room temperature at an initial hydrogen pressure of 47 p.s.i. On removal of the catalyst and alcohol, the 4-propyl syringol was distilled *in vacuo* at 145–148°/4 mm. in 93% yield.

Anal. Calcd. for $C_{11}H_{16}O_4$: OCH_3, 31.62. Found: OCH_3, 31.28.

An acetate of the syringol wasp repared, m.p. 87–88° (corr.), lit. m.p. 87–88°.[26]

Anal. Calcd. for $C_{13}H_{18}O_4$: OCH_3, 26.05. Found: OCH_3, 25.90.

Dihydroconiferyl alcohol. (*a*) *Dihydroferulic acid.* Fifteen grams of ferulic acid, dissolved in 200 ml. of methanol, was mixed with 1 g. of 5% palladium-charcoal and subjected at room temperature to an initial hydrogen pressure of 44 p.s.i. After hydrogenation, the catalyst was filtered and the methanol evaporated, leaving white crystals of dihydroferulic acid, m.p., 91–93°, lit. m.p. 90–91°.[27]

(b) *Ethyl dihydroferulate.* The ethyl ester of dihydroferulic acid was prepared[26] in 74% yield. It distilled at 150–157°/1 mm.

(c) *Dihydroconiferyl alcohol.* In a three neck flask equipped with a ground-glass stirrer, reflux condenser (with drying tube) and a dropping funnel, 5 g. of lithium aluminum hydride was dissolved in 500 ml. of absolute ether by prolonged vigorous stirring. Ethyl dihydroferulate (13.1 g.) dissolved in 400 ml. of absolute ether was added over a period of 2 hr. The mixture was refluxed for 1 hr. and then treated with 50 ml. of cold water-cautiously at first. A cold solution of 20 ml. of concd. sulfuric acid in 200 ml. of water was then carefully added, and after separation, the aqueous layer extracted with additional ether. The combined ether extracts were washed with water, dried over anhydrous sodium sulfate, and then distilled *in vacuo* at 168–170°/1 mm. A cloudy white material was obtained in 50% yield. On refrigeration for several days it became crystalline, m. p. 63–65°, lit. m.p. 65–70°.[28]

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C 66.34, H, 7.91.

The bis-*p*-nitrobenzoate melted at 120.5–122° (corr.); lit. m.p. 121–122°.[29]

Anal. Calcd. for $C_{24}H_{20}O_9N_2$: C, 60.00; H, 4.20. Found: C, 60.21; H, 4.38.

Dihydrosinapyl alcohol. (a) *Sinapic acid.* Sinapic acid was prepared in 63% yield from syringealdehyde,[26] m.p. 190–192°. corr.); lit. m.p. 191–192°.[30]

(b) *Dihydrosinapic acid.* Dihydrosinapic acid was prepared from sinapic acid by the same method used for dihydroferulic acid, m.p. 101.5–103° (corr.); lit. m.p. 102–103°.[19]

(c) *Ethyl dihydrosinapate.* The ethyl ester of dihydrosinapic acid was prepared[26] in 84% yield. It distilled at 195–200°/1 mm.

(d) *Dihydrosinapyl alcohol.* Dihydrosinapyl alcohol was prepared in the same manner as dihydroconiferyl alcohol, m.p. 75–76.5° (corr.); lit. m.p. 75.5–76.5°.[26]

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60, OCH_3, 29.24. Found: C, 62.21; H, 7.69; OCH_3, 29.40.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, ORGANIC CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO.]

