1,3-cyclohexadiene (XVb). A solution of 111 g. (0.6 mole) of V in 1360 ml. of methanol was stirred at 45–55° while 68 g. (1.0 mole) of isoprene was added. The solution was stirred at 50° for 1 hr., then a second mole of isoprene was added and stirring was continued 3 hr. longer at 50°. The solution was left overnight at room temperature and then distilled. About 47 g. of crude liquid distilled from 70° at 1.5 mm. to 90° at 0.8 mm. This was redistilled, yielding 26 g. (23%) pale yellow liquid XVb, b.p. 84–85° at 3.5 mm., having a refractive index (n_D^{27}) of 1.5302 and a density (d_4^{27}) of 1.164.

Anal. Calcd. for $C_9H_{10}Cl_2$: C, 57.2; H, 5.3; S, absent. Found: C, 57.5; H, 5.3; S, absent.

Further distillation of the reaction mixture produced an additional 48.2 g. of distillate before slow decomposition of the residual tar ended the distillation. Redistilling this produced 29.5 g. (19%) of pale yellow liquid XIVb, b.p. 133–136° at 0.6 mm., having a refractive index (n_4^{25}) of 1.5550 and a density (d_4^{25}) of 1.4215.

Anal. Calcd. for $C_9H_{10}Cl_2O_2S$: C, 42.8; H, 3.98; S, present. Found: C, 43.2; H, 3.87; S, present.

3,5,6-Trichlorothianaphthene 1,1-dioxide (XVI), *2,3,7,8-tetrachlorodibenzothiophene 5,5-dioxide* (XVII), and *3,3a,6,6a-tetrachloro-3a,3b,6a,6b-tetrahydrocyclobuta[1.2-b,3.4-b']dithiophene 1,1,4,4-tetroxide* (XIXb). A solution of 25.8 g. (0.1 mole) of IV in 150 ml. of xylene was stirred and cooled for 2 hr. to keep it below 30° while about 7 g. (0.4 mole; 100% excess) of anhydrous ammonia was bubbled through the solution to convert IV to V. The resulting suspension was heated at reflux temperature, with continued stirring, for 1 hr. The ammonium chloride was filtered from the hot solution and rinsed with hot benzene. The crude ammonium chloride was found to contain a small amount of water-insoluble solid; this was recrystallized from chloroform, producing colorless needle-shaped crystals of XVII, m.p. 380°.

Anal. Calcd. for $C_{12}H_4Cl_4O_2S$: Cl, 40.0; S, 9.1. Found: Cl, 39.7; S, 9.1.

Chilling the xylene filtrate overnight at −20° caused 2.3 g. (12%) of XIXb, m.p. 227–231°, to crystallize. One recrystallization from methanol, with a Nuchar treatment, afforded pure XIXb, m.p. 231.5–232°.

Anal. Calcd. for $C_8H_4Cl_4S_2$: C, 26.0; H, 1.1; Cl, 38.3; mol. wt., 370. Found: C, 26.1; H, 1.4; Cl, 38.2; mol. wt. (*via* Rast method in camphor), 236 and 414.

Evaporating the filtrate produced 6.6 g. (49%) of crystalline XVI, m.p. 167–171°, after recrystallization from isopropanol. Two recrystallizations from methanol, with decolorizing carbon treatments, produced pure XVI, m.p. 170–171°.

Anal. Calcd. for $C_8H_3Cl_3O_2S$: C, 35.7; H, 1.1; Cl, 39.5. Found: C, 35.7; H, 1.5; Cl, 39.4.

Improved preparation of 2,3,7,8-tetrachlorobenzothiophene 5,5-dioxide (XVII). A solution of 22.6 g. (0.084 mole) of XVI in 400 ml. of 1,2,4-trichlorobenzene was stirred and heated at 200–215° for 2 hr. while a solution of 32.2 g. (0.174 mole) of V in 240 ml. of chloroform was added dropwise. Chloroform was allowed to distill during the addition. The resulting solution was refluxed for an hour, then the solvent was distilled under reduced pressure until a solid began to form; about 150 ml. of material remained. Triturating this residue with 150 ml. of petroleum ether (b.p. 35–60°) and filtering produced 15.6 g. of brown solid. An additional 4 g. of similar appearing solid was obtained from the filtrate. This 19.6 g. of crude solid was recrystallized twice from benzene and then twice from chloroform, yielding a first crop of 9.4 g. (23%) of fine colorless needle-shaped crystals of XVII, m.p. 380–381°.

