

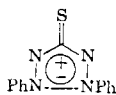
$$\log(k/k_{H_2O}) = 2.59En - 0.052H \quad (7)$$

I are given in Table III along with chosen literature constants² for comparative purposes.

TABLE III

COMPARISON OF THE NUCLEOPHILIC CONSTANT (En) AND ACIDITY (H) FUNCTION OF DEHYDRODITHIZONE TO A SELECTED GROUP OF NUCLEOPHILES

Nucleophile	En	H	Nucleophile	En	H
S^-	3.08	14.66	$(NH_4)_2C=S$	2.18	0.80
SO_3^-	2.57	9.00	CN^-	2.02	10.88
SO_3^{2-}	2.52	3.60	SCN^-	1.83	(1.00)
	2.34	0.17	SO_4^{2-}	0.59	3.74



It may be noted that of those nucleophiles which are particularly effective toward the sp^3 carbon, I possesses the lowest value of H . The high values of both En and H possessed by some of the other nucleophiles such as S^- and SO_3^- provide these bases with the ability to undergo displacement reactions at the sp^3 and sp^2 carbon atoms. This should not be expected of I on the basis of its very low H value. Experimentally, this is found to be the case, and I, unlike these other bases with large En values, is incapable of displacing *p*-nitrophenol from *p*-nitrophenyl acetate.

The somewhat higher value of En for I as compared to thiourea and thiocyanate (which also possess the N-C-S configuration) may be attributed to a greater polarizability of the molecule, which might result from its "meso-ionic" structure.

Aside from the apparent increased polarizability of I, it does not, as a "meso-ionic" compound, appear to be unusual in its sensitivity to electronic effects, nor in its sensitivity to the nature of leaving groups. Thus, the rate ratios k_A/k_{AH} and $k_I:k_{Br}:k_{Cl}$ compare with those previously listed for other nucleophiles possessing high En values.^{5,6}

Experimental

Materials.—Dehydrodithizone was that of another study.⁴ Bromoacetamide was prepared by the method of Papendick.⁷ The haloacetates were obtained commercially and recrystallized to constant m.p. from petroleum ether.

Apparatus.—The determination of pH values was carried out with a model 22 Radiometer pH meter. All spectrophotometric measurements were made with a model PMQ II Zeiss spectrophotometer fitted with a special hollow brass cuvette holder thermostated at $30 \pm 0.01^\circ$ by a Haake constant temperature circulating bath.

Kinetics.—For iodoacetic and chloroacetic acids the substrate was employed as buffer. For bromoacetamide and bromoacetic acid 0.01 *M* tartrate buffer was employed. All reactions were followed at ionic strengths (calculated) of 0.125–0.05 *M* provided by KCl. The disappearance of dehydrodithizone was followed at 250 $m\mu$ (λ_{max}). Specific procedures for the kinetic experiments and method of calculation of observed rate constants have been given previously.⁸

Acknowledgments.—We should like to thank Mr. S. A. Mendoza for performing a portion of the experimental work reported herein. This work was supported by grants to J. O. from The National Heart Institute and to T. C. B. from The National Science Foundation and The National Institutes of Arthritic and Metabolic Diseases.

(7) A. Papendick, *Ber.*, **25**, 1160 (1892).

(8) T. C. Bruice and M. F. Mayahi, *J. Am. Chem. Soc.*, **82**, 3067 (1960).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, PENNSALT CHEMICAL CORP., PHILADELPHIA 18, PA.]

Addition of Iodine Halides to Fluorinated Olefins. I. The Direction of Addition of Iodine Monochloride to Perhaloölefins and Some Related Reactions

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Contrary to prior reports, the addition of iodine monochloride to chlorotrifluoroethylene is bidirectional and both isomers $CF_2ClCFClI$ (I) and $CFCl_2CF_2I$ (II) are formed. The isomer ratio was shown to be temperature dependent with higher temperatures favoring isomer II. If the reaction is carried out at 0° or lower, nearly pure I can be obtained. In the presence of iron, however, the isomer mixture consisted of about 65% of II even at 0° . Pure II was isolated in quantity from isomer mixtures by the selective reaction of I at 50° with chlorosulfonic acid. In the presence of aluminum chloride third possible $C_2Cl_2F_3I$ isomer, the rearranged CF_3CCl_2I , was produced in 100% isomeric purity in low yield. The addition of iodine monochloride to 1,1-dichlorodifluoroethylene gave the isomer CF_2ClCCl_2I exclusively at -10° , but at higher temperatures or in the presence of iron, the isomer CCl_2CF_2I also was produced. The formation of relatively large amounts of the chlorination product CF_2ClCCl_2I was favored under the latter conditions. At 98° the addition of iodine monochloride to perfluoropropene gave an isomer composition of 91.5% CF_2CFICF_2Cl and 8.5% $CF_2CFCICF_2I$. The direction of the thermal addition of fluorocarbon iodides to some fluorinated olefins has been determined. The great utility of vapor-liquid partition chromatography in both the analysis and separation of the addition compounds is described and characteristic elution time ratios for a series of isomeric fluoroiodides are presented.

This is the first paper in a series dealing with the addition of iodine halides to fluorinated olefins and is concerned primarily with the direction of addition of iodine monochloride to various perhaloölefins.

The Addition of Iodine Monochloride to Chlorotrifluoroethylene.—The addition of iodine monochloride to chlorotrifluoroethylene has been reported to give $CF_2ClCFClI$ (I) as the exclusive ICl adduct.^{1,2} We now wish to report that this

(1) R. N. Haszeldine, *J. Chem. Soc.*, 4423 (1952).

addition is in fact bidirectional under the various conditions reported^{1,2} and that at the reaction temperatures previously used, *i.e.*, room temperature to 50° , the adduct actually consists of at least 20–30% of the isomer $CFCl_2CF_2I$ (II).³

(2) J. T. Barr, J. D. Gibson and R. H. Lafferty, *J. Am. Chem. Soc.*, **73**, 1352 (1951), did not investigate the structure of the adduct but assigned the structure $CF_2ClCFClI$ by analogy to other addition reactions of the olefin $CF_2=CFCl$.