Synthesis and Some Novel Reactions of α,α-Dichloroperfluoroalkyl Esters

NEAL O. BRACE AND W. B. McCORMACK

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Photochlorination of α,α-dihydroperfluoroalkyl perfluoroalkanoates at 100–140° gave 90% of the corresponding α,α-dichloro ester distillable *in vacuo*. Thermal or catalytic cracking of the α,α-dichloro ester gave two perfluoro acid chlorides (same or different) in high yield. Reaction of the α,α-dichloro ester with water, amines, or alcohols gave an equivalent of the two corresponding acids, amides, or esters. The α,α-dichloro ester is, in effect, a dimeric acid chloride. Pyrolysis of α,α-dichloroperfluoroalkyl trichloroacetates gave trichloroacetyl chloride and a perfluoroalkanoyl chloride, while bis(α,α-dichloroperfluoroalkyl)carbonates were cleaved in two steps to phosgene and two moles of the perfluoro acid chloride. These reactions provide a convenient route to ω-chloroperfluoroalkanoic acids and their carboxyl-linked derivatives.

Photochlorination of α,α,ω-trihydroperfluoroalkanols (*A*) [$H(CF_2CF_2)_nCH_2OH$, $n = 1,2,3$, *etc.*] at 20–80° gave hemiacetals of the corresponding aldehydes,[1] and increasing amounts of α,α,ω-trihydroperfluoroalkyl ω'-hydroperfluoroalkanoates (*B*) as the conversion of alcohol to hemiacetal was raised.[1,2] From *B* a 90% yield of α,α,ω-trichloroperfluoroalkyl

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(1) N. O. Brace, submitted to *J. Org. Chem.*, Perfluoroaldehydes by Chlorination of α,α,ω-Trihydroperfluoro Alcohols.

(2) Chlorine substitution occurred when chlorination was continued at 20° until no further reaction occurred, but a complicated mixture of products was obtained.

TABLE I

α,α-DICHLOROPERFLUOROALKANOIC ESTERS

$Cl(CF_2)_{2n}COOCCl_2(CF_2)_{2n}Cl$ (*C*)

Reaction Conditions					Products										
										α,α-Dichloro Ester					
								α,α-Dichloro Ester		Calcd., %			Found, %		
n	α,α-Dihydro ester, moles	Cl_2, moles	Time, hr.	Temp.	HCl, moles	α,α-Dichloro ester, yields, %	$Cl(CF_2)_{2n}$-COCl (*E*), yield, %	B.p.	n_D^{25}	C	F	Cl	C	F	Cl
2	0.53	2.04	4.5	115–130	1.74	88	3.4	97–101 (11 mm.)	1.3512	20.1		23.7	19.4		24.4
	0.053	—	3.0	105–145	0.15	82		109 (20 mm.)							
3	0.29	1.14	4.0	112–120	—	77[a,b]	10	72 (0.35 mm.)	1.344		57.1	17.8		57.2	17.5
4	0.037	—	9.5	110–140	—	43[b]	27[b]	126 (0.8 mm.)	1.339	21.6		14.2	21.8		14.7
						$ClCCOOCCl_2(CF_2)_{2n}Cl$ (*F*)									
3	0.0535[c]	0.675	17	117–135	0.347	[d]	87.5	[d]							
4	0.6	3.73	3 (10)[e]	100–135	3.0	60	26[f]	115 (1.4 mm.)[g]	1.3764		44.7	31.3[g]		44.6	30.6[g]
5[h]	0.89	—	104	80–152	4.5	[h]	—	M.p. 143–148	—			[h]			
						$CF_3(CF_2)_2COOCCl_2(CF_2)_{2n}Cl$									
3[i]	0.09	—	4	120	—	82	—	83 (5 mm.)	1.3331	20.9		16.9	20.8		17.3
5[k]	0.05	—	6	112–140	0.12	11[j]	—	93 (0.8 mm.)	1.3312	21.7		12.8	22.1		12.8

