overnight at 98°. Due to a partial leak only about 550 g. of liquid product boiling above room temperature was collected in addition to a considerable amount of solid iodine. This liquid was washed with sodium thiosulfate solution, dried over Drierite and distilled through a fractionating column. There was collected 40 g. of material boiling at 35–78°, $n^{25}D$ 1.337, consisting mostly of a mixture of CF$_3$-CFClCF$_2$Cl, the chlorine adduct of perfluoropropene, and C$_3$ClF$_6$I, and 437 g. of C$_3$ClF$_6$I, b.p. 78–78.5°, $n^{25}D$ 1.375. An additional 37 g. of residue consisted mostly of C$_3$ClF$_6$I. The 437-g. fraction of ICl adduct C$_3$ClF$_6$I was shown by V.L.P.C. to consist of 91.5% CF$_3$CFICF$_2$Cl and 8.5% CF$_3$CFClCF$_2$I. The pure isomers were separated by preparative chromatography.

CF$_3$CFICF$_2$Cl: $n^{25}D$ 1.3757, ultraviolet maximum in isoöctane at 277.5 mμ; principal infrared absorption bands (vapor) at 7.89vs, 8.07vssh, 8.14vvs, 8.37m, 8.62s, 8.72 msh, 8.94vs, 9.46s, 9.69vs, 10.80vs, 11.13vs, 11.44s, 11.88vs, 17.7vs, 13.64m, 14.0s μ.

CF$_3$CFClCF$_2$I: $n^{25}D$ 1.3741, ultraviolet maximum in isoöctane at 273 mμ; principal infrared absorption bands (vapor) at 7.84vs, 8.07vvs, 8.46m, 8.68s, 8.90s, 9.58s, 9.85m, 10.35vs, 11.59m, 12.42vs, 12.8m, 13.6m, 14.17vs μ.

Anal. Calcd. for C$_3$ClF$_6$I: C, 11.53; Cl, 11.35; I, 40.63. Found for CF$_3$CFICF$_2$Cl: C, 11.54; Cl, 11.35; I, 40.51. Found for CF$_3$CFClCF$_2$I: C, 11.38; Cl, 11.11; I, 40.04.

Separation of (CF$_3$)$_2$CFCF$_2$I from CF$_3$CF$_2$CFICF$_3$.—The thermal reaction of CF$_3$I with perfluoropropene was carried out at 195° in a stainless steel autoclave by the procedure previously described.[9] A middle cut of the 1:1 adduct, b.p. 64°, was analyzed by V.L.P.C. and shown to consist of 92% CF$_3$CF$_2$CFICF$_3$ and 8% (CF$_3$)$_2$CFCF$_2$I. The pure isomers were separated by preparative chromatography.

CF$_3$CF$_2$CFICF$_3$: $n^{25}D$ 1.3290, ultraviolet maximum in isoöctane at 279 mμ; principal infrared absorption bands for vapor at 7.43m, 7.55s, 7.81vs, 7.99vvs, 8.07vssh, 8.13-vssh, 8.28vs, 8.47s, 8.95s, 9.22m, 9.32s, 9.54m, 10.67s, 11.18s, 11.38m, 11.59s, 12.20s, 13.42s, 13.81s, 14.15s μ.

(CF$_3$)$_2$CFCF$_2$I: $n^{25}D$ 1.3330, ultraviolet maximum in isoöctane at 275mμ; principal infrared absorption bands for vapor at 7.71vs, 7.90vvs, 8.44ssh, 8.47s, 8.72s, 8.82ssh, 9.53s, 9.80m, 10.11vs, 11.54m, 12.30vs, 13.36s, 13.90s μ.

Anal. Calcd. for C$_4$F$_9$I: C, 13.9; I, 36.7. Found for CF$_3$CF$_2$CFICF$_3$; C, 14.0; I, 37.2. Found for (CF$_3$)$_2$CFCF$_2$I: C, 13.9.

Separation of CF$_3$CF$_2$CF$_2$CF(CF$_3$)CF$_2$I from CF$_3$CF$_2$CF$_2$-CF$_2$CFICF$_3$.—The thermal reaction of CF$_3$CF$_2$CF$_2$I with perfluoropropene was carried out at 190–194° in a stainless steel autoclave by the reported procedure.[9] A middle cut of the 1:1 adduct, b.p. 111°, was analyzed by V.L.P.C. and shown to consist of 98% CF$_3$CF$_2$CF$_2$CF$_2$CFICF$_3$ and 2% CF$_3$CF$_2$CF$_2$CF(CF$_3$)CF$_2$I. The pure isomers were separated by preparative chromatography.

CF$_3$CF$_2$CF$_2$CF$_2$CFICF$_3$: $n^{25}D$ 1.3287, ultraviolet maximum in isoöctane at 280 mμ, principal infrared absorption bonds for vapor at 7.38s, 7.71msh, 7.83vs, 8.01vvs, 8.12vssh, 8.21vssh, 8.73s, 8.92m, 9.30m, 9.56m, 10.36m, 10.54m, 10.88m, 11.22s, 12.0m, 12.5m, 12.7m, 13.52m, 13.77m, 14.17s, 14.74s μ. The liquid infrared spectrum was identical with that[13] for the known analyzed adduct.[9]

CF$_3$CF$_2$CF$_2$CF(CF$_3$)CF$_2$I: Sufficient sample was separated to take the infrared spectrum only. Although this structure, therefore, cannot be considered to be unequivocally proved, we believe it to be correct by virtue of the characteristic elution time ratios (Table I) which are consistent with the ratios obtained with the pair of C$_4$F$_9$I isomers. The principal infrared bands for the vapor were at 7.43s, 7.75vs, 7.93vvs, 8.12vs, 8.22vssh, 8.53s, 8.68vs, 8.84s, 8.93ssh, 9.56s, 9.97s, 10.10s, 10.8m, 11.2m, 11.4m, 11.7m, 11.8s, 12.26m, 12.63s, 12.89m, 13.39s, 13.64s, 13.98s, 14.2m, 14.6m μ, which is also consistent with the assigned structure.

Vapor–Liquid Partition Chromatography.—A Perkin–Elmer model 154 Vapor Fractometer was used.

Infrared Spectra.—A Perkin–Elmer Infracord model 137 was used. The individual spectrograms were calibrated immediately after they were run using a polystyrene film as a standard. The absorption wave lengths are believed accurate to ±0.02 μ.

Ultraviolet Spectra.—A Beckman ratio recording spectrophotometer, model DK-2, was used. The wave length accuracy was checked by means of the mercury-in-quartz arc lamp.

(13) M. Hauptschein. M. Braid and F. E. Lawler. *J. Am. Chem. Soc.*, **79**, 6248 (1957).

