Attempted nitration of 2-buten-2-yl acetate with dinitrogen tetroxide–chlorine mixture. 2-Buten-2-yl acetate, 23 g. (0.2 mol.), was added in 1 hr. to a cooled solution of dinitrogen tetroxide, 9.2 g. (0.1 mol.), and chlorine, 7.1 g. (0.1 mol.), in carbon tetrachloride, 100 ml., and the reaction mixture was allowed to warm to room temperature (1 hr.). The carbon tetrachloride solution was washed with water, dried, and distilled. Only 3-chlorobutanone, b.p. 36° (40 mm.), n_D^{26} 1.4168, 12 g. (58% theory), and no 3-nitrobutanone was isolated.

LAFAYETTE, IND.

[CONTRIBUTION NO. 533 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Fluoroalkanethiolcarboxylic Acids

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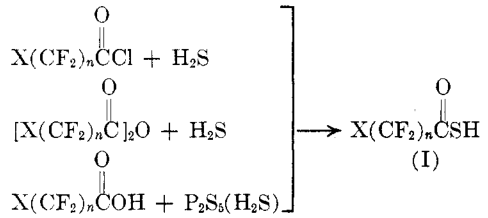
Fluoroalkanethiolcarboxylic acids (I) have been prepared by the reaction of the corresponding acid anhydride or halide with hydrogen sulfide or by reaction of the acid with phosphorus pentasulfide. The properties and reactions of these thioacids are described.

Esters of fluoroalkanethiolcarboxylic acids have been prepared by the reaction of fluoroacyl chlorides with mercaptans,[1] and by the oxidation of the bis(alkyl- and arylthio)-tetrafluorocyclobutenes.[2] However, parent fluoroalkanethiolcarboxylic acids (I) are an unknown class of compounds[3] and attempts to prepare these acids by hydrolysis of the corresponding thioesters yielded only the acids and thiols.[1] We have found that the fluoroalkanethiolcarboxylic acids (I) are readily prepared by heating the corresponding fluoroacyl chlorides or anhydrides with hydrogen sulfide at 200° in an autoclave. They can also be obtained by heating fluoroalkanecarboxylic acids with phosphorus pentasulfide under the same conditions.

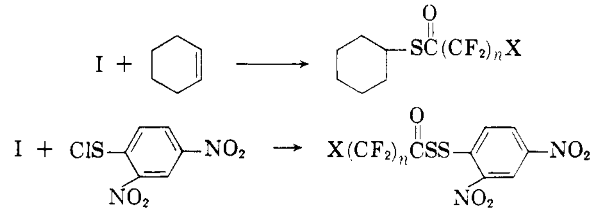


$$\left.\begin{array}{l} X(CF_2)_n\overset{O}{\overset{\|}{C}}Cl + H_2S \\ [X(CF_2)_n\overset{O}{\overset{\|}{C}}]_2O + H_2S \\ X(CF_2)_n\overset{O}{\overset{\|}{C}}OH + P_2S_5(H_2S) \end{array}\right] \longrightarrow \underset{(I)}{X(CF_2)_n\overset{O}{\overset{\|}{C}}SH}$$

where X = F or H

These conditions are more drastic than needed for the preparation of the hydrocarbon analogs.[4] It was noted in preliminary exploratory experiments that no reaction occurred between the fluoroacyl halide and hydrogen sulfide below a temperature of 100° and that heptafluorobutyric acid was unaffected by being heated at 120° with phosphorus pentasulfide. Heptafluorobutyryl chloride reacted with a solution of hydrogen sulfide in pyridine but no free thiol acid could be isolated. The strongly acidic character of this fluoroalkanethiolcarboxylic acid (see below) may cause formation of very stable salts with pyridine.