(3) Professor R. N. Haszeldine, University of Manchester, has recently informed us that he has independently discovered that the ad-

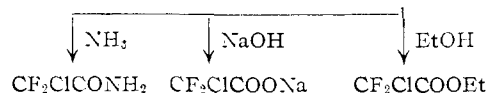
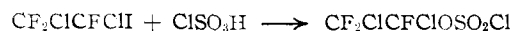
Furthermore, it now has been discovered that the isomer ratio I:II is temperature dependent with higher temperatures favoring isomer II production up to a maximum of about 60% of II. At temperatures of 0° or below almost isomerically pure I was obtained. Thus at 0° and at -8 to -5°, the adducts were 97 and 98% pure I. The data summarized in Table II (Experimental), runs 1-5, illustrate clearly this effect of increasing temperature on isomer composition. On the other hand, if the reaction is carried out in the presence of a reactive form of metallic iron, such as iron gauze or ferric chloride, the major product is isomer II, even when the reaction is carried out at 0°. This effect was first noted when the reaction was performed in an iron vessel (run 7, Table II). By further study of this unexpected result, the catalytic effect of iron was demonstrated unequivocally (run 6 vs. run 2, Table II). It should be noted that despite temperature variations (in the presence of iron), there was a maximum of about 65% of II in the products. This suggested the possibility that the isomeric ratio may have been the result of a chemical equilibrium. This possibility, however, was not confirmed. The isomer compositions were not altered significantly when nearly pure isomer I or isomer II was heated at 40-50° in the presence of iodine monochloride and iron. Thus iron was shown not to be a catalyst for "equilibration" of the mixture.

The reaction has been carried out in the presence and absence of solvents. At low temperatures (below 0°) the heterogeneous reaction of solid ICl with $CF_2=CFCl$ is very slow and use of a solvent is advantageous. Methylene chloride and 1,2,2-trichlorotrifluoroethane have been employed, although the solubility of the ICl in the latter is low and therefore the use of trichlorotrifluoroethane is not recommended. The most efficient reaction system is the solution of the reactants in I, itself.

The pure isomers could be separated by vapor-liquid partition chromatography (V.L.P.C.); see Table I. The ultraviolet spectra in iso-octane exhibited maxima at 286 $m\mu$ for I and at 274 $m\mu$ for II which are entirely consistent with the respective $CF_2ClCFCII$ and $CFCl_2CF_2I$ structures.⁴ It should be noted in this connection that a mixture of isomers I and II will show an unresolved single maximum (rather than two maxima) at some wave length intermediate between 286 and 274 $m\mu$ with the position dependent on the isomeric composition. Thus mixtures containing, for example, 75, 60 and 25% of I, will have respective maxima at 283, 281 and 277 $m\mu$.

A previously discovered reaction of fluorocarbon iodides with halosulfonic acid to produce fluorocarbon halosulfates⁵ and carboxylic acids therefrom⁵ was employed advantageously to effect the separation of pure II in sizable quantities. Thus at a temperature of about 50°, isomer I was preferentially and completely converted by reac-

tion with chlorosulfonic acid to the chlorosulfate $CF_2ClCFCIOSO_2Cl$, which was removed after basic hydrolysis, as the water-soluble sodium chlorodifluoroacetate. This reaction as well as the reaction of the chlorosulfate with ethanol and with ammonia and conversions thereby to the known ester and amide, respectively, also served to confirm the structure for I.



Isomer II would have given carboxylic acid derivatives of dichlorofluoroacetic acid, *i.e.*, $CFCl_2COONa$, $CFCl_2COOEt$ and $CFCl_2CONH_2$. Both of the novel isomeric chlorosulfates $CF_2ClCFCIOSO_2Cl$ and $CFCl_2CF_2OSO_2Cl$ formed at a higher temperature, *i.e.*, 100°, have been characterized.

Finally, in order to investigate the effect of another Lewis acid, the reaction of ICl with $CF_2=CFCl$ was carried out using a rather large amount of aluminum chloride. It was a complete surprise to discover that the sole ICl adduct obtained was neither I nor II but the new rearranged product CF_3CCl_2I ! Only 15% of the total product was the ICl adduct; 60% of the product consisted of isomerically pure CCl_3CClF_2 ; 15% of $C_2Cl_3F_3$ (mostly CF_3CCl_3); and the remainder consisted principally of $CCl_2=CClF$, $CCl_2=CCl_2$, and interestingly $CF_3=CClI$. CF_3CCl_2I also has been prepared by the novel and much superior method involving the addition of iodine monofluoride ($IF_5 + 2I_2 \rightarrow 5IF$) to $CF_2=CCl_2$.⁶ This reaction can give either CF_3CCl_2I or the previously characterized $CFCl_2CF_2I$ (II). The ultraviolet maximum in iso-octane at 296 $m\mu$ was consistent only with the structure CF_3CCl_2I .

The Addition of Iodine Monochloride to 1,1-Dichloro-2,2-difluoroethylene.—The addition of ICl to $CF_2=CCl_2$ was next examined.⁷ This reaction also was found to be bidirectional but to a lesser extent than in the case of the addition of ICl to $CF_2=CFCl$. At -10°, CF_2ClCCl_2I was produced in 100% isomeric purity (*i.e.*, to the limit of detection, which is less than 0.5%, in this case). At 0-3° the adduct consisted of 99% CF_2ClCCl_2I and 1% CCl_3CF_2I . At 5 to 15° the isomeric purity of the adduct CF_2ClCCl_2I ranged from 98 to 97%. At about 20°, using a reverse addition procedure, an isomer mixture consisting of about 90% CF_2ClCCl_2I and 10% CCl_3CF_2I was obtained. In the presence of iron at temperatures between 5 and 13° the adduct contained about 20% of CCl_3CF_2I . The higher temperatures had an even more profound effect on the formation of the undesired chlorination by-product CCl_3CF_2Cl . Thus at 0-3° only 1% of the total product was CCl_3CF_2Cl while the addition of $CF_2=CCl_2$ to ICl at about 20° resulted in the formation of about 20% of the tetrachlorodifluoroethane.