Acknowledgment. The NMR spectra and piezoelectric data were obtained through the kind cooperation and assistance of Dr. A. A. Bothner-By of the Mellon Institute, Pittsburgh, Pa. Appreciation for this assistance is gratefully acknowledged.

PAINESVILLE, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

The Anhydrous Chlorination of Some Mercapto Acids and Analogous Disulfides[1,2,3]

IRWIN B. DOUGLASS AND BASIL S. FARAH[4]

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o-Thiolbenzoic acid, *m,m'*-dithiodibenzoic acid, 3-thiolpropanoic acid, and 4,4'-dithiodibutanoic acid react with anhydrous chlorine to form chlorosulfinylacyl chlorides of the type ClS(O)—R—COCl by a process which is believed to involve the intramolecular solvolysis of an intermediate organosulfur trichloride.

Investigations carried out in this laboratory have shown that certain bivalent sulfur compounds can be converted by the action of anhydrous chlorine at low temperatures to the corresponding alkylsulfur trichlorides.[5] The latter compounds upon controlled solvolysis with water, alcohols, or carboxylic acids yield sulfinyl chlorides.[6] In view of these reactions, it appeared possible that compounds containing both sulfhydryl (or disulfido) and carboxyl groups within their molecular structures might form sulfur trichlorides which would undergo intramolecular solvolysis to form com-

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[1] Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and to the Office of Naval Research for support of this research.

[2] Presented at the Boston meeting of the American Chemical Society, April 10, 1959.

[3] Taken from a thesis submitted by Basil S. Farah in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

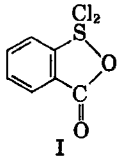
[4] Present address: General Chemical Research Laboratory, Allied Chemical Corp., P. O. Box 405, Morristown, N. J.

[5] K. R. Brower and I. B. Douglass, *J. Am. Chem. Soc.*, **73**, 5787 (1951).

[6] I. B. Douglass and D. R. Poole, *J. Org. Chem.*, **22**, 536 (1957).

pounds containing both sulfinyl and acyl chloride groups.

Price and Smiles[7] investigated the action of anhydrous chlorine on *o*-thiolbenzoic acid and isolated a dichloride, $C_7H_4Cl_2O_2S$, to which they assigned an *S,S*-dichloro structure, (I). Hart, McClelland and Fowkes[8] studied the same reaction but assigned a different formula (II) to the product. The work in this laboratory referred to above suggested, however, that the dichloro compound of Price and Smiles might be *o*-chlorosulfinylbenzoyl chloride (III).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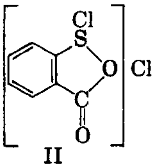
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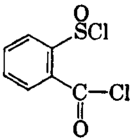
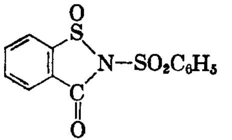

III


IV

Following the procedure of Price and Smiles both thiosalicylic and its disulfide reacted smoothly with anhydrous chlorine to give a compound exhibiting the properties of the dichloride described. This dichloride underwent rapid hydrolysis to *o*-sulfinobenzoic acid and reacted with benzenesulfonamide to give a product identical in melting point to the 2-keto-1-benzenesulfonyl-1,2,-dihydrobenzisothiazolone-*S*-oxide (IV), obtained by Hart, McClelland, and Fowkes in the same manner. Excess methyl mercaptan reduced the compound to *o,o'*-dithiodibenzoic acid, a reaction strongly indicative of a chlorosulfinyl group, as methanesulfinyl chloride behaves in an analogous manner.[9]

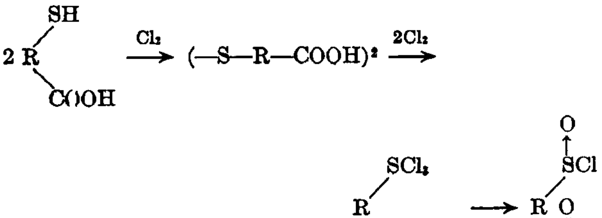
The infrared spectrum of the dichloro compound showed absorption bands at 1778 cm.$^{-1}$ and at 1158 cm.$^{-1}$ characteristic of the chlorocarbonyl[10] and chlorosulfinyl[11] groups, respectively.