The fluoroalkanethiolcarboxylic acids are pale yellow liquids with the characteristic overpowering thioacid odor. They appear to react in a manner analogous to the alkane–thiocarboxylic acids[4] as shown by the following equations:



The ionization constants of fluoroalkanethiolcarboxylic acids are in the region of 0.6; only approximate values of these constants could be determined by conductivity measurement[5] because of apparent instability of the aqueous solutions. These thiol acids are much stronger acids than the hydrocarbon analogs[6] and are of strength comparable to the fluoroalkanecarboxylic acids. The large increase in the acidity of fluoroalkanecarboxylic acids compared to the hydrocarbon analogs has

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(1) M. Hauptschein, C. S. Stokes, and E. A. Nodiff, *J. Am. Chem. Soc.*, **74**, 4005 (1952).

(2) K. E. Rapp, J. T. Barr, R. L. Pruett, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **74**, 749 (1952).

(3) For a recent review of fluoroalkanecarboxylic acids and derivatives, see A. M. Lovelace, O. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corporation, New York, 1958, Chapters VII and XIII.

(4) E. H. Rodd, "Chemistry of Carbon Compounds," Elsevier, New York, 1951, Volume IA, pp. 593–595. Thiolacetic acid is prepared by passing hydrogen sulfide into a mixture of acetic anhydride and acetyl chloride at room temperature, by the reaction of excess hydrogen sulfide on acetyl chloride and pyridine, or by the distillation of the carboxylic acid from phosphorus pentasulfide.

(5) A. L. Henne and C. J. Fox, *J. Am. Chem. Soc.*, **73**, 2323 (1951) reported the ionization constants of trifluoroacetic acid and heptafluorobutyric acid as 0.59 and 0.68, respectively, at 25° in water.

(6) The ionization constant of thiolacetic acid is 4.7 × 10^{-4} compared to the value of 1.7 × 10^{-5} for acetic acid.

TABLE I

PREPARATION OF FLUOROALKANETHIOLCARBOXYLIC ACIDS

Acid Compound[a]	Sulfur Reagent	Temp.	Time (hr.)	Product	Yield, %
$(CF_3\overset{O}{\overset{\|}{C}})_2O$ 73 g., 0.52 mol.	H_2S, 1.0 mol.	200	5	$CF_3\overset{O}{\overset{\|}{C}}SH$[b]	28
$(CF_3\overset{O}{\overset{\|}{C}})_2O$ 216 g., 1.53 mol.	H_2S, 3.0 mol.	200	5	$CF_3\overset{O}{\overset{\|}{C}}SH$	24, 45
$(CF_3CF_2CF_2\overset{O}{\overset{\|}{C}})_2O$ 350 g., 1.17 mol.	H_2S, 3.0 mol.	200	4	$C_3F_7\overset{O}{\overset{\|}{C}}SH$	21
$CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}Cl$ 46.2 g., 0.20 mol.	H_2S, 2.0 mol.	200	6	$C_3F_7\overset{O}{\overset{\|}{C}}SH$ $C_3F_7CO_2H$	68 11
$CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}Cl$ 23.2 g., 0.10 mole	H_2S, 1.0 mol.	90	0.1	$C_3F_7\overset{O}{\overset{\|}{C}}Cl$	[c]
$CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}OH$ 21.7 g., 0.10 mol.	H_2S, 1.0 mol. P_2S_5, 0.06 mol.	200	6	$C_3F_7\overset{O}{\overset{\|}{C}}SH$	39[d]
$CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}OH$ 21.7 g., 0.10 mol.	H_2S, 1.0 mol. (HCl, 2 g.)	200	10	$C_3F_7\overset{O}{\overset{\|}{C}}SH$ $C_3F_7CO_2H$	0 83
$CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}OH$ 21.7 g., 0.10 mol.	P_2S_5, 0.20 mol.	200	6	$C_3F_7\overset{O}{\overset{\|}{C}}SH$	43
$[H(CF_2)_4\overset{O}{\overset{\|}{C}}]_2O$[e] 83 g., 0.176 mol.	H_2S, 3.0 mol.	200	4	$H(CF_2)_4\overset{O}{\overset{\|}{C}}SH$	31
$H(CF_2)_4\overset{O}{\overset{\|}{C}}Cl$[e] 26.4 g., 0.10 mol.	H_2S, 1.0 mol.	200	10	$H(CF_2)_4\overset{O}{\overset{\|}{C}}SH$ $H(CF_2)_4CO_2H$	69 13
$H(CF_2)_4\overset{O}{\overset{\|}{C}}Cl$ 100 g., 0.38 mol.	H_2S, 2.0 mol.	200	5	$H(CF_2)_4\overset{O}{\overset{\|}{C}}SH$ $H(CF_2)_4CO_2H$	39 19