(6) M. Hauptschein and M. Braid, forthcoming publication, which also describes the addition of IF to $CF_2=CFCl$ and to $CF_2=CFCl_2$ to give CF_3CFClI + CF_2ClCF_2I and CF_3CFICF_2 , respectively. The respective V.L.P.C. elution time ratios of these compounds have been included in Table I for completeness.

(7) R. N. Haszeldine, Canadian Patent 603,718 (1960).

(5) See R. N. Haszeldine, *J. Chem. Soc.*, 1764 (1953), for ultraviolet spectroscopic data.

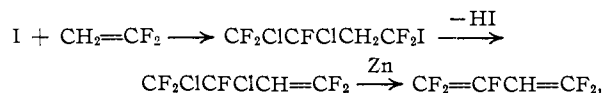
(6) M. Hauptschein and M. Braid, forthcoming publications.

The isomers were separated by V.L.P.C. As would be expected, the ultraviolet maximum (in isoöctane) for $\text{CF}_2\text{CICCl}_2\text{I}$ at 302.5 $\text{m}\mu$ is much higher than the maximum for $\text{CCl}_2\text{CF}_2\text{I}$ which is at 274.5 $\text{m}\mu$. The infrared absorption spectra of both of these isomers were different from that of the other possible isomer, the very unlikely rearranged product $\text{CCl}_2\text{FCClFI}^8$ prepared by addition of ICl to $\text{CFCl}=\text{CFCl}$.

The Addition of Iodine Monochloride to Perfluoropropene.—The products of a related reaction which preceded the aforementioned work were next re-examined.

The reaction of perfluoropropene with iodine monochloride at 98° was shown to produce an adduct consisting of 91.5% $\text{CF}_3\text{CFICF}_2\text{Cl}$ (ultraviolet maximum in isoöctane at 277.5 $\text{m}\mu$; compare $\text{C}_2\text{F}_5\text{CFICF}_3$ λ_{max} 279 $\text{m}\mu$) and 8.5% $\text{CF}_3\text{-CFClCF}_2\text{I}$ (ultraviolet maximum in isoöctane at 273 $\text{m}\mu$). On the basis of the previously discussed studies it would appear likely that the yield of $\text{CF}_3\text{CFICF}_2\text{Cl}$ would be increased by decreasing the reaction temperature and that iron may possibly function as a catalyst to raise the yield of $\text{CF}_3\text{CFClCF}_2\text{I}$.

Chain Transfer Efficiencies and Miscellaneous Telomerizations.—The discovery of the bidirectional nature of the addition of ICl to $\text{CF}_2=\text{CFCl}$ and of methods for preparing the individual isomers is of more than cursory interest. Isomer I is much more active than II as a chain transfer agent for various telomerization reactions. In the thermal telomerization of $\text{CF}_2=\text{CFCl}$, for example, I is effective both as an initiator and as a chain transfer agent at 160°, at which temperature little reaction occurs if II is used instead as the telogen. In the latter case a reaction temperature of at least 185° is necessary and this telomerization process is not nearly as well controlled. Greater quantities of solid telomers consequently are formed in the resulting wider spread in molecular weight ranges.⁵ Also where I has been used as a means of introducing the perfluorovinyl group, *e.g.*



etc., it is obvious that the presence of II would result in reduced yields and/or side reactions.

The efficiency of a fluorocarbon iodide acting as a chain transfer agent is related to the stability of the C-I bond, which to a first approximation may be considered as varying inversely with the wave length of the maximum in the ultraviolet spectrum. It has been found⁵ that $\text{CF}_3\text{CCl}_2\text{I}$ (296 $\text{m}\mu$) and $\text{CF}_2\text{CICCl}_2\text{I}$ (302.5 $\text{m}\mu$) are in fact the most efficient of the $\text{C}_2\text{Cl}_2\text{F}_3\text{I}$ and $\text{C}_2\text{Cl}_3\text{F}_2\text{I}$ series in agreement with the above theory.

The direction of the thermal addition of CF_3I and of *n*- $\text{C}_3\text{F}_7\text{I}$ to perfluoropropene previously has been shown by chemical and/or ultraviolet spectroscopic evidence to produce $\text{R}_f\text{CF}_2\text{CFICF}_3$ where $\text{R}_f = \text{CF}_3$ or *n*- C_3F_7 .⁹ By the more refined V.L.P.C.

(8) M. Hein, Ph.D. Thesis, University of Colorado, Boulder, Colo., 1954.

(9) M. Hauptschein, M. Braid and F. E. Lawlor, *J. Am. Chem. Soc.*, **79**, 2549 (1957).

analytical technique it has now been determined for two specific cases that the 1:1 adducts of CF_3I and *n*- $\text{C}_3\text{F}_7\text{I}$ with $\text{CF}_2=\text{CFCF}_3$ had isomeric compositions of 92% $\text{CF}_3\text{CF}_2\text{CFICF}_3$ and 8% $(\text{CF}_3)_2\text{CFCF}_2\text{I}$ for the former and of 98% $\text{CF}_3\text{CF}_2\text{-CF}_2\text{CF}_2\text{CFICF}_3$ and 2% $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CF}_2\text{I}$ for the latter adduct.

