quantitative yield by catalytic reduction of the corresponding piperidine hydrochloride by the process which has been described; m.p. 271–272° (dec.) after recrystallization from isopropyl alcohol.

*Anal.* Calcd. for $C_{18}H_{28}ONCl$: N, 4.52; Cl, 11.44. Found: N, 4.55; Cl, 11.44.

**1-Methyl-3-acetoxy-4-phenyl-4-cyclohexylpiperidine Hydrochloride.**—A mixture of 3.2 g. of the piperidinol hydrochloride and 10 cc. of acetic anhydride was refluxed for several minutes, cooled and the product precipitated by the addition of ether; yield 2.7 g. (73%); m.p. 199–201° after recrystallization from isopropyl alcohol.

*Anal.* Calcd. for $C_{20}H_{30}O_2NCl$: N, 3.98; Cl, 10.07. Found: N, 3.88; Cl, 9.89.

**1,2,5-Trimethyl-4,4-diphenyl-3-piperidinol Hydrochloride.**—This product was prepared by catalytic reduction of the corresponding piperidone hydrochloride. After recrystallization from absolute ethanol, it melted at 284–285° (dec.).

*Anal.* Calcd. for $C_{20}H_{26}ONCl$: N, 4.22; Cl, 10.68. Found: N, 4.37; Cl, 10.77.

**1,2,6-Trimethyl-4,4-diphenyl-3-piperidinol Hydrochloride.**—This substance, obtained by catalytic reduction of the corresponding piperidone hydrochloride, melted at 293° (dec.) after recrystallization from absolute ethanol.

*Anal.* Calcd. for $C_{20}H_{26}ONCl$: N, 4.22; Cl, 10.68. Found: N, 4.24; Cl, 10.67.

ANN ARBOR, MICHIGAN

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[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

# Thiolesters of Perfluorocarboxylic Acids

BY MURRAY HAUPTSCHEIN, CHARLES S. STOKES AND EDWARD A. NODIFF

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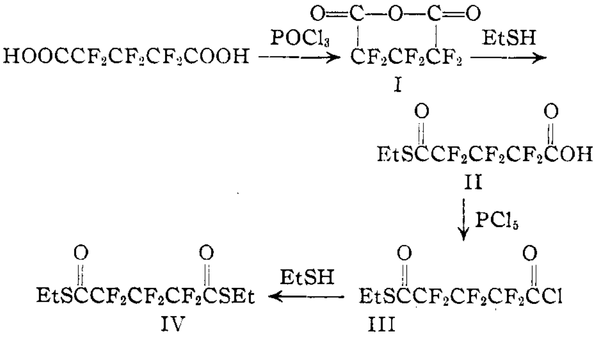
A series of thiolesters and dithiolesters of perfluoro-fatty acids has been prepared by the reaction of perfluoro-fatty acid chlorides and anhydrides with thiols and dithiols. Perfluoroglutaric anhydride has been prepared and converted to its dithiolester by a three step synthesis and to a polythiolester by a condensation polymerization reaction. Infrared absorption and molecular refractivity data of fluorinated thiolesters and oxygen esters are compared with their non-fluorinated analogs, and various correlations are noted and interpreted. New light is shed on the influence of perfluoroalkyl groups on adjacent carbonyl groups. Certain "characteristic" wave length bands for fluorocarbon derivatives have been empirically assigned.

The main purpose of this study was to prepare thiolesters of perfluoro-fatty acids, a class of compounds which has not been reported hitherto.[1] It was found that perfluoro-fatty acid chlorides and anhydrides react readily with thiols and dithiols, in the absence of any solvents, to form high yields of the corresponding thiolesters and dithiolesters.[2] In one case, an attempt to prepare a thiolester by the direct esterification of the free acid and mercaptan resulted in only a very small yield of thiolester.

Trifluoroacetic anhydride or acid chloride, pentafluoropropionyl chloride and *n*-heptafluorobutyryl chloride have been allowed to react with ethyl mercaptan and pentamethylene dimercaptan to form ethyl thioltrifluoroacetate, thiolpentafluoropropionate, thiolheptafluorobutyrate, as well as pentamethylene dithiol bis-(trifluoroacetate), bis-(pentafluoropropionate) and bis-(heptafluorobutyrate).

It was found necessary to go through the following sequence in order to prepare diethyl dithiolhexafluoroglutarate.