Fluorocarbon Halosulfates and a New Route to Fluorocarbon Acids and Derivatives. I. Polyfluoroalkyl Chlorosulfates[1]

BY MURRAY HAUPTSCHEIN AND MILTON BRAID

Novel reactions of chlorosulfonic acid with fluorocarbon iodides have been discovered by which fluorocarbon chlorosulfates, a new class of compounds, or fluorocarbon chlorides are prepared. The physical and chemical properties of C$_3$F$_7$OSO$_2$Cl, C$_3$F$_7$[CF$_2$CF(CF$_3$)]$_4$[CF$_2$CF$_2$]nOSO$_2$Cl, C$_2$F$_5$CF(CF$_3$)[CH$_2$CF$_2$]$_3$OSO$_2$Cl, and similar chlorosulfates are presented. The mechanism of chlorosulfate formation is discussed. Convenient one-step syntheses of carboxylic acids and derivatives from these chlorosulfates have been accomplished. Thus C$_2$F$_5$COX, C$_3$F$_7$[CF$_2$CF(CF$_3$)]$_4$[CF$_2$CF$_2$]$_{n-1}$CF$_2$COX, C$_2$F$_5$CF(CF$_3$)-[CH$_2$CF$_2$]$_2$CH$_2$COX, etc. where X = OH, OR or NH$_2$, have been synthesized by direct reaction of the corresponding chlorosulfate (cited above) with water, alcohol or ammonia. The mechanism of these interesting transformations is discussed.

The use of the versatile reagent chlorosulfonic acid in sulfonation, sulfation, chlorosulfonation, and chlorosulfation reactions is well known in hydrocarbon chemistry. These reactions with aromatic compounds, alcohols, etc., are generally inapplicable to fluorocarbon chemistry since the fluorocarbon analogs either are unknown, *e.g.*, perfluoro alcohols, or have no hydrogens available for reaction, *c.g.*, perfluoro aromatics. It was evident, therefore, that if this reagent were to find general usefulness in the field of fluorocarbon chemistry, reactions in hitherto unexplored areas would have to be investigated. For this new approach it was considered promising to examine as reactants fluorocarbon iodides[2] which were currently under investigation in this Laboratory and

(2) No reactions of hydrocarbon alkyl halides, including the iodides with chlorosulfonic acid have been reported.

which have been shown to undergo various unusual reactions.[3,4]

The present paper reports the discovery of a novel reaction of fluorocarbon iodides with chlorosulfonic acid, of which the products comprise a new class of fluorocarbon derivatives, the chlorosulfates, RCF_2OSO_2Cl, and describes new and improved routes to fluorocarbon carboxylic acids and derivatives.
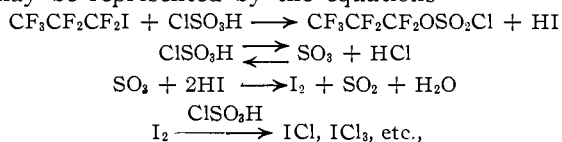
By simple hydrolysis, ammonolysis and alcoholysis, the fluorocarbon chlorosulfates are readily converted to carboxylic acids, carboxylic acid amides and esters, respectively.

Accordingly, many fluorocarbon carboxylic acids and derivatives which have hitherto been difficult to prepare, requiring multi-step syntheses, or unattainable by presently known routes can now be realized. In particular, fluorocarbon telomer iodides prepared from readily available olefins can now be converted into a variety of functional derivatives.

Primary perfluoroalkyl iodides react with chlorosulfonic acid to form the corresponding chlorosulfates. In addition, some of the corresponding perfluoroalkyl chlorides may be formed.

Thus, the reaction of 1-iodoperfluoropropane with more than a tenfold excess of chlorosulfonic acid in a sealed tube at 130° for 65 hours produced 89% of perfluoropropyl chlorosulfate, $CF_3CF_2CF_2OSO_2Cl$, and 11% of 1-chloroperfluoropropane. Iodine chlorides and sulfur dioxide were the inorganic products ultimately formed in the reaction. At temperatures above 150° the relative proportion of C_3F_7Cl was increased, while at temperatures below 100° very little reaction occurred; the chlorosulfate was the only product found.

The formation of perfluoropropyl chlorosulfate may be represented by the equations

$$CF_3CF_2CF_2I + ClSO_3H \longrightarrow CF_3CF_2CF_2OSO_2Cl + HI$$

$$ClSO_3H \rightleftharpoons SO_3 + HCl$$

$$SO_3 + 2HI \longrightarrow I_2 + SO_2 + H_2O$$

$$I_2 \xrightarrow{ClSO_3H} ICl, ICl_3, etc.,$$

It is possible that $C_3F_7OSO_2Cl$ is the precursor of C_3F_7Cl. As noted above, under more vigorous reaction conditions the conversion to chloride was increased at the expense of the chlorosulfate. However, because of the high thermal stability of perfluoroalkyl chlorosulfates (vide infra), it is more likely that C_3F_7Cl is formed at least in part by an independent chlorination route, which is further discussed below in connection with reactions of secondary iodides.

Alternative reactions between C_3F_7I and chlorosulfonic acid may be envisioned in which ICl or IOH is eliminated with the formation of a C–S bond, e.g.

$$C_3F_7I + ClSO_3H \longrightarrow C_3F_7SO_3H + ICl \text{ or}$$
$$C_3F_7SO_2Cl + HOI, etc.$$
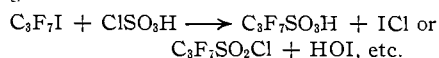
However, fluorocarbon sulfonyl chlorides or sulfonic acids were not found among the reaction products in the present work.
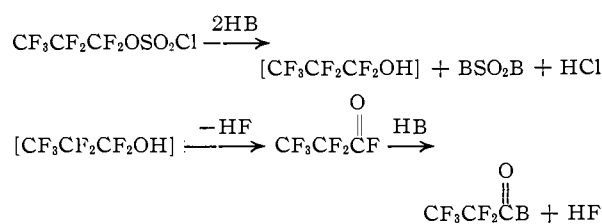
(3) M. Hauptschein, M. Braid and F. E. Lawlor. J. Am. Chem. Soc., **79**, 6248 (1957).

(4) M. Hauptschein and M. Braid. ibid., **80**, 853 (1958).

It was, of course, recognized that the differences in the theoretical analytical values for the chlorosulfate, $C_3F_7OSO_2Cl$, and the sulfonyl chloride, $C_3F_7SO_2Cl$, are not great, and that it would be difficult to distinguish a priori between the physical properties of these two structures. Also, the possibility of a chlorosulfite structure, C_3F_7OSOCl, from the reaction $C_3F_7I + ClSO_3H \rightarrow C_3F_7OSOCl + HOI$, could not be ignored in a rigorous structure proof.

As will be shown below, interpretations of ultraviolet and infrared absorption spectra and particularly of various chemical transformations, together with excellent analytical characterization, established unequivocally the chlorosulfate structure.