It was previously shown by V.L.P.C. that the composition of the 1:1 adduct of the thermal reaction of *n*- $\text{C}_3\text{F}_7\text{I}$ with $\text{CH}_2=\text{CF}_2$ was 95% $\text{C}_3\text{F}_7\text{-CH}_2\text{CF}_2\text{I}$ and 5% $\text{C}_3\text{F}_7\text{CF}_2\text{CH}_2\text{I}$.¹⁰

Unpublished observations by the authors also indicate that the 1:1 adduct of the thermal reaction of $\text{CF}_2\text{CICFCII}$ with $\text{CF}_2=\text{CFCl}$ consists of a few per cent. of $\text{CF}_2\text{CICFCICFCICF}_2\text{I}$ in addition to the main product, $\text{CF}_2\text{CICFCICF}_2\text{CFCII}$.

In view of all of the above findings, it should be expected that the products resulting from the thermal telomerizations of unsymmetrical olefins will generally contain at least a small percentage of other isomers.

Vapor-Liquid Partition Chromatography.—During the course of this research a careful study was made of the use of vapor-liquid partition chromatography as a tool for the analysis and separation of closely boiling isomeric perfluoro- and perfluorochloro-alkyl iodides. Table I summarizes their characteristic elution time ratios, t_c/t_{CCl_4} , in three different chromatographic columns for the temperatures indicated. This ratio is that of the elution

TABLE I
CHARACTERISTIC V.L.P.C.^a ELUTION TIME RATIOS OF ISOMERIC FLUOROIODIDES

Molecular formula	Structural formulas	t_c/t_{CCl_4} at 75°		
		"B" ^b	"K" ^c	"R" ^d
$\text{C}_3\text{F}_7\text{I}$	$\text{CF}_3\text{CF}_2\text{CF}_2\text{I}^f$	0.16	0.13	0.18
	$\text{CF}_3\text{CFICF}_3^g$.22	.24	.27
$\text{C}_4\text{F}_9\text{I}$	$(\text{CF}_3)_2\text{CFCF}_2\text{I}$.29	.21	.32
	$\text{CF}_3\text{CF}_2\text{CFICF}_3$.36	.32	.43
$\text{C}_6\text{F}_{13}\text{I}$	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CF}_2\text{I}$.62	.34	.66
	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CFICF}_3$.77	.52	.90
$\text{C}_2\text{ClF}_4\text{I}$	$\text{CF}_2\text{CICF}_2\text{I}^g$.53	.66	.60
	$\text{CF}_3\text{CFClI}^g$.59	.85	.70
$\text{C}_3\text{ClF}_6\text{I}$	$\text{CF}_3\text{CFClCF}_2\text{I}$.76	.76	.88
	$\text{CF}_3\text{CFICF}_2\text{Cl}$	1.02	1.30	1.26
$\text{C}_2\text{Cl}_2\text{F}_3\text{I}$	$\text{CFCl}_2\text{CF}_2\text{I}$	2.6	3.7	3.0
	$\text{CF}_2\text{CICFCII}$	2.9	4.6	3.4
	$\text{CF}_3\text{CCl}_2\text{I}$	3.2	6.0	4.0
$\text{C}_2\text{Cl}_3\text{F}_2\text{I}$	$\text{CCl}_3\text{CF}_2\text{I}$	8.8 ^e		10.1 ^e
	$\text{CClF}_2\text{CCl}_2\text{I}$	10.5 ^e		13.0 ^e

^a V.L.P.C. = Vapor liquid partition chromatography. ^b Perkin-Elmer 2 meter "B" column (di-2-ethylhexyl sebacate stationary liquid phase). ^c Perkin-Elmer 2 meter "K" column (Carbowax 1500). ^d Perkin-Elmer 2 meter "R" column (Ucon polyglycol LB-550-X). ^e Temperature was 100°. ^f M. Hauptschein and A. V. Grosse, *J. Am. Chem. Soc.*, **73**, 2461 (1951). ^g See ref. 6.

time for the compound to the elution time for the reference standard, carbon tetrachloride (both measured from the time of emergence of the air peak). This ratio is a characteristic constant for each compound in the specified column at the stated temperature, and is independent both of column parameters such as column length, di-

(10) M. Hauptschein and R. E. Oesterling, *ibid.*, **82**, 2868 (1960).

TABLE II
 REACTIONS OF IODINE MONOCHLORIDE WITH CHLOROTRIFLUOROETHYLENE

Run	Temp., °C.	Reactor ^a	Catalyst	Solvent	Isomeric composition, %	
					CF ₂ CICFCII	CFCl ₂ CF ₂ I
1	-8 to -5	Glass	None	CH ₂ Cl ₂	98	2
2	0	Glass	None	CH ₂ Cl ₂	97	3
3	15 to 20	Glass	None	CF ₂ CICFCI ₂ ^c	79	21
4	25 to 30	Monel ^b	None	None	70	30
5	50	Glass	None	None	45	55
6	0	Glass	Fe wire gauze	CH ₂ Cl ₂	37	63
7	40	Iron ^b	...	None	38	62
8	50	Glass	Fe wire gauze	None	34	66
9	40-50	Glass	FeCl ₃	None	34	66
10	100	Stainless steel ^b	Fe wire gauze	None	40	60

^a All reactions at atmospheric pressure except as noted. ^b Pressure, *ca.* 5 atm., *i.e.*, olefin added to reactor while stirring or shaking under a pressure of about 5 atmospheres. ^c CF₂CICFCI₂ is a very poor solvent for ICl. The adducts C₂Cl₂F₂I are excellent solvents for ICl, and the reaction mixture becomes more homogeneous as the reaction progresses and produces more ICl adduct.

ameter, percentage of stationary liquid phase and of operating parameters such as pressure and flow rate. This ratio is dependent only on temperature for any particular column.