It was necessary to employ the anhydride (I) as the acylating agent since perfluoroglutaryl chloride, which should give IV directly, could be prepared only in extremely small yield by the action of phosphorus pentachloride or thionyl chloride on hexafluoroglutaric acid, the reaction resulting primarily in cleavage products due to loss of carbon dioxide.



$$\mathrm{HOOCCF_2CF_2CF_2COOH} \xrightarrow{\mathrm{POCl_3}} \underset{\mathrm{I}}{\overset{\mathrm{O{=}C{-}O{-}C{=}O}}{\mathrm{CF_2CF_2CF_2}}} \xrightarrow{\mathrm{EtSH}} \underset{\mathrm{II}}{\mathrm{EtS\overset{O}{\overset{\|}{C}}CF_2CF_2CF_2\overset{O}{\overset{\|}{C}}OH}}$$

$$\underset{\mathrm{II}}{} \xrightarrow{\mathrm{PCl_5}} \underset{\mathrm{III}}{\mathrm{EtS\overset{O}{\overset{\|}{C}}CF_2CF_2CF_2\overset{O}{\overset{\|}{C}}Cl}} \xrightarrow{\mathrm{EtSH}} \underset{\mathrm{IV}}{\mathrm{EtS\overset{O}{\overset{\|}{C}}CF_2CF_2CF_2\overset{O}{\overset{\|}{C}}SEt}}$$

Perfluoroglutaric anhydride (I) was prepared for the first time by the reaction of perfluoroglutaric acid with phosphorus oxychloride at 150°.[3] It is interesting to note that the boiling point of I (72°) is approximately *208° lower* than that of its "hydrocarbon" analog, glutaric anhydride. This is an even greater reduction than in the case of γ-perfluorobutyrolactone,[1] the empirical formula of which differs from I by one less C=O group. The perfluoro lactone boils at 18°[1] or *188° below* its hydrocarbon analog, γ-butyrolactone. These novel type perfluoro compounds are built up entirely of carbon and the two most *electronegative* elements, fluorine and oxygen. The repulsive forces between these molecules must be exceptionally large, and since there is absolutely no possibility of hydrogen-type bonding, the intermolecular forces of attraction are unusually weak.

In agreement with the poor reactivity of perfluorinated acids with thiols, none of the dithiolester (IV) was isolated in the reaction of I with ethyl mercaptan even though the molar ratio of mercaptan to I was 2:1. Instead, the acid-thiol-

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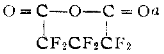
[1] Diethyl dithioltetrafluorosuccinate, $C_2H_5SCOCF_2CF_2COSC_2H_5$, has been prepared by the reaction of ethyl mercaptan with perfluorobutyrolactone (M. Hauptschein, C. S. Stokes and A. V. Grosse, THIS JOURNAL, **74**, 1974 (1952)).

[2] This procedure is an extension to "fluorocarbon" derivatives of the well-known method for preparing "hydrocarbon" thiolesters. For literature review see H. Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., Second Edition, 1943, p. 932.

[3] J. J. Padbury and E. L. Kropa, U. S. Patent 2,502,478 (April 4, 1950).

TABLE I

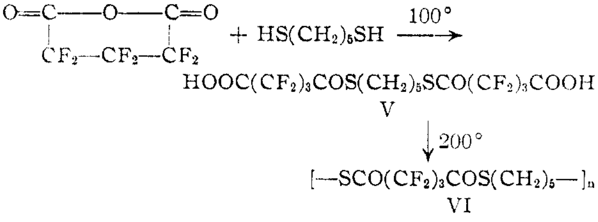
NEW COMPOUNDS

| Compound | Yield, % | B.p., °C. | Mm. | $n^t$D | $d^t_4$ | $t$, °C. | Analyses,[d] %<br>Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found | Sulfur Calcd. | Sulfur Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CF_3COSC_2H_5$ | 84 | 90.5 | 760 | 1.3755<br>1.3888 | 1.2338<br>1.2766 | 25.5<br>0.0 | 30.38 | 30.58 | 3.19 | 3.29 | 20.28 | 20.30 |
| $CF_3CF_2COSC_2H_5$ | 93 | 103 | 760 | 1.3592<br>1.3707 | 1.3300<br>1.3765 | 24.1<br>0.0 | 28.85 | 28.86 | 2.42 | 2.42 | 15.40 | 15.64 |
| $CF_3CF_2CF_2COSC_2H_5$ | 90 | 119 | 760 | 1.3544<br>1.3631 | 1.4217<br>1.4618 | 19.3<br>0.0 | 27.91 | 28.15 | 1.95 | 2.01 | 12.42 | 12.45 |
| $CF_3COS(CH_2)_5SCOCF_3$[a] | 79[b], 84[c] | 119 | 8 | 1.4269<br>1.4372 | 1.3627<br>1.3960 | 24.8<br>0.0 | 32.92 | 33.16 | 3.07 | 3.20 | 19.53 | 19.80 |
| $CF_3CF_2COS(CH_2)_5SCOCF_2CF_3$[a] | 80 | 128 | 8 | 1.4006<br>1.4102 | 1.4404<br>1.4758 | 23.8<br>0.0 | 30.84 | 31.00 | 2.35 | 2.12 | 14.97 | 14.73 |
| $CF_3CF_2CF_2COS(CH_2)_5SCOCF_2CF_2CF_3$[a] | 80 | 142 | 8 | 1.3866<br>1.3960 | 1.5220<br>1.5613 | 24.5<br>0.0 | 29.55 | 29.81 | 1.91 | 1.81 | 12.14 | 12.40 |
| $C_2H_5SCOCF_2CF_2CF_2COSC_2H_5$[a] | 90 | 122 | 8 | 1.4351<br>1.4446 | 1.3858<br>1.4178 | 24.5<br>0.0 | 32.92 | 33.15 | 3.07 | 3.04 | 19.53 | 19.66 |
| $C_2H_5SCOCF_2CF_2CF_2COOH$ | 95 | 131 | 8 | 1.4070 | .... | 25.0 | 29.58 | 29.88 | 2.13 | 2.13 | 11.28 | 10.99[e] |
| $C_2H_5SCOCF_2CF_2CF_2COCl$ | 83 | 101 | 43 | 1.4016 | .... | 25.0 | 11.72 | 11.91 (chlorine) | | | | |
|  $O{=}C{-}O{-}C{=}O$[a] $CF_2CF_2CF_2$ | 76.5 | 72 | 760 | 1.3190<br>1.3315 | 1.6541<br>1.7231 | 24.9<br>0.0 | 27.04 | 27.28 | None | None | | |
| $CF_3CF_2COCl$ | 90 | 9.5 | 760 | .... | .... | .. | 19.43 | 19.05 (chlorine) | | | | |