[a] Unless indicated otherwise, the acid compounds were purchased or prepared by standard procedures (see Ref. 3). [b] No attempt was made to recover the carboxylic acid or other by-products in the majority of the runs. [c] No thiol acid could be detected. [d] Some of product may have been lost during course of run because of a leak in the autoclave. [e] Prepared by standard methods from the corresponding acid which was in turn prepared by permanganate oxidation of the alcohol; see U. S. Patent 2,559,629.

been attributed to the strong electron-withdrawing inductive effect of the fluorine atoms.[7]

EXPERIMENTAL[8]

Preparation of the fluoroalkanethiolcarboxylic acids, I. The reactions for preparation of these acids were all run in Hastelloy-lined autoclaves under autogenous pressure. The charges, conditions, and yields are summarized in Table I. The following procedures describe the method and the characterization of the products.

Trifluorothiolacetic acid. Trifluoroacetic anhydride (73 g., 0.52 mol.) was charged into a dry, nitrogen-flushed, Hastelloy-C-lined, 500-ml. autoclave. The autoclave was cooled to −80° in a solid carbon dioxide bath, evacuated, and charged with 34 g. (1.0 mol.) of hydrogen sulfide. The reaction mixture was heated to 200° for a period of 3 hr. After cooling to room temperature, the gaseous products were vented and the liquid residue of 72 g. was distilled to give 19 g. of trifluorothiolacetic acid, b.p. 35.5°, as a clear, colorless liquid.

Anal. Calcd. for C_2HF_3OS: C, 18.5; H, 0.77; S, 24.6. Found: C, 17.9; H, 1.08; S, 25.1.

Heptafluorothiolbutyric acid. Heptafluorobutyric acid (21.7 g., 0.10 mol.) and 45 g. (0.20 mol.) of phosphorus pentasulfide were charged into a 1-l. Hastelloy B-lined autoclave. The autoclave was cooled to −80°, evacuated, and then heated at 200° for 6 hr. under autogenous pressure. The product, absorbed in the solid phosphorus sulfides and oxides, was distilled at reduced pressure into a trap cooled in a solid carbon dioxide bath. The crude liquid product (11.2 g., contains a small amount of free sulfur) was distilled through a semimicro glass spiral distillation column to give 9.9 g. of heptafluorothiolbutyric acid, b.p. 80–82°, n_D^{27} 1.3259 (1.3 g. of liquid b.p. 82–160° was not characterized).

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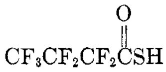
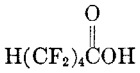
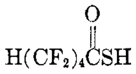
(7) See Ref. 3, p. 202.

(8) All melting points are uncorrected.

TABLE II

NUCLEAR MAGNETIC RESONANCE SPECTRA[a]

Compounds	Frequency Displacement in cps. at 40 Mc. and (Relative Intensities)[b] Proton	Fluorine
 $CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}OH$	−374	+200(3) +1710(2) +1995(2)
 $CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}SH$	−6.4	+175(3) +1548(2) +1950(2)
 $H(CF_2)_4\overset{O}{\overset{\|}{C}}OH$	−256(4) −90.0(1) −37.3(2) +18.0(1)	+1670(2) +1880(2) +2070(2) +2430(2)
 $H(CF_2)_4\overset{O}{\overset{\|}{C}}SH$	−9.6(4) −89.0(1) −36.5(2) +16.0(1)	+1505(2) +1830(2) +2030(2) +2410(2)

[a] Spectra were obtained by means of a high-resolution, nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, California, operating at approximately 9988 gauss for fluorine and 9395 gauss for hydrogen. [b] Spectra were calibrated 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.