The three columns used are particularly suited for the separation of isomeric iodides, their efficiency increasing in the order "B" < "R" < "K." Two interesting observations are worthy of note. First, the secondary iodides invariably emerged later than the isomeric primary iodides. Second, the elution times for the isomeric perfluorochloroalkyl iodides were in the order -CF₂I < -CFCII < -CCl₂I.

Experimental

Reactions of Chlorotrifluoroethylene with Iodine Monochloride. (a) In Glass Reactors.—All reactions were carried out under a dry nitrogen atmosphere at atmospheric pressure. At temperatures of 0-50° chlorotrifluoroethylene was bubbled through iodine monochloride directly or through a solution of iodine monochloride in solvents such as methylene chloride. In some cases small bits of iron wire gauze or ferric chloride catalyst were added. The temperature was maintained by external heating or cooling as required. Unreacted olefin, which was collected in receivers cooled at -78°, was often recycled until all of the ICl was reacted. Reaction mixtures were first washed with water, then with saturated aqueous sodium bisulfite solution, then again with water, and then dried with anhydrous calcium sulfate or magnesium sulfate. Solvents were removed by distillation as was any by-product CF₂CICFCI₂ formed in trace amounts at the lower temperature runs and up to several per cent. at the higher temperatures. The isomeric composition of the ICl adducts was determined by vapor-liquid partition chromatographic analysis (V.L.P.C.).

For reactions carried out at temperatures below 0° the following modified procedure was employed:

To 415 g. (3.56 moles) of condensed chlorotrifluoroethylene cooled by a Dry Ice-acetone-bath there was added during 0.75 hr. while stirring 500 g. (3.08 moles) of iodine monochloride dissolved in 750 ml. of methylene chloride. The temperature of the reaction mixture was allowed to rise to -8 to -5° and was maintained at this temperature for 4 hours by the refluxing of the excess olefin (using a Dry Ice-cooled condenser). The excess olefin then was allowed to boil off and the reaction mixture was worked up as described above. After removal of the solvent there remained 430 g. of crude adduct C₂Cl₂F₂I of which the isomer content was shown by V.L.P.C. to be 98% CF₂CICFCII (I) and 2% CFCl₂CF₂I (II). The pure isomer I (*Anal.* Calcd. C, 8.61. Found: C, 8.79) was obtained by preparative chromatography and had the physical constants: b.p. 101° (45° at 100 mm.), *n*_D²⁵ 1.4493, *d*₄²⁵ 2.199; *MR*_D²⁵ found 34.03, calcd. 34.1 based on atomic refractions of C, 2.58; F, 1.17; Cl, 5.85; I, 13.7.¹¹ *The principal absorp-*

tion maxima (in microns) for the isomer I in the vapor infrared spectrum were at 8.34vs, 8.49vs, 8.59ssh, 9.06vs, 9.67vs, 11.48vs, 12.02vs, 12.50vs, 13.52vvs (s = strong, vs = very strong, vvs = very, very strong, m = medium, sh = shoulder). The absorption maximum of this isomer in the ultraviolet spectrum taken in isoöctane was at 286 mμ.

(b) In Autoclaves.—The autoclave was charged with iodine monochloride and the vessel was sealed, cooled in Dry Ice, and evacuated. The autoclave was heated to slightly less than the desired reaction temperature and chlorotrifluoroethylene was pressured in at such a rate that the temperature remained fairly constant or varied as indicated in Table II. For the lower temperature runs the olefin was admitted slowly to the autoclave with external cooling to maintain the reaction temperature. When olefin absorption ceased, the reaction mixture was brought to room temperature and worked up as previously described.

The results of typical glass reactor and autoclave runs are summarized in Table II.

Reaction of 1,2-Dichloro-1,2,2-trifluoro-1-iodoethane with Chlorosulfonic Acid.—To 93 g. (0.8 mole) of chlorosulfonic acid heated to 50° was added during 10 minutes while stirring vigorously 23 g. (0.0825 mole) of CF₂CICFCII (containing *ca.* 30% CFCl₂CF₂I). The reaction mixture was heated to 60° and stirred for 2 additional hours. After cooling, the reaction mixture was hydrolyzed rapidly by pouring over chipped ice. The lower water-insoluble layer was dried with Drierite and distilled. There was collected some CF₂CICFCI₂; after recovery only of unreacted isomer CFCl₂CF₂I, 12 g. of crude chlorosulfate, CF₂CICFCIOSO₂Cl, b.p. (middle cut on redistillation) 76° at 100 mm., *n*_D³⁰ 1.392, having the characteristic chlorosulfate bands at 6.90 (liquid) and 6.84 μ (vapor) in the infrared,⁵ was obtained. The principal bands in the vapor spectrum were at 6.84vs, 8.04ssh, 8.18vs, 8.24vs, 8.42vs, 8.78vs, 9.23vs, 9.77vvs, 9.85vssh, 10.72vs, 11.70vs, 12.29vs, 12.9s, 14.3s, 14.8s μ. The characteristic elution time ratio *t*₀/*t*_{CCl₄} (Perkin-Elmer "B" column at 75°) was 3.8. Thus it was shown that under these conditions, only CF₂CICFCII is completely converted to the chlorosulfate.

Anal. Calcd. for C₂Cl₂F₃O₂S: C, 9.0; S, 12.0. Found: C, 9.4; S, 12.0.