Perfluoropropyl chlorosulfate has been found to react with water, sodium hydroxide, ethanol and ammonia to form products that are accounted for by the scheme

$$CF_3CF_2CF_2OSO_2Cl \xrightarrow{2HB} [CF_3CF_2CF_2OH] + BSO_2B + HCl$$

$$[CF_3CF_2CF_2OH] \xrightarrow{-HF} CF_3CF_2\overset{O}{\overset{\|}{C}}F \xrightarrow{HB} CF_3CF_2\overset{O}{\overset{\|}{C}}B + HF$$

When B corresponded to OH, ONa, OC_2H_5 and NH_2, the products, C_2F_5COOH, C_2F_5COONa, $C_2F_5COOC_2H_5$ and $C_2F_5CONH_2$, respectively, were formed in nearly quantitative yield. With a large excess of reagent, $C_2F_5\overset{O}{\overset{\|}{C}}B$ is the only fluorocarbon derivative isolated. Of course when B is ONa or NH_2 the inorganic acids depicted in the scheme are in the form of their respective salts.

These reactions confirm unambiguously the chlorosulfate structure possessing CF_2–O–S linkages. The known properties of fluorocarbon sulfonyl chlorides which are hydrolyzed somewhat more slowly to the corresponding sulfonic acids without the liberation of even traces of fluoride ion[5] eliminate from consideration the possibility of CF_2–S–O linkages. Likewise the formation of sodium sulfate exclusively rather than sodium sulfite on basic hydrolysis eliminates perfluoropropyl chlorosulfite, C_3F_7OSOCl, as an alternative structure.

The reaction with water (sodium hydroxide) was carried out quantitatively. It was found that one mole of $C_3F_7OSO_2Cl$ reacted with six equivalents of alkali with formation of two equivalents of fluoride ion and one equivalent of chloride ion, in agreement with the scheme outlined above. These results demonstrate the validity of the above scheme for the other reactions studied.

It is of interest to note that hydrolysis of the chlorosulfate is not as rapid as might be predicted from the structure. While the rate of hydrolysis was not quantitatively measured, $C_3F_7OSO_2Cl$ remained partially unhydrolyzed after several hours contact with water or after standing overnight in the acidic aqueous mixture after addition of

(5) R. N. Haszeldine and J. M. Kidd. J. Chem. Soc., 2901 (1955).

water to the crude chlorosulfonic acid reaction mixture. The hydrolysis was, of course, very rapid in dilute aqueous sodium hydroxide solution.

The reaction with chlorosulfonic acid to form chlorosulfates is general for primary perfluoroalkyl iodides and has been successfully used with telomer iodides of formula $C_3F_7[CF_2CF(CF_3)]_n$-$[CF_2CF_2]_mI$. The latter are formed by the thermal reaction of $CF_3CF_2CF_2[CF_2CF(CF_3)]_nI^6$ with tetrafluoroethylene.

Thus, $C_3F_7[CF_2CF(CF_3)]_4[CF_2CF_2]_{12av}I$ was obtained in good conversion from the reaction of $C_3F_7[CF_2CF(CF_3)]_4I$ with $CF_2=CF_2$ at 190°. Conversion to the corresponding chlorosulfates was conveniently effected by reaction of the telomer iodides with chlorosulfonic acid at 150° for 17 hours.

It is interesting to note that no decomposition was observed during distillation of the chlorosulfates $C_3F_7[CF_2CF(CF_3)]_4[CF_2CF_2]_nOSO_2Cl$ where $n = < 9$ to > 25 despite ultimate heating to above 400°.

The chlorosulfates of this series undergo the chemical transformations discussed previously for n-perfluoropropyl chlorosulfate. For example, by reactions with anhydrous ammonia, $C_3F_7[CF_2-CF(CF_3)]_4[CF_2CF_2]_{9av}OSO_2Cl$ was directly converted to the amide $C_3F_7[CF_2CF(CF_3)]_4[CF_2-CF_2]_{8av}CF_2CONH_2$.

It is apparent that a general, convenient, one-step route to many types of fluorocarbon carboxylic acid derivatives by direct reaction of alcohols or amines with a primary perfluoroalkyl chlorosulfate is now possible.

The reaction with chlorosulfonic acid has been extended to another type of fluorocarbon iodide, $R(CH_2CF_2)_nI$. Examples of these telomer iodides have been prepared via thermal reactions of 1,1-difluoroethylene employing CF_3CFICF_2Cl and $C_2F_5CFICF_3$ as reactant iodides.[7] Chlorosulfonic acid was found to react vigorously with $C_2F_5CF(CF_3)(CH_2CF_2)_3I$ and $CF_3CF(CF_2Cl)(CH_2-CF_2)_{4.5av}I$ at temperatures as low as 0°. The reasons for the increased reactivity of a $-CH_2-CF_2I$ group relative to the completely fluorinated primary alkyl iodide, $-CF_2CF_2I$, have not been completely established. It was certainly remarkable to observe the immediate liberation of crystalline iodine and sulfur dioxide when a difluoroethylene telomer iodide was added to an excess of chlorosulfonic acid at 0°.

$$C_2F_5CF(CF_3)(CH_2CF_2)_3I + ClSO_3H \longrightarrow$$
$$C_2F_5CF(CF_3)(CH_2CF_2)_3OSO_2Cl + HI$$
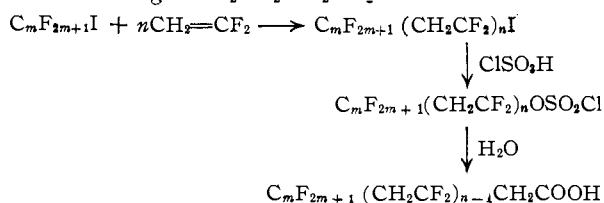$$2HI + SO_3 \longrightarrow I_2 + SO_2 + H_2O$$
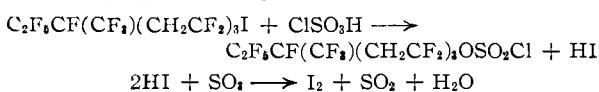
The chlorosulfates of structure $R(CH_2CF_2)_n$-OSO_2Cl are readily converted to the carboxylic acids of the type $R(CH_2CF_2)_{n-1}CH_2COOH$ by hydrolysis. This represents the most satisfactory general method for preparing 1,1-dihydroperfluoroalkyl carboxylic acids and derivatives (when $n = 1$) and, of particular importance, affords the

(6) See M. Hauptschein, M. Braid and F. E. Lawlor, *J. Am. Chem. Soc.*, **79**, 2549 (1957), for details on the synthesis of telomer iodides of perfluoropropene.