An alternative synthesis of *o*-chlorosulfinylbenzoyl chloride was achieved by low temperature chlorination of *o,o'*-dithiodibenzoyl chloride in the presence of two equivalents of glacial acetic acid, a reaction known to convert disulfides to sulfinyl chlorides.[12] The product obtained in this way had properties identical to those of the dichloro compound originally obtained from thiosalicylic acid. There seems no reason to doubt, therefore, that the dichloro compound of Price and Smiles is *o*-chlorosulfinylbenzoyl chloride, (III).

In order to disprove further the cyclic structure the reaction was extended to *m,m'*-dithiodibenzoic, which could not conceivably form a cyclic dichloro derivative. This reaction produced an oil which could not be distilled but which responded to tests indicating that it was *m*-chlorosulfinylbenzoyl chloride. This product gave an infrared spectrum similar to that of the ortho compound with absorption bands near 1782 and 1158 cm.$^{-1}$ It fumed in moist air, reacted readily with aniline to form a dianilide, and was hydrolyzed rapidly in cold water to *m*-sulfinobenzoic acid. The latter compound, on heating in alkaline solution with benzyl chloride, readily formed the sulfone, *m*-benzylsulfonylbenzoic acid.

The investigation was extended further to the products obtained by chlorinating the aliphatic mercapto acids and their disulfides. 3-Thiolpropanoic acid and its disulfide and 4,4'-dithiodibutanoic acid reacted with anhydrous chlorine to yield undistillable oils showing the properties of 3-chlorosulfinylpropanoyl chloride, $ClSOCH_2CH_2COCl$, and 4-chlorosulfinylbutanoyl chloride, $ClSOCH_2CH_2CH_2COCl$, respectively. These products had infrared spectra with absorption bands near 1800 and 1150 cm.$^{-1}$ as expected for the chlorocarbonyl[13] and chlorosulfinyl groups. They also formed dianilides, $C_6H_5NH\overset{\overset{O}{\uparrow}}{S}(CH_2)_nCONHC_6H_5$, and upon hydrolysis and heating with benzyl chloride, formed benzylsulfonyl derivatives, $C_6H_5CH_2SO_2(CH_2)_nCOOH$.

The process by which the chlorosulfinylacyl chlorides described above are formed can best be explained if one assumes the following series of reactions.



$$2\,R\begin{matrix}SH\\COOH\end{matrix} \xrightarrow{Cl_2} (-S-R-COOH)^2 \xrightarrow{2Cl_2} R\begin{matrix}SCl_3\\COOH\end{matrix} \longrightarrow R\begin{matrix}\overset{\overset{O}{\uparrow}}{S}Cl\\ \overset{O}{\|}\\ CCl\end{matrix}$$

This conclusion is supported by the fact that organosulfur trichlorides react readily with carboxylic acids to form sulfinyl chlorides and acyl chlorides[6] and by the fact that a mixture of methyldisulfide and glacial acetic acid reacts nearly quantitatively with anhydrous chlorine to form methanesulfinyl chloride and acetyl chloride.[12]

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[7] W. B. Price and S. Smiles, *J. Chem. Soc.*, 2858 (1928).

[8] L. E. Hart, E. W. McClelland, and F. S. Fowkes, *J. Chem. Soc.*, 2114 (1938).

[9] I. B. Douglass and B. S. Farah, *J. Org. Chem.*, **23**, 805 (1958).

[10] R. S. Rasmussch and R. R. Brattam, *J. Am. Chem. Soc.*, **71**, 1073 (1949).

[11] S. Detoni and D. Hadzi, *J. Chem. Soc.*, 3163 (1955).

[12] I. B. Douglass and B. S. Farah, *J. Org. Chem.*, **23**, 330 (1958).

[13] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, J. Wiley and Sons, New York, N. Y., 1959, p. 125.

The lack of visual evidence for the formation of the intermediate sulfur trichloride is understandable when one considers the ease with which carboxylic acids react with organosulfur trichlorides. When a mixture of methyldisulfide and glacial acetic acid is chlorinated there is likewise no separation of solid methylsulfur trichloride and the mixture remains a single phase throughout the reaction.[12]

EXPERIMENTAL

Chlorination of 2-thiolbenzoic acid. The chlorination was carried out in a manner identical with that described by Price and Smiles except that methylene chloride was substituted for carbon tetrachloride. A suspension of 3.08 g. of 2-thiolbenzoic acid in 30 ml. of methylene chloride was chlorinated until solution was complete, after which the resulting solution was filtered and evaporated to dryness under vacuum. The residual solid, which weighed about 3 g. (65–75% yield), melted at 62–64° and had to be protected from moisture until used. Price and Smiles[7] reported a melting point of 62° for their product. A carbon tetrachloride solution of the compound showed strong absorption at 1778 cm.$^{-1}$ and 1158 cm.$^{-1}$ The compound was formed equally well by the chlorination of 1,1′-dithiodibenzoic acid.