Preparation of Pure Isomer CFCl₂CF₂I (II).—The product of the reaction of ICl with chlorotrifluoroethylene at 50° in the presence of iron, *i.e.*, containing 66% CFCl₂CF₂I and 34% CF₂CICFCII (see Table II), was treated with an excess of chlorosulfonic acid while stirring at 50-52° for 2.5 hours and then poured over chipped ice. The lower organic layer was separated and stirred with 10% aqueous sodium hydroxide until it remained permanently basic after standing in contact with water. [This treatment converts the chlorosulfate CF₂CICFCIOSO₂Cl into the carboxylic acid salt CF₂CICCOONa which is soluble in the water layer (see below).] After washing the remaining lower layer with water and drying over Drierite, the crude product was distilled in a small Vigreux unit. There was collected an almost colorless liquid, b.p. 101°, *n*_D²⁵ 1.4446, *d*₄²⁵ 2.189, *MR*_D²⁵ found 33.88, calcd. 34.1, shown by V.L.P.C. to consist only of the isomer II (*Anal.* Calcd.: C, 8.61. Found: C, 8.81). This isomer is considerably

(11) The atomic refractions used are based on unpublished work of A. H. Fainberg and W. T. Miller, Jr.

less light sensitive and much less lachrymatory than the isomer I. These isomers boil within 1° of one another and are difficult or impossible to separate by simple fractional distillation. The isomer $\text{CFCl}_2\text{CF}_2\text{I}$ appears to be the slightly lower boiling iodide as shown by the enrichment of successive fractions in $\text{CF}_2\text{ClCFClI}$ during distillation. The infrared spectrum of II (vapor) has strong absorption maxima (in μ) at 8.45vs, 8.62vs, 9.01vs, 9.85vs, 9.94ssh, 11.08vs, 11.85s, 13.3vvs. The absorption maximum in the ultraviolet spectrum taken in isoöctane was at 274 $m\mu$.

Reaction of 1,1-Dichloro-1,2,2-trifluoro-2-iodoethane with Chlorosulfonic Acid.—To 70 g. (0.601 mole) of chlorosulfonic acid there was added drop by drop during 0.5 hr. a total of 30 g. (0.108 mole) of $\text{CFCl}_2\text{CF}_2\text{I}$ while stirring. During the addition, the reaction temperature was raised gradually until the liberation of iodine and the evolution of sulfur dioxide were observed at 100° when about 8 g. of the iodide had been added. The addition was completed, and the reaction mixture was then stirred for 2 hr. longer at 100°. After cooling, the contents of the flask were poured into chipped ice and the lower layer was separated, washed once with cold water, dried with a mixture of calcium and magnesium sulfates, and distilled in a small still packed with glass helices. There was collected, after a small fore-run containing unreacted iodide and 1,1,2-trichlorotrifluoroethane, 15 g. of the chlorosulfate, $\text{CFCl}_2\text{CF}_2\text{OSO}_2\text{Cl}$, b.p. middle cut 76° (100 mm.), a colorless liquid, n_D^{20} 1.3943.

Anal. Calcd. for $\text{C}_2\text{Cl}_4\text{F}_2\text{O}_2\text{S}$: C, 8.98; S, 11.99. Found: C, 9.25; S, 12.24.

The absorption band for the chlorosulfate group in the vapor infrared spectrum is at 6.82 μ ; in the infrared spectrum of the liquid it is at 6.89 μ . The principal peaks in the vapor spectrum were at 6.82vs, 7.85vs, 8.16vs, 8.84vvs, 9.02vs, 10.54vs, 10.9vs, 12.1s, 13.5vs μ . The characteristic elution time ratio t_e/t_{CCl_4} (Perkin-Elmer "B" column at 75°) was 4.2.

Reactions of $\text{CF}_2\text{ClCFClOSO}_2\text{Cl}$. (a) **Hydrolysis.**—Dilute sodium hydroxide was added drop by drop to a mixture of 1 g. (0.00374 mole) of $\text{CF}_2\text{ClCFClOSO}_2\text{Cl}$ and 10 ml. of water until solution was complete and the solution remained neutral. Water was removed by evaporation and the remaining salts, after drying at 110° in an oven, were extracted with absolute ethanol. The ethanol was evaporated, and there remained ca. 0.6 g. of $\text{CF}_2\text{ClCOONa}$, of which the infrared spectrum matched that of an authentic sample of sodium chlorodifluoroacetate prepared by hydrolysis (aqueous NaOH) of known $\text{CF}_2\text{ClCOOC}_2\text{H}_5$.

(b) **Esterification.**—Three grams (0.065 mole) of absolute ethanol was added dropwise to 2.3 g. (0.0086 mole) of $\text{CF}_2\text{ClCFClOSO}_2\text{Cl}$ cooled to 0°. When the resulting vigorous reaction had subsided, the reaction mixture was refluxed for 3 hr. at 80°. After cooling, ice-water was added, and the resulting lower layer was separated and dried with Drierite. There was obtained 1.5 g. of colorless liquid shown by infrared spectroscopic analysis to be the known $\text{CF}_2\text{ClCOOC}_2\text{H}_5$.

(c) **Ammonolysis.**—Anhydrous ammonia was passed for 0.25 hr. into 0.4 g. (0.0015 mole) of $\text{CF}_2\text{ClCFClOSO}_2\text{Cl}$ in 15 ml. of anhydrous ether cooled to 0°. The solution was filtered to remove ammonium chloride, fluoride and sulfate. The solvent was removed from the filtrate by distillation. The remaining white solid (0.3 g.) was recrystallized from carbon tetrachloride-methylene chloride. There was obtained ca. 0.2 g. of $\text{CF}_2\text{ClCONH}_2$, white solid, m.p. 81–82° (not depressed on admixture with $\text{CF}_2\text{ClCONH}_2$ prepared by ammonolysis of known $\text{CF}_2\text{ClCOOC}_2\text{H}_5$). The infrared spectrum of this solid matched that of an authentic sample of $\text{CF}_2\text{ClCONH}_2$.

Reactions of Dichloriodotrifluoroethanes with Iodine Monochloride in the Presence of Iron.—Approximately 5-ml. portions of $\text{CF}_2\text{ClCFClI}$ and $\text{CFCl}_2\text{CF}_2\text{I}$ shown by chromatographic analysis to be 98 and 96% pure in each isomer, respectively, were heated separately under a nitrogen atmosphere with equal volumes of iodine monochloride in the presence of iron strands at 40–50° for 2.5 hr. with occasional shaking. After the products were worked up as described earlier, reanalysis by V.L.P.C. showed that the isomer composition of $\text{CFCl}_2\text{CF}_2\text{I}$ remained at 96% while that for $\text{CF}_2\text{ClCFClI}$ was 96%.