[a] These liquids are crystalline or glassy solids at Dry Ice temperatures. [b] Yield obtained when trifluoroacetic anhydride was used as the acylating agent. [c] Yield obtained when trifluoroacetyl chloride was used as the acylating agent. [d] Carbon hydrogen and sulfur analyses determined by Clark Microanalytical Laboratory, Urbana, Illinois. [e] Calcd. for $C_7H_6O_3SF_6$, mol. wt., 284.2; found (by saponification equivalent), 284.

ester (II) was formed in 95% yield. Conversion of II to the acid chloride (III) was accomplished in 83% yield with phosphorus pentachloride, which did not cleave the thiolester linkage. III was converted finally to IV in 90% yield by reaction with an additional mole of ethyl mercaptan. The acidic monothiolester (II) was very stable thermally, but was water-soluble and extensively hydrolyzed to perfluoroglutaric acid and ethyl mercaptan. No stable end-point, corresponding to the neutralization of the $^-COOH$ group, was obtained on titration with 0.1 $N$ sodium hydroxide solution, but excellent results were obtained for complete hydrolysis to the dibasic acid (see footnote (*e*) of Table I).

Perfluoroglutaric anhydride reacted readily with pentamethylene dimercaptan according to the scheme



$$\begin{array}{c} O{=}C{-}O{-}C{=}O \\ CF_2{-}CF_2{-}CF_2 \end{array} + HS(CH_2)_5SH \xrightarrow{100°} \underset{V}{HOOC(CF_2)_3COS(CH_2)_5SCO(CF_2)_3COOH} \xrightarrow{200°} \underset{VI}{[-SCO(CF_2)_3COS(CH_2)_5-]_n}$$

The reaction when conducted at 100° terminated with the formation of V, but when the reaction mixture was heated to over 200° for several hours, the yellow, waxy, solid polymer (VI) was formed.

The physical constants and analytical data for the new compounds prepared in these investigations are listed in Table I. Pure thiolesters of perfluoro-fatty acids have relatively slight odors which are reduced as the per cent. fluorine in the compounds increases. Pentamethylene dithiol bis-(heptafluorobutyrate) is essentially odorless. All of the thiolesters and dithiolesters were found to be insoluble in water and in potassium carbonate solution; they were practically unhydrolyzed in cold 5% aqueous potassium hydroxide solution. They could be saponified by hot alcoholic potassium hydroxide. Both the basic- and acid-catalyzed hydrolyses were demonstrated to proceed by S-acyl (step A) rather than S-alkyl fission (step B) since no thioacid was formed (negative hydrogen sulfide test) in either case.

$$ROH + C_nF_{2n+1}COSH \xleftarrow{B} C_nF_{2n+1}COSR \xrightarrow{A} C_nF_{2n+1}COOH(M^+) + RSH$$

Infrared absorption spectra are given in Figs. 1–4. The relatively weak bands at 14.1–14.42 microns for the fluorinated thiolesters are due to C–S stretching vibrations, which may be masked by the bending vibrations of the carbon skeleton. The corresponding bands for perfluoro-*n*-propyl disulfide[4] and trisulfide[4] appear at 14.71 and 14.72 $\mu$, respectively, and at 14.18 microns in diethyl dithioltetrafluorosuccinate.[1] As the per cent. sulfur in the molecule is increased, the intensity of this band increases, and there seems to be an accompanying shift to higher wave length.