(7) (a) M. Hauptschein, M. Braid and F. E. Lawlor, *ibid.*, **80**, 846 (1958); (b) M. Hauptschein, M. Braid and A. H. Fainberg, *ibid.*, **83**, 2495 (1961).

first route to carboxylic acid derivatives possessing the recurring $-CH_2CF_2CH_2CF_2-$ structure.[7]

$$C_mF_{2m+1}I + nCH_2=CF_2 \longrightarrow C_mF_{2m+1}(CH_2CF_2)_nI$$
$$\downarrow ClSO_3H$$
$$C_mF_{2m+1}(CH_2CF_2)_nOSO_2Cl$$
$$\downarrow H_2O$$
$$C_mF_{2m+1}(CH_2CF_2)_{n-1}CH_2COOH$$

While the rate of hydrolysis of the chlorosulfate with water alone is slow, there is a marked increase in rate in the presence of sodium bicarbonate. Use of strong alkali, however, resulted in loss of hydrogen fluoride with formation of conjugated acids; e.g., $C_2F_5CF(CF_3)CH_2CF_2CH_2CF=CHC-OOH$ and $C_2F_5CF(CF_3)CH_2CF=CHCF=CHCO-OH$ are possible.

The chlorosulfates, $R(CH_2CF_2)_nOSO_2Cl$, are convenient intermediates for the synthesis of esters or amides, in which the α-carbon atom is substituted with hydrogens.[8] Without the necessity of isolating the parent carboxylic acids, these derivatives are obtainable directly from the crude chlorosulfates by reaction with the appropriate alcohol or amine.

Secondary perfluoroalkyl iodides are converted mainly to the corresponding secondary perfluoroalkyl chlorides under the reaction conditions investigated. However, at the lower temperatures studied, evidence was obtained for the formation of the secondary chlorosulfates. Thus at 148° in a sealed tube 2-iodoperfluorohexane was converted to 2-chloroperfluorohexane in almost quantitative yield by reaction with chlorosulfonic acid. At 95° there was obtained mainly the chloride in low conversion and small amounts of the chlorosulfate, $C_4F_9CF(OSO_2Cl)CF_3$. These findings suggest that the chlorosulfate may be a precursor of the chloride. Displacement of the chlorosulfate ester group by chloride ion is possible.

The novel chlorinating action of chlorosulfonic acid is probably not due to sulfuryl chloride which may be formed in situ.[9a] This possibility, however, has not been completely eliminated.[9b]

Another more likely route to the chloride may be via chlorination by the iodine chlorides, particularly ICl_3 (serving as a source of available chlorine) produced by reaction of iodine with excess chlorosulfonic acid.

$$I_2 + 2ClSO_3H \longrightarrow 2ICl + H_2SO_4 + SO_2$$
$$ICl + 2ClSO_3H \longrightarrow ICl_3 + H_2SO_4 + SO_2$$
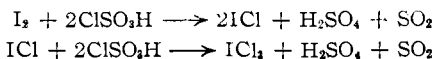
It would appear that the use of chlorosulfonic acid as a chlorinating agent in reactions of the above type may offer unique advantages when the use of gaseous chlorine is less desirable.

(8) For related compounds, see (a) M. Hauptschein, C. S. Stokes and E. A. Nodiff, *J. Am. Chem. Soc.*, **74**, 4005 (1952); (b) M. Hauptschein, J. F. O'Brien, C. S. Stokes and R. Filler, *ibid.*, **75**, 87 (1953); (c) R. Filler, J. F. O'Brien, J. V. Fenner and M. Hauptschein, *ibid.*, **75**, 966 (1953); (d) R. Filler, J. V. Fenner, C. S. Stokes, J. F. O'Brien and M. Hauptschein, *ibid.*, **75**, 2693 (1953).

(9) (a) P. Behrend, *Ber.*, **8**, 1004 (1875), quantitatively converted chlorosulfonic acid to sulfuryl chloride by heating the former for 12 hours at 170–180° in a sealed tube. (b) A single attempt to treat 2-iodoperfluorohexane with sulfuryl chloride in the absence of chlorosulfonic acid or other possible catalysts in a sealed tube at 100–115° gave only a trace of 2-chloroperfluorohexane.

Ultraviolet and Infrared Spectra of Chlorosulfates.

The ultraviolet spectrum of the typical fluorocarbon chlorosulfate, $C_3F_7OSO_2Cl$, showed a strong absorption maximum at 203 mμ in the vapor phase and at 218 mμ in isoöctane solution; both the vapor and liquid spectra exhibited slight general absorption at 260–290 mμ with a maximum at 275 mμ. These data clearly distinguish the chlorosulfate from the sulfonyl chloride, $C_3F_7SO_2Cl$, which had absorption maxima at 210, 220, 230 and 240 mμ.[5]

The infrared spectrum of $C_3F_7OSO_2Cl$ had an absorption band at 6.82 μ (vapor) and at 6.89 μ (liquid) which is undoubtedly associated with the asymmetrical stretching vibration of the "sulfone" $-SO_2-$group.[10] This eliminates the chlorosulfite, C_3F_7OSOCl, (with a "sulfoxide" $-SO-$group) which should not have a band at 6.8–6.9 μ, from consideration.

The infrared spectra of the series $C_3F_7[CF_2CF-(CF_3)]_4[CF_2CF_2]_nOSO_2Cl$ have a band at 6.85 μ (shoulder at 6.94) which is assigned to the $-OSO_2-$group. For the series $C_2F_5CF(CF_3)(CH_2CF_2)_n-OSO_2Cl$ the corresponding band was at 6.94 μ.

Experimental[11]

Thermal Reaction of 1-Iodoperfluoropropane with Chlorosulfonic Acid.—Fifty grams (0.429 mole) of chlorosulfonic acid and 11.8 g. (0.0399 mole) of 1-iodoperfluoropropane were sealed under a dry high-purity nitrogen atmosphere in a 70-cc. heavy-wall Pyrex ampule. The tube was shaken and heated at a temperature of 130° for 65 hours. The tube contents were a mixture of dark liquid and orange crystals of ICl_3. After cooling in Dry Ice, the ampule was opened and warmed to room temperature. The volatiles evolved during warming were passed through aqueous neutral potassium permanganate solution to remove sulfur dioxide, dried over Drierite, and finally condensed in a refrigerated trap. There was collected in the latter 0.9 g. (0.0044 mole, 11% yield and conversion) of n-C_3F_7Cl, identified by its infrared spectrum.[12] The liquid portion remaining in the tube was distilled in a small Vigreux unit from which there was obtained 10.7 g. (89% yield and conversion) of crude n-perfluoropropyl chlorosulfate, b.p. 66–70°, shown by infrared spectra to contain minor amounts of SO_2Cl_2. A similar fraction from another run, after washing with water, was redistilled, and the fraction b.p. 80°, $n^{24}D$ 1.3124, for which the infrared spectrum matched that of the fraction discussed above except for the impurity bands in the former, was analyzed.