Reaction of Chlorotrifluoroethylene with Iodine Monochloride in the Presence of Aluminum Chloride.—Into a three-necked flask equipped with a thermometer, con-

denser, and gas inlet tube was placed 200 g. of iodine monochloride, 80 g. of aluminum chloride and 2 g. of iodine. Over a period of 3 hours 195 g. of chlorotrifluoroethylene was introduced, the reaction temperature being maintained at 35–40°. About 50 g. of chlorotrifluoroethylene was recovered in a Dry Ice trap attached to the system. The reaction product was washed and dried as above using $\text{CF}_2\text{ClCFClI}$ as a diluent (a considerable quantity of suspended solids was present). After removing the solvent by distillation, about 50 g. of product remained. This mixture was analyzed by V.L.P.C. using a 2-meter Perkin-Elmer "B" column at 75°. The following compounds were separated and identified spectroscopically (compound, approximate weight per cent., and the characteristic elution time ratios t_e/t_{CCl_4} , in order): $\text{C}_2\text{F}_4\text{Cl}_2$ (90% CF_2CCl_2 , 10% $\text{CF}_2\text{ClCFCl}_2$), 15, 0.23; $\text{CCl}_2=\text{CClF}$, 5, 0.66; $\text{CCl}_2=\text{CClF}_2$ (isomerically pure), 60, 1.2; $\text{CF}_2=\text{CClI}$,¹² 2, 1.3; $\text{CF}_2\text{CCl}_2\text{I}$ ⁶ (isomerically pure) 15, 3.2; $\text{CCl}_2=\text{CCl}_2$, 1, 3.5. Two unidentified olefins possessing infrared maxima at 6.1 and 6.16 μ constituted about 2% of the product.

$\text{CF}_2\text{CCl}_2\text{I}$ boiled at 45° at 100 mm., m.p. 21°, n_D^{25} 1.4535, and had the following characteristic bands in the infrared spectrum (vapor): 7.81m, 8.09vs, 8.23vvs, 11.22s, 11.90vs, 12.78vs, 14.4s μ . The absorption maximum in the ultraviolet spectrum taken in isoöctane was at 296 $m\mu$.

Anal. Calcd. for $\text{C}_2\text{Cl}_2\text{F}_2\text{I}$: C, 8.61; Cl, 25.43; I, 45.51. Found: C, 8.68; Cl, 25.14; I, 45.88.

Reaction of 1,1-Dichloro-2,2-difluoroethylene with Iodine Monochloride.—To 300 g. (2.25 moles) of $\text{CF}_2=\text{CCl}_2$ in a glass flask cooled to 0–3°, there was added drop by drop over a period of 3.5 hr. 292.5 g. (1.18 moles) of iodine monochloride while stirring. (An atmosphere of dry high-purity nitrogen was maintained in all the procedures and manipulations to exclude air and moisture when necessary.) Stirring was continued for another 2.75 hr. after which the crude product was worked up to yield 14% by weight of unreacted $\text{CF}_2=\text{CCl}_2$, 1% by weight of $\text{CF}_2\text{ClCCl}_2$, 85% by weight of $\text{C}_2\text{Cl}_2\text{F}_2\text{I}$ shown by V.L.P.C. to consist of 99% $\text{CF}_2\text{ClCCl}_2\text{I}$ and 1% of $\text{CCl}_2\text{CF}_2\text{I}$. The pure isomer $\text{CF}_2\text{ClCCl}_2\text{I}$ (*Anal.* Calcd.: C, 8.1; Cl, 36.0; I, 42.98. Found: C, 8.0; 7.9; Cl, 36.3; I, 42.87) separated by preparative chromatography, boiled at 75° at 75 mm. and melted at 37°. The principal absorption maxima (in μ) in the infrared spectrum of the vapor are 8.60vvs, 9.82vs, 11.83vs, 12.00vs, 13.0vs and 14.5vs. The absorption maximum in the ultraviolet spectrum taken in isoöctane is at 302.5 $m\mu$. $\text{CF}_2\text{ClCCl}_2\text{I}$ is a powerful lachrymator and very light sensitive.

When this reaction was carried out at –10° none of the isomer $\text{CCl}_2\text{CF}_2\text{I}$ could be detected chromatographically.

When this reaction was carried out from 5 to 15° the iodine monochloride adduct ranged from 98 to 97% $\text{CF}_2\text{ClCCl}_2\text{I}$ isomeric purity and the product contained 2 to 3 wt. % $\text{CCl}_2\text{CF}_2\text{I}$, respectively. Total conversion to adducts was about 90–92%. At this temperature range but in the presence of iron powder the conversion to the isomer $\text{CCl}_2\text{CF}_2\text{I}$ and to $\text{CCl}_2\text{CF}_2\text{Cl}$ increased. Specifically, at 5–7° for 5.5 hr., in the presence of 0.5 wt. % iron there was a 58% conversion to adduct consisting of 83% of $\text{CF}_2\text{ClCCl}_2\text{I}$ and 17% of $\text{CCl}_2\text{CF}_2\text{I}$, and 10.5 wt. % of the product was the chloride $\text{CF}_2\text{ClCCl}_2$. Under identical conditions but at 10–13° for 6 hr. in the presence of 0.5 wt. % iron there was a 59% conversion to adduct consisting of 80% of $\text{CF}_2\text{ClCCl}_2\text{I}$ and 20% of $\text{CCl}_2\text{CF}_2\text{I}$, and 14 wt. % of the product was $\text{CF}_2\text{ClCCl}_2$.