In previous communications[5-8] we have noted certain distinctions in the spectra of perfluoroalkyl halides and dihalides depending on whether $-CF_3$ groups were present or absent. Additional evidence is drawn from the spectra presented herein, as well as from the spectra of other "fluorocarbon" derivatives containing different functional groups such as COOH, COOR and COCl (unpublished data) which make it possible to draw several conclusions.[9] (1) When a $CF_3$ group is attached directly to other $CF_2$ groups, *i.e.*, $CF_3{-}(CF_2)_n{-}X$ (where X = Cl, Br, I, COSR, COOH, COCl), a band of moderate to strong intensity is observed

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(4) M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 5461 (1951).

(5) M. Hauptschein and A. V. Grosse, *ibid.*, **73**, 2461 (1951).

(6) M. Hauptschein, C. S. Stokes and A. V. Grosse, *ibid.*, **74**, 848 (1952).

(7) M. Hauptschein, R. L. Kinsman and A. V. Grosse, *ibid.*, **74**, 849 (1952).

(8) M. Hauptschein, E. A. Nodiff and A. V. Grosse, *ibid.*, **74**, 1347 (1952).

(9) Since the following conclusions are, of necessity, based on a limited number of compounds, they should not be construed as final.

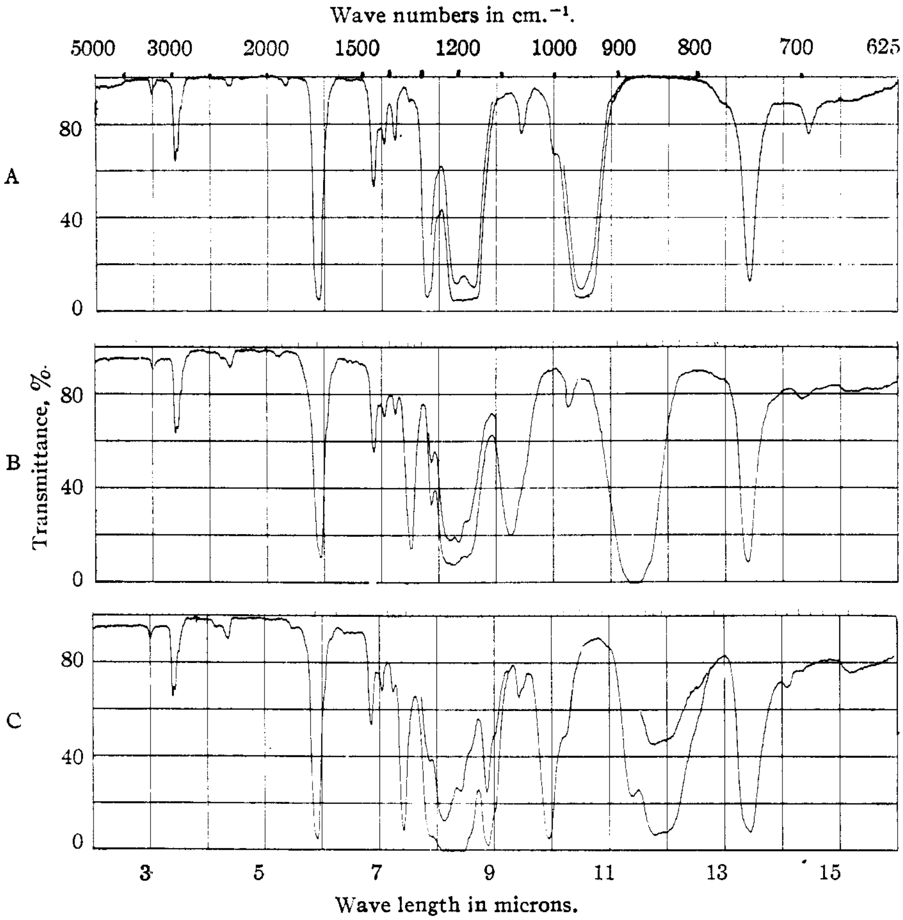

Fig. 1.—Infrared absorption spectra of ethyl thioltrifluoroacetate (A), ethyl thiolpentafluoropropionate (B) and ethyl thiol-*n*-heptafluorobutyrate (C).

at 7.33 to 7.53 $\mu$. This band is associated with C–F stretching vibrations in CF$_3$ groups. (2) When a CF$_3$ group is attached directly to a functional group, *i.e.*, CF$_3$–X, it is more difficult to reach a definite conclusion. The band at 7.33 to 7.53 $\mu$, if any, is usually weak. Another weak band is often found at 7.2 $\mu$. Certain exceptions have been noted, since CF$_3$COOEt and (CF$_3$CO)$_2$O have relatively strong bands in this wave length region. (3) In the absence of CF$_3$ groups, bands do not appear at 7.33–7.53 $\mu$; *i.e.*, in X–(CF$_2$)$_n$–X. The only exception to this which has been found in our work to date is the ring compound, perfluoroglutaric anhydride, which gives a band at 7.46 $\mu$. The above conclusions are largely in accord with the findings of Smith, Nielsen, *et al.*,[10] on the infrared spectroscopic properties of fluorocarbons and fluorinated hydrocarbons. These investigators have shown that bands in the higher frequency regions of 1340 to 1350 cm.$^{-1}$ are to be expected only of molecules possessing CF$_3$ groups and of four- and five-membered unsubstituted fluorocarbon rings. It is thus seen that some of the correlations made by these authors for the CF$_2$ and CF$_3$ groups in pure fluorocarbons which had been considered by them to be tentative, have been substantiated by the results obtained in this Laboratory on a variety of fluorocarbon derivatives.