Anal. Calcd. for $C_3F_7O_3SCl$: C, 12.7; F, 46.7; S, 11.3; Cl, 12.5. Found: C, 12.6; F, 46.6; S, 11.4; Cl, 12.5.

From another run in which 15 g. (0.0507 mole) of 1-iodoperfluoropropane and 25 g. (0.215 mole) of chlorosulfonic acid were heated in a sealed tube at 155° for 2 hours with shaking, there were obtained 4.5 g. (46% yield, 43% conversion) of C_3F_7Cl and 7 g. (52% yield, 49% conversion) of $C_3F_7OSO_2Cl$, and 0.9 g. of C_3F_7I was recovered.

Finally, a mixture of 15 g. of C_3F_7I and 25 g. of $ClSO_3H$ was heated in a sealed tube at 95° with shaking for 17 hours. Only unreacted C_3F_7I shown by infrared spectroscopic analysis to contain a small amount (*ca.* 5% conversion, estimated) of $C_3F_7OSO_2Cl$ was obtained. No C_3F_7Cl was found.

Reaction of n-Perfluoropropyl Chlorosulfate. (a) Hydrolysis.—To 0.2 g. (0.0007 mole) of $C_3F_7OSO_2Cl$ in 2 ml. of water, there was added small portions of 10% aqueous NaOH solution until the mixture remained basic. Water

was removed by evaporation on a steam-bath and the salts remaining after further drying in an oven were extracted in a Soxhlet apparatus with anhydrous ether. After removal of the ether, there was obtained white crystals, shown by the infrared spectrum[13] to be pure C_2F_5COONa in practically quantitative yield.

The ether-insoluble salt residue showed no C—F or C=O absorption in the infrared spectrum. Qualitative analysis, infrared and X-ray diffraction showed the presence of sodium sulfate, sodium chloride and sodium fluoride and established the absence of Na_2SO_3.

In an analytical procedure a sample of $C_3F_7OSO_2Cl$ was hydrolyzed in excess standard aqueous sodium hydroxide. Aliquots of the aqueous solution were backtitrated with standard hydrochloric acid and also analyzed for F^- and Cl^-. There were consumed 6 equivalents of NaOH per mole of $C_3F_7OSO_2Cl$, and there were produced 2 equivalents of fluoride and 1 equivalent of chloride per mole of chlorosulfate. A balanced equation for the hydrolysis is

$$CF_3CF_2CF_2OSO_2Cl + 6NaOH \longrightarrow$$
$$CF_3CF_2COONa + 2NaF + Na_2SO_4 + NaCl + 3H_2O$$
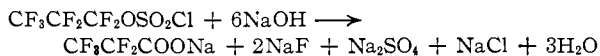
(b) Ammonolysis.—Anhydrous ammonia was passed for 10 minutes into a solution of 1 g. (0.0035 mole) of $C_3F_7OSO_2Cl$ in 25 ml. of anhydrous ether at $-75°$ while shaking. The reaction mixture was allowed to warm slowly to room temperature to boil out excess ammonia. The remaining solution was filtered to remove ammonium salts and the filtrate was evaporated. There remained 0.7 g. of slightly yellow crystals, m.p. 91–93°. After one recrystallization from 1,1,2-trichlorotrifluoroethane there was obtained 0.6 g. (100%) of the spectroscopically pure amide, $C_2F_5CONH_2$, m.p. 93.5–94.5° (uncor.).[14]

(c) Esterification.—To 2.8 g. (0.0098 mole) of $C_3F_7OSO_2Cl$ was added 1 g. (0.022 mole) of absolute ethanol. After the ensuing vigorous reaction had subsided, the reaction mixture was refluxed in a heating bath at 80° for 1 hour. During refluxing, formation of an immiscible layer and etching of the glass were observed. The lower layer was washed with dilute aqueous $NaHCO_3$ and dried with Drierite. After removal of the drying agent, there remained 2 g. of colorless fragrant liquid shown by infrared spectroscopic analysis to consist of 1.7 g. (0.0088 mole) of $C_2F_5COOC_2H_5$ (100% yield, 90% conversion) and 0.3 g. (0.001 mole) of unreacted $C_3F_7OSO_2Cl$.

Thermal Reaction of Perfluoro-4,6,8-trimethyl-2-iodododecane with Tetrafluoroethylene.—A Monel autoclave, approximately 140 cc., containing 40 g. (0.0446 mole) of $C_3F_7[CF_2CF(CF_3)]_4I$ was sealed, evacuated, and cooled to $-195°$. Forty grams (0.40 mole) of tetrafluoroethylene was admitted to the autoclave by gaseous transfer *in vacuo*. The reaction mixture was heated while shaking for 18 hr. at a temperature of 190° during which the pressure dropped from 1400 p.s.i. (est.) to below 50 p.s.i. From this reaction there were recovered 1 g. of olefin and 8 g. of $C_3F_7-[CF_2CF(CF_3)]_4I$. A total of 70 g. (75% conversion) of white soft solid, $C_3F_7[CF_2CF(CF_3)]_4[CF_2CF_2]_nI$ where $n =$ 12av containing $n < 9$ to >25 (characterized as chlorosulfates), melting range 44–150° (clear melt), was finally collected from the autoclave.

Anal. Calcd. for $C_{39}F_{79}I$: C, 22.3; F, 71.6. Found: C, 22.6; F, 70.2.

Reaction of $C_3F_7[CF_2CF(CF_3)]_4(CF_2CF_2)_{12av}I$ with Chlorosulfonic Acid.—Twenty-five grams (0.215 mole) of chlorosulfonic acid and 14.5 g. (0.0069 mole) of $C_3F_7[CF_2CF-(CF_3)]_4[CF_2CF_2]_{12av}I$ were sealed under a dry nitrogen atmosphere in a 70-cc. heavy-wall Pyrex ampule and heated at 150° for 17 hr. with shaking. The tube was cooled in Dry Ice (crystals of ICl_3 precipitated) and opened. The acid liquid was decanted and the soft white solid remaining was drained dry under nitrogen. Twelve grams (84% conversion) of the chlorosulfate, $C_3F_7[CF_2CF(CF_3)]_4-[CF_2CF_2]_{12av}OSO_2Cl$, was obtained, and a 7.5-g. aliquot was distilled in a small Vigreux unit at *ca.* 0.1 mm. pressure to effect the separation of the following fractions: (1) b.p. 120–142° (mainly 135–140°), 1.8 g. (28 wt.%) of $C_3F_7-[CF_2CF(CF_3)]_4[CF_2CF_2]_{9av}OSO_2Cl$, a white opalescent vis-

(10) R. Vogel-Hogler, *Acta Phys. Austr.*, **1**, 323 (1947); K. C. Schreiber, *Anal. Chem.*, **21**, 1168 (1949); and N. S. Ham and A. N. Hambly, *Austral. J. Chem.*, **6**, 33 (1953); and ref. 5, discuss infrared and Raman spectra of oxy-sulfur compounds.