In one experiment the addition procedure was reversed and a 10% excess of the olefin $\text{CF}_2=\text{CCl}_2$ was added to the iodine monochloride in a glass flask equipped with a Dry Ice-filled reflux condenser. The reaction mixture was worked up after refluxing of the olefin (b.p. 20°) had ceased. Under these conditions the adduct consisted of about 90% $\text{CF}_2\text{ClCCl}_2\text{I}$ and 10% $\text{CCl}_2\text{CF}_2\text{I}$ and the weight percentage of by-product $\text{CF}_2\text{ClCCl}_2$ was about 20%. The isomer $\text{CCl}_2\text{CF}_2\text{I}$ was separated by preparative chromatography and showed an absorption maximum in the ultraviolet spectrum taken in isoöctane at 274.5 $m\mu$. The principal absorption maxima in the infrared spectrum of the vapor are at 8.70vvs, 10.12vs, 11.67vs, 11.93m, 13.6msl, 13.85vs μ .

Reaction of Perfluoropropene with Iodine Monochloride.—Into a 1-liter Monel autoclave containing 826 g. of iodine monochloride, 629 g. of perfluoropropene was transferred *in vacuo*. The autoclave was sealed and allowed to shake

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_D^{25} 1.337, consisting mostly of a mixture of $\text{CF}_3\text{-CFClCF}_2\text{Cl}$, the chlorine adduct of perfluoropropene, and $\text{C}_3\text{ClF}_6\text{I}$, and 437 g. of $\text{C}_3\text{ClF}_6\text{I}$, b.p. 78–78.5°, n_D^{25} 1.375. An additional 37 g. of residue consisted mostly of $\text{C}_3\text{ClF}_6\text{I}$. The 437-g. fraction of ICl adduct $\text{C}_3\text{ClF}_6\text{I}$ was shown by V.L.P.C. to consist of 91.5% $\text{CF}_3\text{CFICF}_2\text{Cl}$ and 8.5% $\text{CF}_3\text{-CFClCF}_2\text{I}$. The pure isomers were separated by preparative chromatography.

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

$\text{CF}_3\text{CFClCF}_2\text{I}$: n_D^{25} 1.3741, ultraviolet maximum in isoöctane at 273 μ ; 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 $\text{C}_3\text{ClF}_6\text{I}$: C, 11.53; Cl, 11.35; I, 40.63. Found for $\text{CF}_3\text{CFICF}_2\text{Cl}$: C, 11.54; Cl, 11.35; I, 40.51. Found for $\text{CF}_3\text{CFClCF}_2\text{I}$: C, 11.38; Cl, 11.11; I, 40.04.

Separation of $(\text{CF}_3)_2\text{CFCF}_2\text{I}$ from $\text{CF}_3\text{CF}_2\text{CFICF}_3$.—The thermal reaction of CF_3I 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% $\text{CF}_3\text{CF}_2\text{CFICF}_3$ and 8% $(\text{CF}_3)_2\text{CFCF}_2\text{I}$. The pure isomers were separated by preparative chromatography.

$\text{CF}_3\text{CF}_2\text{CFICF}_3$: n_D^{25} 1.3290, ultraviolet maximum in isoöctane at 279 μ ; principal infrared absorption bands for vapor at 7.43m, 7.55s, 7.81vs, 7.99vvs, 8.07vssh, 8.13vssh, 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 .

$(\text{CF}_3)_2\text{CFCF}_2\text{I}$: n_D^{25} 1.3330, ultraviolet maximum in isoöctane at 275 μ ; 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 $\text{C}_4\text{F}_9\text{I}$: C, 13.9; I, 36.7. Found for $\text{CF}_3\text{CF}_2\text{CFICF}_3$: C, 14.0; I, 37.2. Found for $(\text{CF}_3)_2\text{-CFCF}_2\text{I}$: C, 13.9.

Separation of $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CF}_2\text{I}$ from $\text{CF}_3\text{CF}_2\text{CF}_2\text{-CF}_2\text{CFICF}_3$.—The thermal reaction of $\text{CF}_3\text{CF}_2\text{CF}_2\text{I}$ 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% $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CFICF}_3$ and 2% $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CF}_2\text{I}$. The pure isomers were separated by preparative chromatography.

$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CFICF}_3$: n_D^{25} 1.3287, ultraviolet maximum in isoöctane at 280 μ ; principal infrared absorption bands 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 that¹³ for the known analyzed adduct.⁹

$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CF}_2\text{I}$: 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 $\text{C}_4\text{F}_9\text{I}$ 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 $\pm 0.02 \mu$.

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.

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

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, PENNSALT CHEMICALS CORP., PHILADELPHIA 18, PA.]

Fluorocarbon Halosulfates and a New Route to Fluorocarbon Acids and Derivatives. I. Polyfluoroalkyl Chlorosulfates¹

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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 $\text{C}_3\text{F}_7\text{OSO}_2\text{Cl}$, $\text{C}_3\text{F}_7[\text{CF}_2\text{CF}(\text{CF}_3)]_n[\text{CF}_2\text{CF}_2]_m\text{OSO}_2\text{Cl}$, $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)[\text{CH}_2\text{CF}_2]_n\text{OSO}_2\text{Cl}$, 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 $\text{C}_2\text{F}_5\text{COX}$, $\text{C}_3\text{F}_7[\text{CF}_2\text{CF}(\text{CF}_3)]_n[\text{CF}_2\text{CF}_2]_{n-1}\text{CF}_2\text{COX}$, $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)[\text{CH}_2\text{CF}_2]_n\text{CH}_2\text{COX}$, 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 avail-

able for reaction, *e.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 iodides² which were currently under investigation in this Laboratory and

(1) The work herein reported was carried out in part under contract between the Office of Naval Research and the Pennsalt Chemicals Corp., 1956–1957.

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