[a] Dichloro and trichloro ester cuts (2–3%) also obtained; $Cl(CF_2)_6COOCl_2(CF_2)_6Cl$, b.p. 138 (12 mm.). [b] Thermal decomposition at 190–200° pot temperature; distilled smoothly at lower pressure. [c] $H(CF_2)_6CH_2OOCCH_3$, b.p. 176° (1 atm.); n_D^{25} 1.3221. [d] The α,α-dichloro ester was pyrolyzed at atmos. pressure (190–280 pot temp.) to $Cl(CF_2)_6COCl$ and Cl_3CCOCl. [e] Rubber tubing used for chlorine feed line during 3 hr.; replaced with plastic tubing and rate increased three-fold for remaining 10 hr. See Experimental. [f] CCl_3COCl also obtained; see Experimental. [g] M.p. 30–33°; hydrolyzable Cl; calcd., 10.4; found, 10.1. [h] Experiment by K. C. Smeltz. Product showed only ω-chlorine atoms of $Cl(CF_2)_n$—chain by NMR spectroscopy and no ω-hydrogen atoms. Converted directly to ethyl ester; 80% yield. See Table II. $H(CF_2)_{10}CH_2OOCCH_3$, b.p. 80–81° (0.5 mm.) m.p. 50–50.5° (from carbon tetrachloride and from 93:7 methanol-water). [i] Experiment by W. S. Smith, Jr. $CF_3(CF_2)_2COOCH_2(CF_2)_6H$, b.p. 93.5° (20 mm.); n_D^{25} 1.3033. [j] Thermal dissociation to acid chloride occurred at 15 mm. 40% of di- and trichloro esters also obtained, b.p. 129–130° (15 mm.); m.p. 27–28°. Infrared bands at 5.50 and 5.45 μ. [k] $CF_3CF_2CF_2COOCH_2(CF_2CF_2)_5H$, b.p. 135° (20 mm.); m.p. 27–28°; infrared C=O bands at 5.55 μ. *Anal.* Calcd. for $C_{15}F_{27}H_3O_2$: C, 24.7; F, 70.4. Found: C, 24.2; F, 71.7.

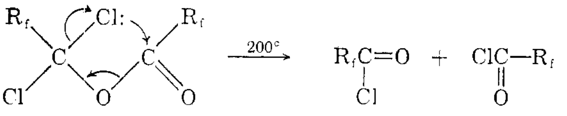
ω'-chloroperfluoroalkanoates (C) has now been obtained under carefully controlled conditions.

$$\underset{B\ (n = 1, 2, 3, 4, 5)}{\mathrm{H(CF_2CF_2)}_n\mathrm{COOCH_2(CF_2CF_2)}_n\mathrm{H}} + \mathrm{Cl_2} \xrightarrow[100\text{–}140^\circ]{h\nu} \underset{C}{\mathrm{Cl(CF_2CF_2)}_n\mathrm{COOCCl_2(CF_2CF_2)}_n\mathrm{Cl}} + \mathrm{HCl}$$

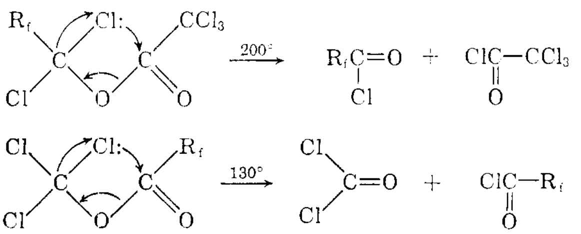
Syntheses of three types of these unusual new 1,1-dichloro esters from the corresponding hydro compounds are listed in Table I.[3] Intense irradiation was required for fastest reaction, and poisons such as are entrained with chlorine gas passing through ordinary *rubber* tubing had to be avoided. If the reaction temperature was allowed to go above 160°, cleavage to α,ω-dichloroperfluorocarbons occurred [$\mathrm{Cl(CF_2CF_2)}_n\mathrm{Cl}$ (D)]; there was also observed the formation of radical coupling "dimeric" ester product. At 100–140° reaction temperature, side reactions were observed only when using a limited concentration of chlorine. When a visible excess of chlorine was present in the reaction mixture, clean-cut replacement of all hydrogens without cleavage or coupling to condensation products resulted. Photochlorination of partially chlorinated esters also occurred smoothly.