(11) Microanalyses were performed by the Analytical Department, Pennsalt Chemicals Corp., and the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(12) M. Hauptschein, E. A. Nodiff and A. V. Grosse, *J. Am. Chem. Soc.*, **74**, 1347 (1952).

(13) D. G. Weiblen in "Fluorine Chemistry," edited by J. H. Simons, Academic Press, Inc., New York, N. Y., 1954, p. 491.

(14) D. R. Husted and A. H. Ahlbrecht, *J. Am. Chem. Soc.*, **75**, 1605 (1953).

cous oil. *Anal.* Calcd. for $C_{33}F_{67}O_3SCl$: C, 22.2; F, 71.3; S, 1.8; Cl, 2.0. Found: C, 22.5; F, 70.6; S, 1.8; Cl, 2.0. (2) B.p. 180–190°, 1.8 g. (28 wt.%) of $C_3F_7(CF_2-CF(CF_3)]_4[CF_2CF_2]_{11av}OSO_2Cl$, a white soft wax. *Anal.* Calcd. for $C_{37}F_{75}O_3SCl$: C, 22.4; F, 71.8; S, 1.6; Cl, 1.8. Found: C, 22.4; F, 72.4; S, 1.6; Cl, 1.8. (3) B.p. 190–200°, 1.4 g. (21 wt. %) of $C_3F_7[CF_2CF(CF_3)]_4-[CF_2CF_2]_{13av}OSO_2Cl$, a white wax. *Anal.* Calcd. for $C_{41}-F_{83}O_3SCl$: C, 22.5; F, 72.2; S, 1.5; Cl, 1.6. Found: C, 22.5; F, 71.9; S, 1.4; Cl, 1.6.

The residue, a white friable solid, 1.5 g. (23 wt.%), m.p. 245–281°, of which no decomposition was noted during distillation despite a still-pot temperature > 400°, was the chlorosulfate $C_3F_7[CF_2CF(CF_3)]_4[CF_2CF_2]_{25av}OSO_2Cl$.

Anal. Calcd. for $C_{65}F_{131}O_3SCl$: C, 23.1; F, 73.5; S, 0.95; Cl, 1.05. Found: C, 23.5; F, 73.5; S, 0.90; Cl, 1.07.

Reaction of $C_3F_7[CF_2CF(CF_3)]_4[CF_2CF_2]_nOSO_2Cl$ with Water or Sodium Hydroxide.—After refluxing several hours with water the lower fraction $C_3F_7[CF_2CF(CF_3)]_4[CF_2CF_2]_{9av}OSO_2Cl$ was converted to the carboxylic acid, $C_3F_7[CF_2-CF(CF_3)]_4[CF_2CF_2]_{8av}CF_2COOH$; infrared absorption band at 5.63 μ for the carbonyl stretching vibration, and at 3 μ for the –OH stretching vibration.

The higher fractions of $C_3F_7[CF_2CF(CF_3)]_4[CF_2CF_2]_n-OSO_2Cl$ made poor contact with water because of their physical characteristics, and preparation of the sodium salt precursor *via* basic hydrolysis was a superior route to these acids. Excess 20% aqueous sodium hydroxide solution was allowed to reflux with 0.3 g. of $C_3F_7[CF_2CF(CF_3)][CF_2CF_2]_{11-av}OSO_2Cl$ for several hours. The aqueous solution was decanted, and the remaining waxy solid was washed several times with water. After oven drying, there remained 0.25 g. of the carboxylic acid sodium salt for which the infrared spectrum showed the expected absorption band at 5.9 μ, and the absence of one at 3 μ.

Ammonolysis of $C_3F_7[CF_2CF(CF_3)]_4[CF_2CF_2]_{9av}OSO_2Cl$.—Anhydrous ammonia was passed for 0.25 hr. through a solution of 0.5 g. (0.00028 mole) of $C_3F_7[CF_2CF(CF_3)]_4[CF_2-CF_2]_{9av}OSO_2Cl$ in 10 ml. of anhydrous ether cooled to –75°. The reaction mixture was allowed to warm to room temperature to evaporate excess ammonia, and filtered. The solvent was distilled from the filtrate, and there was obtained upon further distillation, 0.4 g. (83% conversion) of the amide, $C_3F_7[CF_2CF(CF_3)]_4[CF_2CF_2]_{8av}CF_2CONH_2$, a viscous white oil, b.p. 115–119° (*ca.* 0.1 mm.).

Anal. Calcd. for $C_{33}F_{65}ONH_2$: C, 23.8; N, 0.84; H, 0.12. Found: C, 23.4; N, 0.41; H, 0.6.

Reaction of $C_2F_5CF(CF_3)(CH_2CF_2)_3I$ with Chlorosulfonic Acid.—To 50 g. (0.429 mole) of chlorosulfonic acid in a 250-cc. 3-necked flask equipped with addition funnel, stirred thermometer and gas inlet tube by means of which the apparatus was purged and maintained under a dry nitrogen atmosphere, 26 g. (0.0483 mole) of $C_2F_5CF(CF_3)(CH_2CF_2)_3I$ was added dropwise with stirring. During the addition which required 20 minutes the temperature of the vigorous exothermic reaction was maintained at 4–5° by the use of an ice–water-bath. The formation of solid crystalline iodine was noted. The reaction mixture was stirred at 0–4° for 1.5 hours and cautiously hyrolyzed by the drop by drop addition of 40 ml. of ice–water. The lower organic layer was removed and combined with several 10-ml. portions of 1,1,2-trichlorotrifluoroethane used to extract the remaining aqueous layer. After drying and removal of the solvent by distillation, the residue was distilled in a small Vigreux still. From this fractionation there was recovered 4.5 g. (0.0084 mole) of the reactant iodide, and 18 g. (0.034 mole, 90% yield, 79% conversion) of crude chlorosulfate $C_2F_5-CF(CF_3)(CH_2CF_2)_3OSO_2Cl$, b.p. 74–86°(*ca.* 0.1 mm.). was collected. A fraction of b.p. mainly at 80°(*ca.* 0.1 mm.), $n^{27}D$ 1.352, analyzed as the chlorosulfate.

Anal. Calcd. for $C_{10}H_6ClF_{15}O_3S$: C, 22.8; H, 1.1; Cl, 6.7; S, 6.1. Found: C, 23.2; H, 0.9; Cl, 6.3; S, 6.0.

