr. D. W. Wiley of this laboratory. [f] The pressure vessel leaked during this reaction. Otherwise, the yield would probably have been substantially higher. [g] A sample of 1,7-dihydrododecafluoro-3-heptanone was kindly supplied by Dr. C. D. Ver Nooy of the Organic Chemicals Department of E. I. du Pont de Nemours and Co.

cating that this secondary thiol is even more acidic. The enhanced acidity of these fluorinated thiols can be explained on the basis of the highly electronegative character of fluoroalkyl groups, and is consistent with the increased acidities reported for fluorinated alcohols,[8] carboxylic acids,[9] and sulfonic aids.[10]

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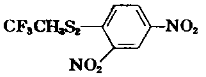
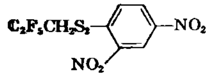
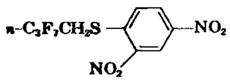
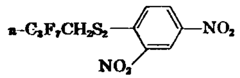
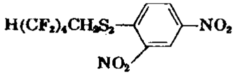
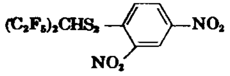
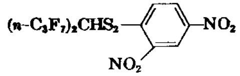
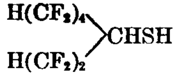
[8] A. M. Lovelace, D. A. Rausch, and W. Postelnek, *Aliphatic Fluorine Compounds*, Reinhold Publishing Corp., New York, N. Y., 1958, p. 138.

TABLE II PROPERTIES OF FLUOROALKANETHIOLS AND DERIVATIVES

Compound	B.P./Mm. or Recryst. Solvent	M.P. or n_D^{25}	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Fluorine, % Calcd.	Fluorine, % Found	Other, % Calcd.	Other, % Found
				PRIMARY									
CF_3CH_2SH	36.5	1.3413	$C_2H_3F_3S$	20.7	20.7	2.6	3.1	27.6	27.8	49.1	48.9		
$(CF_3CH_2)_2S_2$[a]	130–131	1.3890	$C_4H_4F_6S$	20.9	20.7	1.8	2.1	27.9	27.5	49.5	50.0		
CF_3CH_2SCl[a]	73	1.3890	$C_2H_2ClF_3S$	16.0	15.9	1.3	1.8					Cl 23.6	23.1
	Carbon tetrachloride or Cyclohexane	64.5–65.0	$C_8H_5F_3N_2O_4S_2$					20.4	20.5	18.1	18.2		
$C_2F_5CH_2SH$	45–47	1.3285	$C_3H_3F_5S$					19.3	19.2	57.2	56.7		
	Cyclohexane	65–66	$C_9H_5F_5N_2O_4S_2$					17.6	17.9	26.1	25.9		
$n\text{-}C_3F_7CH_2SH$	75–76	1.3217	$C_4H_3F_7S$	22.2	23.2	1.4	1.5	14.8	14.5	61.5	61.6	M.W. 216	212[b]
	Ethanol	77–77.5	$C_{10}H_5F_7N_2O_4S$	31.4	31.5	1.3	1.5	8.4	8.5	34.8	34.9	N 7.3	7.5
	Cyclohexane	75–75.5	$C_{10}H_5F_7N_2O_4S_2$	29.0	29.5	1.2	1.2	15.5	15.3				
$H(CF_2)_4CH_2SH$	127	1.3440	$C_5H_4F_8S$					12.9	13.0	61.3	60.8		
$[H(CF_2)_4CH_2]_2S_2$	84/0.5	1.3688	$C_{10}H_6F_{16}S_2$	24.3	24.7	1.2	1.5	13.0	12.7	61.5	61.4	M.W. 494	428[b] 436
$[H(CF_2)_4CH_2]_2S_3$	144/2.0	1.3972	$C_{10}H_6F_{16}S_3$	22.8	23.4	1.2	1.4	18.3	17.9	57.8	58.9	M.W. 526	460[b] 490
$H(CF_2)_4CH_2SCl$	44/6.0	1.3696	$C_5H_3ClF_8S$	21.3	21.0	1.1	1.2	11.3	11.3	53.8	54.4		
$H(CF_2)_4CH_2SO_3H$	136–139/1.0		$C_5H_4F_8O_3S$	20.3	20.5	1.4	1.6	10.8	11.0	51.3	51.7	N.E. 296	281
$[H(CF_2)_4CH_2SO_3]_2Ba$			$C_5H_3F_8O_3SBa_{1/2}$	16.5	16.7	0.83	0.94	8.8	8.8	41.8	40.9	Ba 18.6	18.8
	Carbon tetrachloride	55.5–56.5	$C_{11}H_6F_8N_2O_4S_2$	29.6	29.9	1.4	1.3	14.4	14.3				
$HSCH_2(CF_2)_3CH_2SH$	92–93.5/25	1.4215	$C_5H_6F_6S_2$	24.6	25.0	2.5	2.6	26.3	26.2	46.7	45.7	M.W. 244	226[b] 228
				SECONDARY									
$(ClCF_2)_2CHSH$[a]	115	1.4018	$C_3H_2Cl_2F_4S$					14.8	14.8	35.0	34.7	Cl 32.7	32.6
$[(ClCF_2)_2CH]_2S_2$[a]	54–57/0.7	1.4367	$C_6H_2Cl_4F_8S_2$	16.7	17.1	0.47	0.61	14.8	14.6	35.2	35.3	Cl 32.8	32.8
$(C_2F_5)_2CHSH$	86.5–87	1.3101	$C_5H_2F_{10}S$					11.3	11.6	66.9	66.9		
	Petroleum ether (b.p. 30–60°)	72–73	$C_{11}H_4F_{10}N_2O_4S_2$					13.3	13.3	39.4	39.3		
$(n\text{-}C_3F_7)_2CHSH$	122–124	1.3082	$C_7H_2F_{14}S$	21.9	22.3	0.5	0.9	8.3	8.3	69.2	68.8		
	Benzene-pentane	99–100	$C_{13}H_4F_{14}N_2O_4S_2$	26.8	27.4	0.7	1.0	11.0	10.9				
 $\begin{matrix}H(CF_2)_4\\H(CF_2)_2\end{matrix}\!\!>CHSH$	76–77/25	1.3428	$C_7H_4F_{12}S$	24.1	24.6	1.2	1.4	9.2	9.3				