It is instructive to consider further the infrared spectra in terms of the relationships of the stretching vibration frequencies of the carbonyl groups in esters and thiolesters of perfluoro-acids to their non-fluorinated analogs. In the case of these fluorinated oxygen esters, there is a definite shift of about 0.1–0.2 $\mu$ to shorter wave lengths relative to their non-fluorinated analogs, while in the case of the thiolesters the shift, if any, is at the most only a few hundredths of a micron in the same direction (*vide infra*). These facts may be explained as follows[11]: (1) Due to the extreme electronegativity of the fluorine atoms, a strong inductive effect ($-I_s$) is present which gives the carbonyl carbon a greater effective positive charge than in the non-fluorinated cases. As a consequence, the attractive forces between the positive carbon and negative oxygen of the carbonyl bond are enhanced, and the motion of the oxygen atom relative to the carbon atom during a vibrational cycle is diminished. Thus the force constant of the carbonyl bond is increased which is reflected in the greater frequency (decreased wave length) of the infrared band. (2) Due to the greater polarizability (lower electronegativity) of the sulfur compared to

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[10] D. C. Smith, J. R. Nielsen, *et al.*, "Spectroscopic Properties of Fluorocarbons and Fluorinated Hydrocarbons," Naval Research Laboratory Report 3567, Washington, D. C., 1949.

[11] Grateful acknowledgment is made to Dr. M. D. Stern of the Chemistry Department for helpful discussions on this subject.

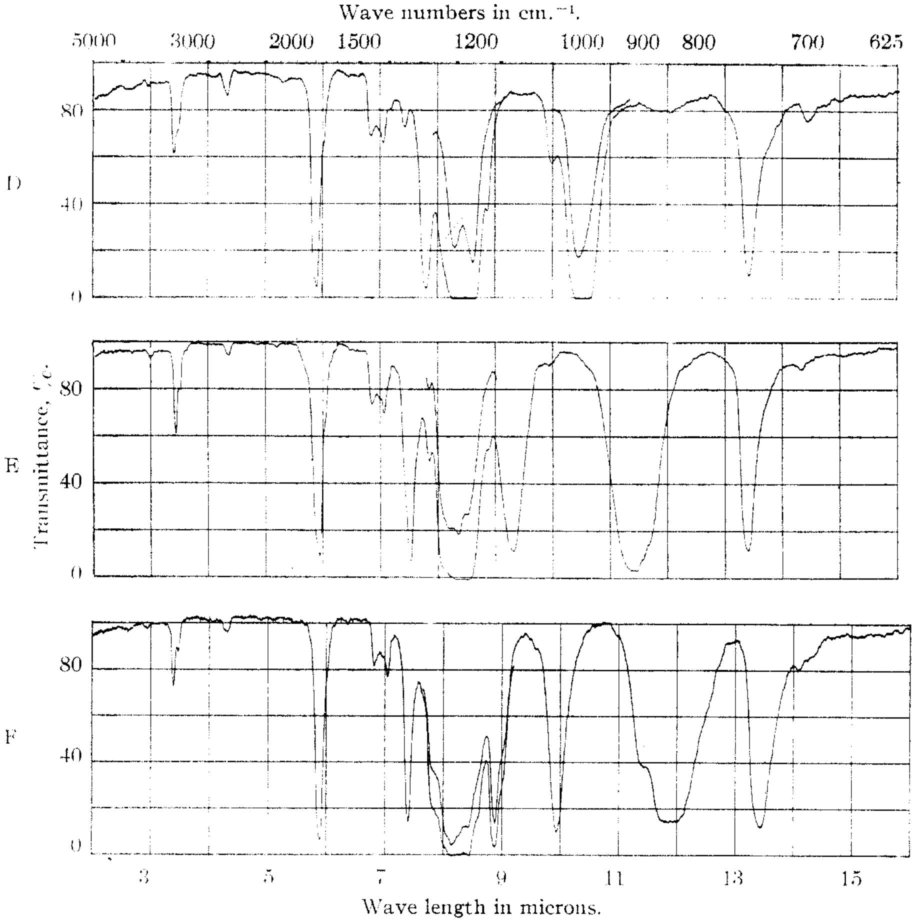

Fig. 2.—Infrared absorption spectra of pentamethylene dithiol bis-(trifluoroacetate), D, pentamethylene dithiol bis-(pentafluoropropionate), and E, pentamethylene dithiol bis-($n$-heptafluorobutyrate), F.