Reactions of $CF_3CF_2CF(CF_3)(CH_2CF_2)_3OSO_2Cl$. (a) **Hydrolysis with Water.**—Ten grams (0.019 mole) of $CF_3CF_2CF(CF_3)(CH_2CF_2)_3OSO_2Cl$ was refluxed with 15 ml. of water for 4 hours. There was recovered 9.5 g. of water-insoluble liquid, b.p. mainly 78–82° (*ca.* 0.1 mm.), $n^{24}D$ 1.353, shown by its infrared spectrum to consist almost entirely of unreacted chlorosulfate. However, an absorption band at 3.3 and 5.78 μ in the infrared and the presence of sulfate and chloride ion in the aqueous layer indicated

the formation of a small amount of the acid $CF_3CF_2CF-(CF_3)(CH_2CF_2)_2CH_2COOH$.

(b) **Hydrolysis with $NaHCO_3$.**—A mixture of 0.8 g. (0.0015 mole) of $CF_3CF_2CF(CF_3)(CH_2CF_2)_3OSO_2Cl$ and 10 ml. of water was refluxed for several hours during which small portions of $NaHCO_3$ were added intermittently until no further evolution of CO_2 was noted and the mixture remained basic. The reaction mixture was acidified with dilute sulfuric acid and extracted several times with ethyl ether. The extract was dried with Drierite and distilled. After removal of the solvent, there was collected 0.5 g. (0.0012 mol. 80%) of $CF_3CF_2CF(CF_3)(CH_2CF_2)_2CH_2COOH$, b.p. 110–111° (*ca.* 0.1 mm.), a white viscous oil, with strong infrared absorption at 3.3 and 5.78 μ due to the –COOH group.

Anal. Calcd. for $C_{10}H_7F_{13}O_2$: C, 29.38; H, 1.74. Found: C, 29.57; H, 1.65.

(c) **Hydrolysis with Sodium Hydroxide.**—Eleven grams (0.021 mole) of $C_2F_5CF(CF_3)(CH_2CF_2)_3OSO_2Cl$, was shaken with 50 g. of 20% aqueous NaOH solution until the lower organic layer which formed on mixing was completely dissolved. Occasional cooling of the reaction flask was required to keep the reaction at or slightly below room temperature. The reaction mixture was acidified with concentrated hydrochloric acid and extracted with 1,1,2-trichlorotrifluoroethane and then ethyl ether. The extracts were combined, dried with Drierite, and distilled to remove solvents. There remained 7.5 g. of crude acid, a dark viscous oil from which there was finally distilled 3 g. (middle fraction b.p. 89–90° (*ca.* 0.1 mm.)) of slightly yellow oil, $n^{27}D$ 1.370, which analyzed as $C_{10}H_8F_{12}O_2$.

Anal. Calcd.: C, 31.1; H, 1.6; mol. wt., 386. Found: C, 31.5; H, 2.2; mol. wt. (by neut. equiv.), 378.

This acid had bands at 5.78 and 6.08 μ, as well as a broad band at 3.3 μ, in the infrared, which are indicative of a fluorine-containing unsaturated carboxylic acid. Evidence that this was a conjugated unsaturated acid was obtained from its ultraviolet spectrum which showed relatively strong absorption at the relatively long wave length maximum of 289.5 mμ.

The above findings are consistent with the structure $C_2-F_5CF(CF_3)CH_2CF_2CH_2CF{=}CHCOOH$.

Approximately 1 g. of the conjugated acid above was refluxed for 2 hours with excess 20% aqueous sodium hydroxide solution. The reaction mixture was neutralized with concentrated sulfuric acid and extracted exhaustively with ethyl ether. The ether extract was dried with Drierite and distilled. There was obtained about 0.5 g. of a fraction, b.p. 95–97° (*ca.* 0.1 mm.), a brown viscous oil, which analyzed as $C_{10}H_8F_{11}O_2$.

Anal. Calcd.: C, 32.8; H, 1.4. Found: C, 32.8; H, 2.1.

This acid had bands at 5.80 and 6.1 μ, as well as a broad band at 3.3 μ, in the infrared, indicative as before of a fluorine-containing unsaturated carboxylic acid. The ultraviolet spectrum of this acid showed an increase in intensity of absorption as expected for increased conjugation, although a slight shift in λ_{max} to 284 mμ, cannot be explained in the light of present knowledge. The diconjugated acid, $C_2F_5CF(CF_3)CH_2CF{=}CHCF{=}CHCOOH$, is thus possible. Further work, of course, is necessary for unequivocal proof of structure for these conjugated acids.

(d) **Ammonolysis.**—Anhydrous ammonia was passed for 0.25 hr. into a solution of 1 g. (0.0019 mole) of $C_2F_5-CF(CF_3)(CH_2CF_2)_3OSO_2Cl$, in 40 ml. of anhydrous ethyl ether cooled at 0°. The reaction mixture was warmed to room temperature, filtered, and distilled to remove solvent. From the distillation of the residue under reduced pressure there was obtained 0.7 g. (91%) of the amide $C_2F_5CF-(CF_3)(CH_2CF_2)_2CH_2CONH_2$, b.p. 109–110° (<0.1 mm.), an oil at room temperature, solid at ice temperature. The compound had a typical amide infrared spectrum with the carbonyl stretching vibration at 5.95 μ, NH stretching vibration at 3.02 and 3.15 μ, and NH bending (probably) at 6.20 μ.

Anal. Calcd. for $C_{10}H_8F_{13}ON$: C, 29.6; H, 2.0; N, 3.5. Found: C, 29.7; H, 2.0; N, 3.5.

(e) **Esterification.**—A mixture of 3.5 g. (0.0067 mole) of $CF_3CF_2CF(CF_3)(CH_2CF_2)_3OSO_2Cl$ and 5 g. (0.108 mole) of absolute ethanol was allowed to reflux for 1.5 hours. The reaction mixture was poured into 20 cc. of ice-water

and the lower layer, 3.4 g. of colorless liquid, was separated. After drying with Drierite, there was obtained by distillation in a small Vigreux still 2.7 g. (0.0062 moles, 92%) of the ethyl ester $CF_3CF_2CF(CF_3)(CH_2CF_2)_2CH_2COOC_2H_5$, b.p. 77–81° (ca. 0.1 mm.)(main fraction b.p. 80–81° (ca. 0.1 mm.), $n^{28}D$ 1.345). A band at 5.73 μ in the infrared is attributed to the C=O stretching vibration of the ester.