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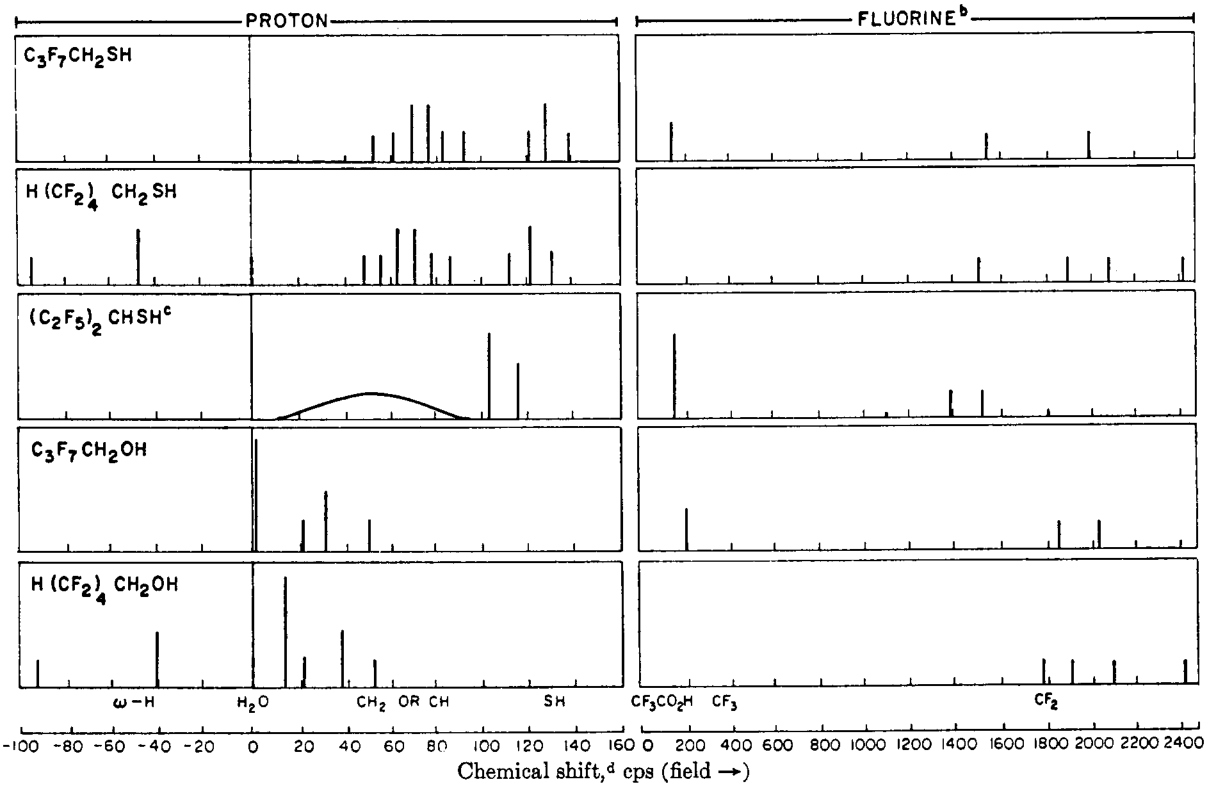
[a] Prepared by Dr. W. J. Middleton. [b] Freezing point in benzene.