Hydrolysis of the chlorination product. The residue from a chlorination, carried out as described above, was added to ice cold water and yielded 2.9 g. of *o*-sulfinobenzoic acid melting at 125–126° after recrystallization from methanol. By the same procedure Price and Smiles obtained *o*-sulfinobenzoic acid melting at 126°.

Reaction of the dichloride with benzenesulfonamide. The product of another chlorination was heated with 3.0 g. of benzenesulfonamide in 10 ml. of pyridine. On pouring the reaction mixture into 1*N* hydrochloric acid a solid separated which melted at 181–182° after recrystallization from aqueous methanol. Hart, McClelland, and Fowkes[8] report a melting point of 182° for 2-keto-1-benzenesulfonyl-1,2-dihydrobenzisothiazole-*S*-oxide obtained by this same procedure. The compound was identified further by oxidation to 2-keto-1-benzenesulfonyl-1,2-dihydrobenzisothiazole-*S*,*S*-dioxide, m.p. 202.[8]

Reaction of the dichloride with methanethiol. The product from another chlorination was dissolved in methylene chloride and treated with a slow stream of methyl mercaptan until the evolution of hydrogen chloride ceased. A precipitate of *o,o*′-dithiodibenzoic acid was obtained in 90% yield and melted at 289–290° both alone and when mixed with an authentic sample.

Alternative synthesis of o-chlorosulfinylbenzoyl chloride. A suspension of 2.4 g. of *o,o*′-dithiodibenzoic acid in 20 ml. thionyl chloride was refluxed vigorously until solution was complete. The excess thionyl chloride was then removed at reduced pressure and the residue extracted with benzene. On concentrating and cooling the benzene solution there was obtained 2.1 g. (80% yield) of *o,o*′-dithiodibenzoyl chloride, melting at 155–156° after recrystallization from a mixture of benzene and petroleum ether (b.p. 30–60°). Chatterja and Prasad[14] report a melting point of 154° for the same compound obtained by the action of thionyl chloride on 2-thiolbenzoic acid.

Anal. Calcd. for $C_{14}H_8Cl_2O_2S_2$: C, 48.97; H, 2.35; Cl, 20.66. Found: C, 48.72; H, 2.26; Cl, 20.82.

A suspension of 1.0 g. (0.003 mole) of the *o,o*′-dithiodibenzoyl chloride in 30 ml. dry methylene chloride containing 0.36 g. (0.006 mole) of glacial acetic acid was treated with anhydrous chlorine until there was a faint yellow of excess chlorine. The product obtained, after removal of the solvent and acetyl chloride under vacuum, melted at 62–65° both when alone and when mixed with the product obtained by chlorinating *o*-thiolbenzoic acid.

m-Chlorosulfinylbenzoyl chloride and derivatives. When 3.06 g. of *m,m*′-dithiodibenzoic acid was chlorinated in the same manner as described for *o*-thiolbenzoic acid 4.8 g. of a pale yellow oil was obtained which fumed in moist air and decomposed on attempted distillation. Because of its instability the product could not be purified for analysis but the following tests identified it as *m*-chlorosulfinylbenzoyl chloride. The infrared spectrum of the oil resembled that of *o*-chlorosulfinylbenzoyl chloride with strong absorption bands at 1752 cm.$^{-1}$, 1782 cm.$^{-1}$ and 1158 cm.$^{-1}$

On treatment with cold water the oil from a similar chlorination was converted to *m*-sulfinobenzoic acid (3.1 g., 83% yield) which melted at 197–198° and did not depress the melting point of an authentic sample prepared by the reduction of *m*-chlorosulfonylbenzoic acid with sodium sulfite according to the method of Smiles and Davis.[15] When 1.8 g. of this acid was refluxed with 1.3 g. benzyl chloride and excess 5% sodium bicarbonate for 3 hr., there was obtained 2.1 g. of *m*-benzylsulfonylbenzoic acid, *m*-$C_6H_5CH_2SO_2C_6H_4COOH$, melting at 211–212° after recrystallization from alcohol.