Anal. Calcd. for C_4HF_7OS: C, 20.9; H, 0.44; F, 57.8; S, 13.9; mol. wt. 230. Found: C, 21.2; H, 0.75; F, 58.9; S, 13.6; mol. wt. 234, 235 (b.p. in benzene); neut. eq. 241, 236.

5-H-Octafluorothiolvaleric acid. 5-H-Octafluorovaleroyl chloride (100 g., 0.378 mole) was charged into a 1-l., "Hastelloy B"-lined autoclave with 68 g. (2.0 moles) of hydrogen sulfide as described above. The reaction mixture was heated at 200° for 5 hr., cooled, and the volatile products vented. There was obtained 120 g. of liquid which on distillation through an 18-inch spinning band column yielded 38.2 g. 5-H-octafluorothiolvaleric acid, b.p. 124–126°, n_D^{24} 1.3470, and 19.3 g. of 5-H-octafluorovaleric acid, b.p. 94° at 40 mm. (a fraction of 5.1 g., b.p. 99° at 40 mm. to 82° at 1.9 mm. was not characterized).

Anal. Calcd. for $C_5H_2F_8OS$: C, 22.9; H, 0.77; F, 58.0; S, 12.2; mol. wt. 262. Found: C, 23.4; H, 1.08; F, 57.9; S, 12.2; mol. wt. 248, 248 (f.p. in benzene).

Reaction of 5-H-octafluorothiolvaleric acid with cyclohexene- 5-H-Octafluorothiolvaleric acid (5.2 g., 0.020 mole) was added to 5 ml. of cyclohexene. After a short induction period, a vigorous exothermic reaction resulted. The resulting solution was distilled through a 12-inch micro spinning band column. The excess cyclohexene was discarded and 5.3 g. (77%) of cyclohexyl 5-H-octafluorothiolvalerate was collected as a colorless liquid, b.p. 72–72.5° (1.2 mm.), n_D^{23} 1.4085.

Anal. Calcd. for $C_{11}H_{12}F_8OS$: C, 38.4; H, 3.52; F, 44.2. Found: C, 39.2, 39.0; H, 4.15; F, 44.2.

Reaction of 5-H-octafluorothiolvaleric acid with 2,4-dinitrobenzenesulfenyl chloride. A solution of 2.62 g. (0.010 mol.) of 5-H-octafluorothiolvaleric acid was added to 2.34 g. (0.010 mol.) of 2,4-dinitrobenzenesulfenyl chloride partially dissolved in 35 ml. of ether. The reaction occurred immediately as indicated by the rapid solution of the undissolved sulfenyl chloride. The ether was evaporated to leave a residue of 4.33 g. of pale yellow oil that crystallized on chilling. The 2,4-dinitrophenyl-5-H-octafluorovaleroyl disulfide was recrystallized from a solution of approximately 1% benzene in pentane, m.p. 44.0–44.8°, pale yellow crystals.

Anal. Calcd. for $C_{11}H_4F_8N_2O_5S_2$: C, 28.7; H, 0.88; F, 33.0; S, 13.9. Found: C, 29.1; H, 1.44; F, 33.1; S, 14.0.

Infrared and NMR (Nuclear Magnetic Resonance) Spectra. The infrared and NMR (fluorine and proton) spectra were obtained on the thiol acids and derivatives and found to be in agreement with the assigned structures in every case. The infrared absorption maximum for the thiol group of the thiol acids was observed at 2580 cm.$^{-1}$ and the carbonyl absorption at 1733–1738 cm.$^{-1}$. These absorption maxima occur in the usual regions (for thiolacetic acid, thiol is at 2550 cm.$^{-1}$ and carbonyl at 1712 cm.$^{-1}$) with the expected shift to lower wave numbers resulting from the inductive effect of the fluorine atoms.

The NMR spectra for two of the thiol acids are compared with those for the corresponding carboxylic acids in Table II.

WILMINGTON 98, DELAWARE