Carbonate esters of α,α-dihydroperfluoroalkanols were perchlorinated without difficulty. The oxalate, dichloroacetate and chloroformate esters were also photochlorinated, but the process was interrupted after reaction of only one equivalent of chlorine in order to determine the position of the hydrogen atoms first replaced. The replacement of hydrogen under these conditions was found to be a random process; chlorine was found in the α and ω positions in proportion to the number of hydrogens originally present in these positions.

Acid chloride formation. These new α,α-dichloro esters C undergo thermal or catalytic cracking to ω-chloroperfluoroalkanoyl chlorides (E).



($\mathrm{R_f = Cl(CF_2CF_2)_n}$— or $\mathrm{CF_3(CF_2)_n}$—)



The thermal cleavage reaction can be drawn as having a cyclic transition state in which the α-chlorine atom approaches the carbonyl carbon atom at the same time that the ester-oxygen bond breaks. Such a process would be facilitated by the electron-withdrawing inductive effect of the fluorocarbon chain on the carbonyl group, which would tend to make the carbonyl carbon more positive. Negative groups such as the chloride ion could then have an easier approach. The still more electronegative fluoride ion should more readily attack the carbonyl group. It was found that catalytic amounts of sodium fluoride reduced the cleavage temperature of C ($n = 2$) from near 200° to 100°.

The splitting of C to E is a high yield reaction. Pyrolysis of α,α,ω-trichloroperfluoroalkyl trichloroacetates (F) (from photochlorination of the acetate of an α,α-dihydroperfluoro alcohol), for example, is a convenient, simple method for obtaining E and trichloroacetyl chloride. Symmetrical α,α-dichloro esters gave two moles of the same acid chloride, E, while trichloromethyl perfluorooctanoate gave one mole of phosgene and one mole of perfluoroctanoyl chloride. Carbonate esters of A pyrolyzed in two stages when heated.

$$[\mathrm{Cl(CF_2)_4CCl_2O}]_2\mathrm{CO} \longrightarrow \mathrm{Cl(CF_2)_4COCl} + \mathrm{Cl(CF_2)_4CCl_2OCOCl}$$

$$\mathrm{Cl(CF_2)_4CCl_2OCOCl} \longrightarrow \mathrm{Cl(CF_2)_4COCl} + \mathrm{COCl_2}$$

Displacement reactions. Nucleophilic displacement by anions or bases on an α,α-dichloro ester is a rapid, exothermic reaction, giving a quantitative yield of the two corresponding amides, esters, acids, or acid fluorides.

$$\mathrm{R_fCOOCCl_2(CF_2)_{2n}Cl} \xrightarrow{:X\mathrm{H}} \mathrm{R_fCO}X + \mathrm{Cl(CF_2)_{2n}CO}X + \mathrm{HCl}$$

$$\left(\begin{aligned}\mathrm{R_f} &= \mathrm{CF_3(CF_2)_n}\text{—}\\ &= \mathrm{Cl(CF_2)_{2n}}\text{—}\end{aligned}\right)$$

$$(X\mathrm{H} = \mathrm{HOH, H_2NH, R_2NH, ROH, R_fCH_2OH})$$

Two molecules of the *same* acid or acid derivative resulted from reactions in which a symmetrical ester (C) was employed. A good yield of the acid fluoride was isolated from reaction of C ($n = 4$) with sodium fluoride. The lower alkyl perfluoroalkanoates were very readily prepared by this method, and the hydrogen chloride was rapidly evolved. Subsequent reaction of the alkyl perfluoroalkanoate with an amine was also used to prepare the perfluoroalkanamide by displacement of the alcohol without formation of an equivalent of amine hydrochloride.

The acid chlorides of perfluoro acids have been the preferred reagents for the preparation of fluorinated esters, amides and other carboxyl-linked derivatives. The α,α-dichloroperfluoroalkyl esters can now be employed for the synthesis of a variety of fluorinated products based on ω-chloroperfluoroalkanoic acids[4] and their derivatives. The

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(3) The α,α-dichloro esters are heavy liquids having an offensive odor, especially the lower boiling compounds. In the infrared spectra there are no CH bands, and the single sharp carbonyl band is at 5.45 μ. This is at 0.10 μ lower wave length than the α,α,-dihydro ester. The α-chloro-α-hydro ester carbonyl infrared band is at 5.50 μ.