the oxygen atom, the positive character of the carbonyl carbon is not enhanced nearly as much in the case of fluorinated thiol esters; *i.e.*, the mobile electronic field of the alkyl sulfur atom is more "available" to the carbonyl carbon. The force constant of the carbonyl bond in fluorinated thiolesters is increased to a minor extent, if at all, so that almost no shift to lower wave length is observed. The fact that the wave length corresponding to C–S stretching vibrations is shifted from about 14.85 for ethyl thiolacetate (Fig. 4-K) to 14.42 $\mu$ for ethyl thioltrifluoroacetate (Fig. 1-A) is to be expected if the electrons of the sulfur atom in the latter are put under greater constraint.

The molar refraction measurements may be qualitatively correlated with the bond stretching evidence deduced from the infrared spectra. The refraction data, which is a measure of the polarizability, has been considered in terms of the differences in *MR* values between thiolesters and esters of "hydrocarbon" ($\Delta MR_{H-C}$) and "fluorocarbon" ($\Delta MR_{F-C}$) carboxylic acids. It has been found that these differences are of the same order of magnitude in both cases. Whereas $\Delta MR_{H-C}$ is 6.7–6.8 cc.,[12] $\Delta MR_{F-C}$ is approximately 6.7 cc. for the few cases where enough data were available for calculation. Although it is impossible to deduce from these data whether there is a net tightening of the electronic system,[13] it would seem that the degree of additional constraint in which electrons of the carbonyl bond in the fluorinated esters exist is of a similar order of magnitude as for the electrons of the C–S bond in fluorinated thiolesters.

The stretching vibration wave lengths for the carbonyl groups in esters and thiolesters of perfluorocarboxylic acids are on the average 5.6[14a] and 5.9[14b] microns, respectively. For the non-fluorinated analogs the "characteristic" carbonyl band is at 5.7–5.8 $\mu$ for esters[14c] and 5.91 (Fig. 4-K)–5.95[14c] $\mu$ for thiolesters.

Finally, it is noted (Fig. 3) that both the acid-thiolester and acid chloride thiolester show in addition to the thiolester carbonyl band, a carboxylic acid carbonyl band at 5.67 and an acid chloride carbonyl band at 5.61 $\mu$, respectively. The latter value should be compared with those for perfluoro-fatty acid chlorides: $n$-$C_3F_7COCl$, 5.61 $\mu$ (liquid),[15]

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[12] Determined from the values of A. I. Vogel, *J. Chem. Soc.*, 624 (1948), and F. Wenzel and E. E. Reid, This Journal, **59**, 1089 (1937).

[13] See K. Fajans in A. Weissberger's "Physical Methods of Organic Chemistry," 2nd ed., Vol. I, part II, Interscience Publishers, Inc., New York, N. Y., 1949, p. 1171.

[14] (a) This is an average value for several esters of monocarboxylic and dicarboxylic perfluoro-acids (unpublished work); (b) this is the average value for compounds A to G of Figs. 1–3; (c) H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Company, Inc., New York, N. Y., 1949, p. 6.

[15] M. Hauptschein and C. S. Stokes, unpublished data.