Reaction of $CF_2ClCF(CF_3)(CH_2CF_2)_{4.5av}I$ with Chlorosulfonic Acid.—To 18 g. (0.0299 mole) of $CF_2ClCF(CF_3)$-$(CH_2CF_2)_{4.5av}I$ in a 3-necked flask cooled in an ice-bath and equipped with stirrer, thermometer, addition funnel and gas inlet tube for purging and maintaining a nitrogen atmosphere, there was added very slowly 25 g. (0.215 mole) of chlorosulfonic acid. Crystalline iodine was liberated and sulfur dioxide was evolved during the addition. The reaction mixture was stirred at 0° for 2 hr. and hydrolyzed by addition of water. The lower organic layer was taken up in 1,1,2-trichlorotrifluoroethane, washed with dilute $Na_2S_2O_3$ solution, dried with Drierite and distilled to remove solvent. From the residue there was separated by distillation 12 g. (0.0256 mole) (85% yield and conversion) of a liquid, b.p. 64 to > 126° (ca. 0.1 mm.), shown by infrared spectra to consist entirely of a mixture of fluorocarbon acid and acid fluoride, $CF_2ClCF(CF_3)(CH_2CF_2)_{3.5av}$-$CH_2COOH$, characterized as the amide (see below) and $CF_2ClCF(CF_3)(CH_2CF_2)_{3.5av}CH_2COF$ with the acyl fluoride carbonyl absorption at 5.39 μ decreasing progressively and the acid carbonyl absorption at 5.78 μ increasing progressively with increasing boiling point of the fractions.

$CF_2ClCF(CF_3)(CH_2CF_2)_{3.5av}CH_2CONH_2$.—Anhydrous ammonia was passed through a solution of 7 g. (0.149 mole) of $CF_2ClCF(CF_3)(CH_2CF_2)_{3.5av}CH_2COF$ in 50 ml. of anhydrous ether for 0.25 hr. The solution was filtered, and the filtrate was distilled. After removal of the solvent there was obtained as the sole product 5.3 g. (76% conversion) of the amide, $CF_2ClCF(CF_3)(CH_2CF_2)_{3.5av}CH_2CONH_2$, b.p. 156–162° (ca. 0.1 mm.), m.p. 49–50° after one recrystallization from 1,1,2-trichlorotrifluoroethane.
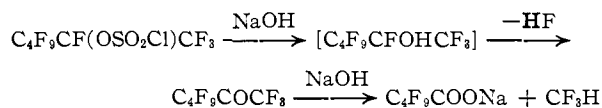
Anal. Calcd. for $C_{12}H_{11}OF_{13}ClN$: C, 30.8; H, 2.4; N, 3.0. Found: C, 31.3; H, 2.7; N, 3.1.

Thermal Reaction of 2-Iodoperfluorohexane with Chlorosulfonic Acid.—Twenty grams (0.17 mole) of chlorosulfonic acid and 5 g. (0.0112 mole) of 2-iodoperfluorohexane were sealed in a heavy-walled Pyrex ampule and heated at 148° for 112 hours. A mass of orange crystals of iodide trichloride formed at the bottom of the tube. The tube was then cooled and opened and the top layer, a clear yellow oil, was decanted. On warming to room temperature, sulfur dioxide gas was evolved. A small amount of

additional oil was collected on hydrolysis of the iodine trichloride–acid layer, combined with the main fraction (total 4 g., 100%), washed with dilute potassium carbonate solution, dried with Drierite, and distilled to give entirely 2-chloroperfluorohexane, b.p. 83–84°, $n^{26}D$ 1.2826.

Similarly, from two reactions of 17.8 g. (0.0399 mole) of 2-iodoperfluorohexane with 50 g. (0.429 mole) of chlorosulfonic acid in sealed tubes at 75° for 4.25 hours and 95° for 2 hours, respectively, mainly unreacted iodide was recovered, and small amounts of 2-chloroperfluorohexane and perfluoro-2-hexyl chlorosulfate were detected by infrared spectroscopic analyses.

Hydrolysis of Perfluoro-2-hexyl Chlorosulfate.—Several fractions of the product from the reaction of 2-iodoperfluorohexane and chlorosulfonic acid carried out at 75 and 95° (see above) were combined (total weight 28 g.) and shaken exhaustively with water. The water-insoluble lower layer (27 g.) was removed and the aqueous part was neutralized with dilute aqueous sodium hydroxide solution. A small amount of gas (probably fluoroform) was liberated. After evaporation of the water, the residual solid salts were extracted in a Soxhlet apparatus with anhydrous ether. From the ether extract there was obtained after evaporation of the solvent a small amount of a sodium salt of a perfluorocarboxylic acid, as shown by the infrared spectrum, probably C_4F_9COOH. These chemical observations may be ascribed to a transformation of the type

$$C_4F_9CF(OSO_2Cl)CF_3 \xrightarrow{\text{NaOH}} [C_4F_9CFOHCF_3] \xrightarrow{-HF}$$

$$C_4F_9COCF_3 \xrightarrow{\text{NaOH}} C_4F_9COONa + CF_3H$$

Thermal Reaction of 2-Iodoperfluorohexane with Sulfuryl Chloride.—A mixture of 8.9 g. (0.0199 mole) of 2-iodoperfluorohexane and 29 g. (0.215 mole) of sulfuryl chloride was sealed in an 80-cc. heavy-wall Pyrex ampule. The tube was heated at 100–115° with shaking for 11 hours. There was recovered from this reaction only $CF_3CF_2CF_2$-CF_2CFICF_3 shown spectroscopically to contain a trace of $CF_3CF_2CF_2CFClCF_3$. No $CF_3CF_2CF_2CF_2CF(OSO_2$-$Cl)CF_3$ was detected.

Fluorocarbon Halosulfates and a New Route to Fluorocarbon Acids and Derivatives. II. Polyfluoroalkyl Fluorosulfates

BY MURRAY HAUPTSCHEIN AND MILTON BRAID

Novel reactions of fluorosulfonic acid with fluorocarbon iodides have been discovered by which fluorocarbon fluorosulfates are prepared. The syntheses of $CF_3CF_2CF_2OSO_2F$, $CF_2ClCFClOSO_2F$ and $CF_3CF_2CF(CF_3)(CH_2CF_2)_2OSO_2F$ and their one-step conversions to $CF_3CF_2CONH_2$, $CF_2ClCONH_2$ and $CF_3CF_2CF(CF_3)CH_2CF_2CH_2CONH_2$ by ammonolysis of the respective fluorosulfates are described.

The novel reactions of chlorosulfonic acid with fluorocarbon iodides and other polyfluoroalkyl iodides to produce the corresponding chlorosulfates have been described.[1] The present report deals with the extension of this work to the reaction of fluorosulfonic acid with these fluorinated iodides to form the corresponding fluorocarbon and fluoroalkyl fluorosulfates, and also describes their con-

(1) M. Hauptschein and M. Braid. *J. Am. Chem. Soc.*, **83**, 2500 (1961).

versions to fluorocarbon carboxylic acids and derivatives.

A typical primary fluorocarbon iodide, 1-iodoheptafluoropropane, reacted with an excess of fluorosulfonic acid in a sealed tube at 150° for 5 hr. to produce the novel perfluoropropyl fluorosulfate in high yield. The fluorination product, perfluoropropane, was formed in only trace amounts.

In a manner analogous to the formation of the