(4) W. A. Severson and T. J. Brice, *J. Am. Chem. Soc.*, **80**, 2312 (1958).

TABLE II

ω-CHLOROPERFLUOROALKANOIC ACIDS AND DERIVATIVES

Method A. $Cl(CF_2)_{2n}COOCCl_2(CF_2)_{2n}Cl$ + nucleophilic reagent
Method B. $Cl(CF_2)_{2n}COCl$ + nucleophilic reagent
Method C. $Cl(CF_2)_{2n}CCl_2OOCCCl_3$ + nucleophilic reagent
Method D. $Cl(CF_2)_{2n}COOCH_3$ + nucleophilic reagent

					Calcd., %				Found, %			
n	Method	Yield, %	M.P.	B.P.	C	F	N	Cl	C	F	N	Cl
$Cl(CF_2CF_2)_nCOOH$												
3	A,B	98	42–43	196				9.4				9.4
4	A,B	95	83–84		22.5	63.2		7.38	22.4	63.1		7.46
5	B	87	111.6–112.1		22.7	65.4		6.1	22.8	63.7		6.7
$Cl(CF_2CF_2)_nCONH_2$												
2	A	80	124		21.5	54.4		12.68	21.6	54.4		12.4
2	B	93	124									
3	A	100	145		22.15		3.69	9.34	22.3		4.1	9.4
4	A	96	157				2.92	7.39			3.01	7.3
4	B	85	157									
5	D	—	171		22.8			6.12	22.9			5.3
$Cl(CF_2CF_2)_nCOOC_2H_5$												
2	A	97		146	26.7	48.3		11.3	27.0	48.8		11.7
4[a]	C	95[b]		50 (10 mm.)	[c]			6.97	[e]			6.9
5[d,e]	C	80		94 (2.8 mm.)	[c]				[e]			
$Cl(CF_2CF_2)_nCOCl$												
2	A			100[f]	20.1	50.9		23.7	20.6	54.2		24.0
3	—			142[g]				17.8				18.1
4	—			66 (10 mm.)[h]	21.6	60.95		14.21	21.6	60.9		14.4
5	—		53–54.5	95 (28 mm.)				11.8				
$Cl(CF_2CF_2)_nCOF$												
3	A	97		46 (55 mm.)[c,i]	22.0	64.6		9.26		62.8		9.9
4	A	85		112 (200 mm.)[c]				7.7				7.3

[a] Experiment by R. W. Fasick. [b] A small amount of solid, m.p. 100–101°, probably $Cl(CF_2)_8CH(OH)OC_2H_5$, isolated. *Anal.* Calcd. for $C_9F_{16}HOCl$: Cl, 7.18 g. Found: Cl, 7.2. Infrared showed strong OH band, but no carbonyl band. [c] NMR spectrum showed no trace of ω-hydrogen; only ω-chloro group. [d] Experiment by K. C. Smeltz. [e] Methyl ester, b.p. 140° (30.0 mm.); m.p. 48–50°. *Anal.* Calcd. for $C_{12}F_{20}H_3O_2Cl$: C, 24.24; F, 63.9; Cl, 5.96. Found: C, 24.1; F, 66.0; Cl, 6.0. [f] n_D^{25} 1.3274; b.p. 57–58° (200 mm.). [g] n_D^{25} 1.3267; b.p. 37° (13 mm.). [h] n_D^{25} 1.3262; b.p 82° (23 mm.); 135–137° (200 mm.). [i] n_D^{25} 1.298; infrared carbonyl band at 5.32 μ.

methods used and derivatives prepared in the present work are listed in Table II. A few typical individual preparations are described in the Experimental part.