Anal. Calcd. for $C_{14}H_{12}O_4S$: C, 60.85; H, 4.38; S, 11.60. Found: C, 61.19; H, 4.40; S, 11.58, 11.66.

Approximately 3.0 g. of the product from another chlorination, dissolved in 30 ml. of methylene chloride, was added slowly to 7.5 g. of aniline in 100 ml. of anhydrous ether at −20°. The resulting precipitate, after washing free of aniline hydrochloride and recrystallizing from dilute methanol, melted at 157–158° and corresponded in composition to *m*-anilinosulfinylbenzanilide, *m*-$C_6H_5NHSOC_6H_4CONHC_6H_5$. The yield was 80%.

Anal. Calcd. for $C_{19}H_{15}N_2O_2S$: C, 67.83; H, 4.79; N, 8.33; S, 9.53. Found: C, 67.70; H, 4.87; N, 8.21; S, 9.36, 9.55.

Chlorination of 3-thiolpropanoic acid. A solution of 10.6 g. of 3-thiolpropanoic acid in 50 ml. methylene chloride was chlorinated at −10° to the faint yellow color of excess chlorine. After removing the solvent under reduced pressure approximately 16 g. of an oil remained which decomposed rapidly upon attempted distillation. The infrared absorption spectrum of the product from another chlorination showed bands at 1152 and 1800 cm.$^{-1}$ These characteristic bands and the following tests indicated that the undistillable oil was 3-chlorosulfinylpropanoyl chloride, $ClSOCH_2CH_2COCl$.

3-Anilinosulfinylpropananilide. Approximately 6 g. of the chlorination product was added to 19 g. of aniline in 100 ml. of methylene chloride at −20°. The resulting solid, after washing free of aniline hydrochloride and recrystalling from dilute methanol melted at 137–138°. The analysis corresponded to 3-anilinosulfinylpropananilide, $C_6H_5NHSOCH_2CH_2CONHC_6H_5$.

Anal. Calcd. for $C_{15}H_{16}N_2O_2S$: C, 62.48; H, 5.59; S, 11.12. Found: C, 62.20; H, 5.81; S, 11.0.

3-Benzylsulfonylpropanoic acid. The chlorination product obtained from 10.6 g. of *β*-mercaptopropionic acid was added to cold 5% sodium bicarbonate. Upon refluxing the resulting solution with benzyl chloride and acidifying the reaction mixture, 17.5 g. of 3-benzylsulfonylpropanoic acid precipitated. After recrystallization, the product melted at 177–178° and unchanged when mixed with an authentic sample prepared by the method of Holmberg and Schjanberg.[16]

Chlorination of 4,4′-dithiodibutanoic acid. Chlorination of 1.19 g. of this acid, prepared from 4-chlorobutanoic acid by way of the isothiouronium salt, gave about 1.8 g. of an undistillable oil. The infrared spectrum of the oil showed absorption bands at 1792 and 1150 cm.$^{-1}$ which, together

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(14) J. N. Chatterja and K. Prasad, *J. Indian Chem. Soc.*, **31**, 203 (1954); *Chem. Abstr.*, **49**, 9614 (1955).

(15) E. G. Davis and S. Smiles, *J. Chem. Soc.*, 1294 (1910).

(16) B. Holmberg and E. Schjanberg, *Arkiv, Kemi. Mineral. Geol.*, **14A**, No. 7 (1940); *Chem. Abstr.*, **35**, 2113 (1941).

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.

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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

JOHN F. HARRIS, JR., AND WILLIAM A. SHEPPARD

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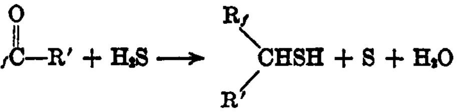
Reductive thiolation of highly fluorinated acids, acyl chlorides, aldehydes, and ketones provides a general method for the synthesis of α-hydrofluoroalkanethiols. The physical properties and some reactions of these thiols are described.

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:

$$R_f\overset{O}{\overset{\|}{C}}-X + H_2S \longrightarrow R_fCH_2SH + S + HX + H_2O \qquad (5)$$

$$X = Cl, OH; R_f = \text{fluoroalkyl}$$



$$R_f\overset{O}{\overset{\|}{C}}-R' + H_2S \longrightarrow \begin{matrix} R_f \\ \quad\diagdown \\ \quad CHSH \\ \quad\diagup \\ R' \end{matrix} + S + H_2O \qquad (6)$$

$$R' = \text{H, fluoroalkyl}$$

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).