Table III. Nuclear magnetic resonance spectra at 40 mc[a]



[a] Spectra were obtained by means of a high-resolution NMR spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at approximately 9,988 gauss for fluorine and 9,395 gauss for hydrogen. [b] The fluorine resonances were found to have the expected spin-spin splittings but for simplicity these are not recorded here. [c] The CH area was complex and poorly resolved as a result of multiple spin-spin couplings with the SH and CF_2 groups. Also the pattern for both proton and fluorine was typical of a CF_2 group adjacent to an asymmetric carbon [see W. D. Phillips, *New York Academy of Sciences,* 70, 817 (1958)]. [d] Spectra were calculated in terms of displacement in cycles per second (cps) from the proton resonance of water and the fluorine resonance of trifluoroacetic acid. Negative frequency displacements indicate resonances occurring at lower field relative to the reference. CORRECTION: The line shown at 30 cps for $C_3F_7CH_2OH$ should be located at 34 cps.

The infrared spectra of these thiols showed the expected small shift of the SH stretching band to higher wave numbers as a result of the inductive effect of the fluoroalkyl groups. A considerable increase in intensity of this band was also noted.

The fluorine and hydrogen NMR spectra of several of the thiols were obtained, and the observed resonances are recorded in Table III. Spin-spin coupling constants are recorded in Table IV.

TABLE IV

SPIN-SPIN COUPLING CONSTANTS (IN C.P.S.) AT 40 MC.

Compound	$J_{(SH)(CH)}$	$J_{(SH)(CF_2)}$	$J_{(CH)(CF_2)}$
$C_3F_7CH_2SH$	9	<1	16
$H(CF_2)_4CH_2SH$	9	<1	16
$(C_2F_5)_2CHSH$	12	—	—

Chemical properties. In general, these highly fluorinated thiols exhibited chemical properties typical of the hydrocarbon thiols. Thus, they were easily oxidized to the corresponding sulfonic acids by chlorine in glacial acetic acid. With chlorine in carbon tetrachloride, they were oxidized to the corresponding disulfides, and on further chlorination converted to sulfenyl chlorides. These sulfenyl chlorides appeared to be much more stable than their hydrocarbon analogs; for example, they could be stored at room temperature without serious decomposition.