The displacement reaction of ethyleneimine on an α,α-dichloro ester occurred under very mild conditions, but ring opening and further reaction of the product with amine hydrochloride ensued. A mixture of equivalents of triethylamine, ethyleneimine, and *C* (n = 3) in benzene solution at 0° gave 2-(7 - chloroperfluoroheptanamido)ethyltriethylammonium chloride (*G*) in 65% yield, and 35% of a mixture of higher polyethyleneimine analogs of *G*.

Ester-exchange occurred when *C* (n = 2) was heated with 1,1,5-trihydroperfluoropentanol (*A*, n = 2), but as the presumed α,α-dichloro alcohol was displaced, it immediately decomposed to hydrogen chloride and the acid chloride, which later distilled out. That displacement, rather than splitting to acid chloride and subsequent esterification occurred, was demonstrated by isolating the *same* α,α-dihydro ester and perfluorobutyroyl chloride in 90% yield from reaction of 1,1,5-trihydroperfluoropentanol with 1,1-dichloroperfluorobutyl 5-chloroperfluoropentanoate.

$$Cl(CF_2)_4COOCCl_2(CF_2)_4Cl + H(CF_2)_4CH_2OH \xrightarrow{150^\circ} Cl(CF_2)_4COCl + Cl(CF_2)_4COOCH_2(CF_2)_4H$$

$$Cl(CF_2)_4COOCCl_2(CF_2)_3F + H(CF_2)_4CH_2OH \xrightarrow{90\%} F(CF_2)_3COCl + Cl(CF_2)_4COOCH_2(CF_2)_4H$$

If the acid chloride was not removed as rapidly as it was produced, however, further reaction with alcohol occurred to give a second molecule of ester.

Heating *C* (n = 3) with cobaltic fluoride gave the acid fluoride and free chlorine in quantitative yield.

EXPERIMENTAL

Photochlorination of α,α,ω-trihydroperfluoroalkanol esters. **A reaction vessel having an internal ultraviolet source (mercury vapor in quartz tubing) (ultraviolet cell) identical**

TABLE III

FRACTIONAL DISTILLATION IN COLUMN A AT 10:1 REFLUX RATIO

Fr.	Head Temp./mm.	Pot Temp.	n_D^{25}	Wt., G.	Identity
I	36–37/5.0	95–130	1.3157	1.6	$Cl(CF_2)_8Cl$ (*D*)
II	38–56/5.0	157	1.3202	1.9	*D* + $Cl(CF_2)_8COCl$ (*E*)
III	52–54/1.0–0.7	144	Solid	2.3[a]	$Cl(CF_2)_8CCl_3$ + $Cl(CF_2)_8COOH$
IV	80–106/0.9	154	1.3335	1.8	
V	112–119/0.8	152	1.3329	11.4[b]	$Cl(CF_2)_8COOCHCl(CF_2)_8Cl$ (*I*)
VI	121–119/1.0–0.8	152	1.3337	31.1	*C* and *I*
VII	118–120/0.7	156	1.3375	137.8[c]	*C* (infrared carbonyl band at 5.45 μ)
VIII[d]	112–105/0.7	200	1.3404	4.8	*C*
IX	Hold-up and residue			6.1	

[a] *Anal.* Cl, 19.5. [b] *Anal.* Calcd. for $C_{18}F_{32}HO_2Cl_3$: Cl, 11.0; hydrolyzable Cl, 3.7. Found: Cl, 11.5; hydrolyzable Cl, 4.7. [c] *Anal.* Calcd. for $C_{18}F_{32}O_2Cl_4$: Cl, 14.2; hydrolyzable Cl, 7.1. Found: Cl, 13.4; hydrolyzable Cl, 6.3. [d] Column operated at a 1:1 reflux ratio.

to that described[5] was used. Chlorine from a cylinder standing on a triple-beam balance was led through plastic hose connections to the reactor, and the exit gases at the top of the reactor were conducted directly through a 12-in. trap at −80° and the noncondensed gas bubbled into water. The hydrogen chloride evolved was thus titrated during the course of the reaction. A safety trap was used in series with the reactor. An excess of chlorine was conveniently maintained in the reactor by means of a −80° reflux condenser. Detailed description of procedures used is given in the following sections. Extensive use of platinum spinning band fractionation columns was made in the separation of the corrosive liquid mixtures. Data for a typical distillation are recorded in Table III.