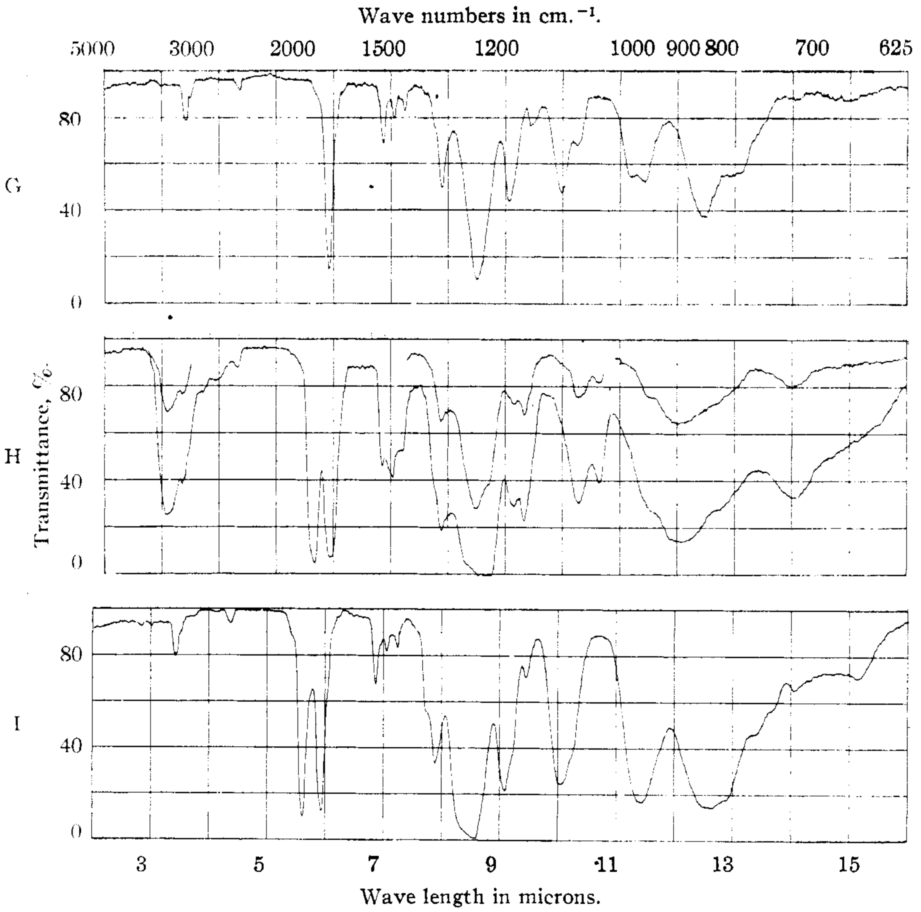

Fig. 3.—Infrared absorption spectra of diethyl dithiolhexafluoroglutarate (G), monoethyl thiolhexafluoroglutarate (H) and monoethyl thiolhexafluoroglutaryl chloride (I).

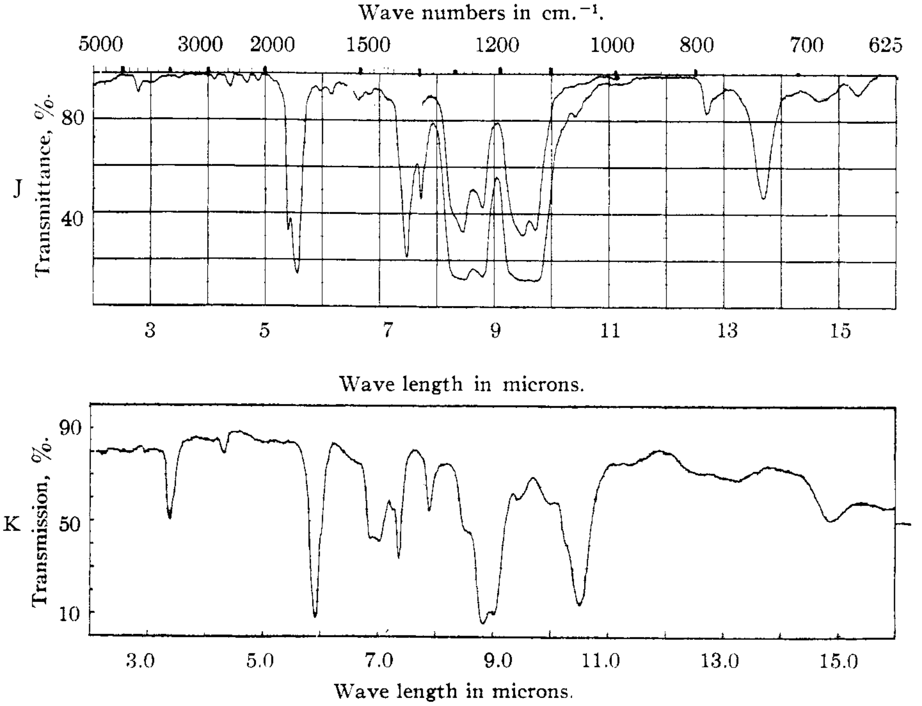

Fig. 4.—Infrared absorption spectra of perfluoroglutaric anhydride (J) and ethyl thiolacetate (K).

5.58 $\mu$ (vapor)[15]; $C_2F_5COCl$, 5.56 $\mu$ (vapor).[15] Perfluoroglutaric anhydride (Fig. 4-J) exhibits two bands at 5.40 and 5.58 $\mu$ in the liquid phase, which are shifted a few hundredths of a micron to shorter wave lengths in the vapor phase.

## Experimental

**Preparation of Perfluoroacyl Chlorides.**—Trifluoroacetyl chloride,[16] pentafluoropropionyl chloride and *n*-heptafluorobutyryl chloride[17] have been prepared in 90% yields by the reaction of the perfluoro-fatty acids (Minnesota Mining and Manufacturing Company) with excess phosphorus pentachloride. The acyl chlorides were collected in Dry Ice cooled traps connected to the system and carefully rectified. Pentafluoropropionyl chloride, b.p. 9.5°, has not been reported previously (see Table I).