Fluoroalkyl 2,4-dinitrophenyl sulfides were prepared by reaction of the thiols with 2,4-dinitrochlorobenzene, and the corresponding disulfides were prepared by reaction with 2,4-dinitrobenzenesulfenyl chloride. Both of these reactions generally yielded crystalline products which are useful for characterization purposes.

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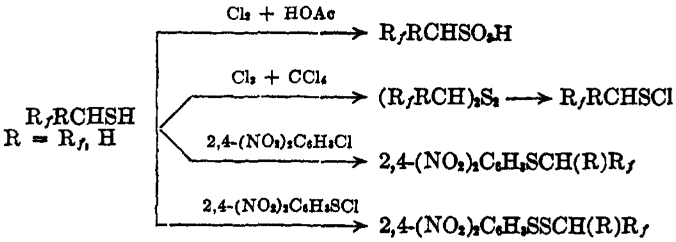
(9) A. M. Lovelace, D. A. Rausch, and W. Postelnek, *Aliphatic Fluorine Compounds,* Reinhold Publishing Corp., New York, N. Y., 1958, pp. 201-202.

(10) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.,* 4228 (1954).



EXPERIMENTAL

Preparation of mercaptans. Two methods (A and B) were used: In Method A, hydrogen sulfide at autogenous pressure was employed, while in Method B, hydrogen sulfide at pressures of 2000–3000 atm. was used. The conditions and products for each experiment are shown in Table I. All of the products were liquids and were purified by distillation. The physical properties and analytical data for the products and derivatives are listed in Table II. A detailed description of each method is given below.

Method A. Autogenous pressure. ω-Monohydrooctafluoropentanal (115 g., 0.50 mole) was placed in a 1-l. "Hastelloy" autoclave. The autoclave was cooled to −76°, evacuated, and charged with 68 g. (2.0 moles) of hydrogen sulfide. The mixture was heated at 200° for 5 hr. and then cooled to 25°. The excess hydrogen sulfide was bled off, and the reaction mixture was filtered to remove the sulfur (7.5 g.). Water (6.8 ml.) was also separated. After being dried briefly over anhydrous sodium sulfate, the product was distilled through a 45-cm. spinning-band still. The following fractions were obtained: (A) 1,1,5-trihydrooctafluoro-1-pentanethiol 56.2 g. (45.3%), b.p. 126.5–127°, n_D^{25} 1.3438–1.3442; (B) bis(1,1,5-trihydrooctafluoropentyl) disulfide, 25.7 g. (20.8%), b.p. 114–136°/16 mm.; (C) bis(1,1,5-trihydrooctafluoropentyl) trisulfide, 15.8 g. (12.0%), b.p. 95–115°/2.0–2.3 mm. Fractions B and C, which contained suspended sulfur, were further purified by filtration and redistillation.

Method B. High pressure. Perfluoro-4-heptanone (25 g., 0.067 mole) was placed in an 80-ml. "Hastelloy C"-lined shaker tube. The tube was cooled to −76° and evacuated, and hydrogen sulfide was pressured in until the entire system was filled with liquid hydrogen sulfide. Methylcyclohexane was then pressured mechanically into the reservoir portion of the system until a pressure of 800 atm. was attained. The system was closed and the reaction tube was heated to 190° while the pressure rose to 3000 atm. The tube was maintained at these conditions for 5 hr. and then cooled to 25°. Hydrogen sulfide was bled off and the reaction mixture was filtered to remove the sulfur and water. Distillation of the product through a 45-cm. spinning-band still yielded 13.3 g. (51%) of 4-monohydrotetradecafluoro-4-heptanethiol as a clear, colorless liquid boiling at 122–124°, n_D^{25} 1.3082.

Preparation of 4-(4-monohydrotetradecafluoroheptyl) 2,4-dinitrophenyl disulfide. A solution of 1.0 g. (0.0026 mole) of 4-monohydrotetradecafluoro-4-heptanethiol in 10 ml. of anhydrous ether was added all at once to a solution of 0.67 g. (0.0028 mole) of 2,4-dinitrobenzenesulfenyl chloride in 25 ml. of ether. After the mixture had stood for 15 min., it was evaporated to dryness, yielding 1.20 g. of crude product. Two recrystallizations of this material from a 1:3 benzene: pentane mixture yielded 4-(4-monohydrotetradecafluoroheptyl) 2,4-dinitrophenyl disulfide as yellow plates melting at 99–100°.