Trifluoroacetic anhydride, ethyl mercaptan and pentamethylene dimercaptan were purchased from Columbia Organic Chemicals Company. Ethyl thiolacetate was prepared and the physical constants agreed with previously reported values.[18]

**Preparation of Thiolesters of Perfluoro-fatty Acids.**—Ethyl thioltrifluoroacetate, thiolpentafluoropropionate and thiolheptafluorobutyrate were prepared by dropping into ethyl mercaptan a 20–30% excess of trifluoroacetic anhydride, pentafluoropropionyl chloride and *n*-heptafluorobutyryl chloride, respectively. Since pentafluoropropionyl chloride is a gas at room temperature, it was allowed to vaporize and bubble through the mercaptan in a long, vertical, Pyrex reaction tube above which was placed a "Dry Ice refluxer." Reaction with gaseous trifluoroacetyl chloride was carried out similarly. In all cases, reaction took place at room temperature, the rate being conveniently measured (when using acid chlorides) by the hydrogen chloride evolution. To ensure completeness of reaction, the mixtures were heated at 100° for several hours. It was noted that all the preparations turned red during this treatment. Excess acid chloride or anhydride was removed by washing with 5% potassium hydroxide solution. After drying over anhydrous magnesium sulfate, the product was fractionally distilled and the yields of pure, colorless products (based on the mercaptan) are given in Table I. In a similar manner pentamethylene dithiol bis-(trifluoroacetate), bis-(pentafluoropropionate) and bis-(*n*-heptafluorobutyrate) were prepared from pentamethylene dimercaptan. The former compound was prepared twice using both trifluoroacetic anhydride and trifluoroacetyl chloride as the acylating agents.

**Reaction of *n*-Heptafluorobutyric Acid with Ethyl Mercaptan.**—Heptafluorobutyric acid (16.1 g., 50% excess) and 3.1 g. of ethyl mercaptan were heated together at 100° for 24 hours. The reaction mixture did become somewhat cloudy, but on working up this reaction, only 0.7 g. (5% yield) of ethyl thiolheptafluorobutyrate was isolated.

**Preparation of Perfluoroglutaric Anhydride.**—Perfluoroglutaric acid was prepared according to the method of Henne and Zimmerschied.[19] This acid (240.1 g., 1.0 mole), neutralization equivalent: calcd., 120.0; found, 119.8, was heated with 56.0 g. of phosphorus oxychloride for 8 hours at 150° and yielded 170 g. (76.5% yield) of perfluoroglutaric anhydride, a colorless liquid which boiled at 72° after distillation in a Podbielniak fractionating column.

**Reaction of Perfluoroglutaric Anhydride with Ethyl Mercaptan.**—Perfluoroglutaric anhydride (22.2 g., 0.1 mole) was added to 12.4 g. (0.2 mole) of ethyl mercaptan at room temperature. The reaction mixture was finally heated at 100° for several hours. Upon rectification, 27.0 g. (95.2%) of monoethyl thiolhexafluoroglutarate (II), b.p. 131° at 8 mm., was obtained. Approximately 0.1 mole of unreacted ethyl mercaptan was collected in the cold trap attached to the system.

**Reaction of Monoethyl Thiolhexafluoroglutarate (II) with Phosphorus Pentachloride.**—Monoethyl thiolhexafluoroglutaryl chloride (III), b.p. 101° at 43 mm., was prepared in 83% yield by treating II with excess phosphorus pentachloride in the usual manner.

**Reaction of Monoethyl Thiolhexafluoroglutaryl Chloride (III) with Ethyl Mercaptan.**—Diethyl dithiolhexafluoroglutarate (IV), b.p. 122° at 8 mm., was prepared in 90% yield by the reaction of III with an equimolar quantity of ethyl mercaptan in the previously described manner.

**Condensation Polymerization of Perfluoroglutaric Anhydride with Pentamethylene Dimercaptan.**—When equimolar proportions of perfluoroglutaric anhydride and pentamethylene dimercaptan react for several hours at 100°, the reaction tends to stop with formation of the highly acidic liquid thiolester V. However, when the reaction is heated for an additional number of hours at temperatures of greater than 200°, further reaction is forced between the carboxylic acid end-groups of V and the unreacted dithiol. A yellow waxy condensation polymer, soluble in the usual organic solvents, is formed. Qualitative elementary analysis confirmed the presence of fluorine, sulfur and carbon.

**Infrared Absorption Spectra.**—Infrared spectra were run on the Baird Associates infrared double beam recording spectrophotometer of Samuel P. Sadtler and Sons, Inc., Philadelphia. The spectra were determined in the liquid phase in a sodium chloride cell. The lower curves are for cell thickness of 0.01 mm., the upper curves for cell thickness of *ca.* 0.005 mm.

PHILADELPHIA, PENNA.

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[16] J. H. Simons and E. O. Rambler, THIS JOURNAL, **65**, 389 (1943).

[17] W. H. Pearlson in J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 502.

[18] J. R. Schaefgen, THIS JOURNAL, **70**, 1308 (1948).

[19] A. L. Henne and W. J. Zimmerschied, *ibid.*, **67**, 1235 (1945).