Preparation of 1,1-Dihydroheptafluorobutyl 2,4-dinitrophenyl sulfide. 1,1-Dihydroheptafluoro-1-butanethiol (1.1 g., 0.005 mole) was converted to the sodium salt and treated with 1.1 g. (0.005 mole) of 2,4-dinitrochlorobenzene as described by Bost, Turner, and Norton.[11] There was obtained 1.9 g. of crude 1,1-dihydroheptafluorobutyl 2,4-dinitrophenyl sulfide. After being recrystallized from ethanol, the product was obtained as light yellow platelets melting at 77–77.5°.

Preparation of 1,1,5-trihydrooctafluoro-1-pentanesulfenyl chloride. 1,1,5-Trihydrooctafluoro-1-pentanethiol (23.5 g., 0.095 mole) was dissolved in 100 ml. of carbon tetrachloride, and dry chlorine was passed into the solution at room temperature. After an excess of chlorine had been added, the solution was distilled. There was obtained 22 g. (78%) of 1,1,5-trihydrooctafluoro-1-pentanesulfenyl chloride distilling at 44°/6 mm., n_D^{24} 1.3700.

Preparation of 1,1,5-trihydrooctafluoro-1-pentanesulfonic acid. 1,1,5-Trihydrooctafluoro-1-pentanethiol (14.0 g., 0.057 mole) was dissolved in 100 ml. of glacial acetic acid containing 12 ml. of water. Chlorine was passed into the solution until in excess. After removal of the acetic acid by distillation through a Vigreux column, the product was distilled through a micro glass-spiral distillation column. There was obtained 9.5 g. (57%) of 1,1,5-trihydrooctafluoro-1-pentanesulfonic acid, distilling at 138–139°/1.0 mm. This product solidified to a low-melting, hydroscopic, waxy solid. The barium salt of the acid was prepared by adding a solution of 1.0 g. of barium chloride dihydrate in 10 ml. of water to an aqueous solution of 0.90 g. of acid.

Oxidation of 1,1,5-trihydrooctafluoro-1-pentanethiol to the disulfide. A solution of 10 g. (0.04 mole) of 1,1,5-trihydrooctafluoro-1-pentanethiol in 20 ml. of carbon tetrachloride was cooled to −15 to −20°, and then dry chlorine was passed in until the solution was slightly yellow. Upon distillation of the reaction mixture through a small Vigreux still, there was obtained 6.4 g. (64%) of bis(1,1,5-trihydrooctafluoropentyl) disulfide distilling at 84°/0.5 mm., 90°/2.0 mm., n_D^{25} 1.3688.

Infrared and NMR spectra. The infrared spectra of the thiols were obtained with a Perkin-Elmer infrared spectrometer Model 21. An SH absorption of medium intensity at 2590–2600 cm.$^{-1}$ (3.85–3.90 μ) was observed. In general, aliphatic thiols show a weak maxima at 2580 cm.$^{-1}$. CH_2 bands at 2900 cm.$^{-1}$, 3000 cm.$^{-1}$, and 1410 cm.$^{-1}$ were observed. Strong CF absorption in the 1000–1250 cm.$^{-1}$ region was also observed.

The fluorine and proton NMR spectra for several of the primary and secondary thiols were measured and are recorded in Table III. The corresponding patterns of two related fluoroalcohols are also given. Coupling constants are tabulated in Table IV.

pKa measurements. The pKa's for three of the thiols were determined by potentiometric titrations in 50% ethanol: $CF_3CF_2CF_2CH_2SH$, 8.30; $H(CF_2)_4CH_2SH$, 8.42; and $(C_2F_5)_2CHSH$, 4.6.

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[11] R. W. Bost, J. O. Turner, and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1985 (1932).