C (*n* = *2*). Chlorine (195 g., 2.75 moles) was fed into 245.6 g. (0.534 mole) of *B* (*n* = 2) (b.p. 92.5–94.5° (17.0 mm.); n_D^{25} 1.3155–1.3162) in the ultraviolet cell over a 4-hr. period at 115–128°. A small excess of chlorine passed through the reaction liquid and was collected in a −80° trap (56.5 g. after 4 hr.). Hydrogen chloride was titrated with 2*N* aqueous sodium hydroxide; it amounted to 1.74 moles (82%). A sample of the reaction product showed a carbonyl band at 5.47 μ and a very weak CH band at 3.35 μ in the infrared spectrum. It was analyzed.

Anal. Calcd. for $C_{10}F_{16}Cl_4O_2$: Cl, 23.7; hydrolyzable Cl, 11.8. Found: Cl, 23.0; hydrolyzable Cl, 10.4.

The hydrolyzable chlorine was 88% of theory. Chlorine (14.0 g.) was fed into the reaction mixture again for 0.5 hr. at 116–123°; 7.0 g. was used up. The total chlorine used was, therefore, 145.5 g. (2.04 moles) or 96.2%. The reaction product weight 311 g. (97.6%) including 1.6 g. which collected in the −80° trap and which remained after chlorine boiled away. *C* (*n* = 2), (b.p. 97–101° (11 mm.); n_D^{25} 1.348 to 1.354; 272 g. (88%)) was obtained by distillation in a 3-ft. platinum spinning band column (Column A). In addition, 13.0 g. of forerun, b.p. 46–58° (11 mm.); and higher-boiling cuts, 3.4 g.; b.p. 112–116° (11 mm.); n_D^{25} 1.3645; (found: Cl, 26.0 (8.3 hydrolyzable); infrared, no CH bands, C=O at 5.45 and 5.63 μ) and 7.2 g., b.p. 136–160° (11 mm.); n_D^{25} 1.3693, were isolated. [Found: 23% Cl, (5.8% hydrolyzable). Infrared CH at 3.35 μ, no CH bands at 6.87 or 7.11 μ; C=O at 5.45–5.50 μ.]

C (*n* = 4). Photochlorination of 32 g. (0.037 mole) of *B* (*n* = 4) (m.p. 44–48°, b.p. 163° (10 mm.)) at 110–140° for 9.5 hr. gave 35.5 g. of liquid product. Distillation in Column A under reduced pressure at the water pump gave thermal decomposition to *E* (*n* = 4), b.p. 68–70° (14 mm.); n_D^{25} 1.3253; 9.9 g. (26.5%); infrared carbonyl band at 5.50 μ. At a lower pot temperature, pure *C* (*n* = 4) distilled, b.p. 126–127° (0.8 mm.); n_D^{25} 1.339; (infrared carbonyl band 5.46, no C—H bands); 16.6 g. (43%). The residue was 3.1 g.

C (*n* = 4) *from 1,1,9-trihydroperfluorononyl 9-chloroperfluorononanoate* (*H*, *n* = 4). Chlorine (65 g.; 0.92 mole) was bubbled during 2 hr. through 192 g. (0.21 mole) of *H* (*n* = 4), at 110–105° while 0.35 mole (83%) of hydrogen chloride was evolved. The excess chlorine which passed through was 17.7 g. (0.66 mole used up; 100%). The liquid reaction product weighed 200.3 g. There was 1.6 g. liquid in the trap, n_D^{25} 1.3114, mostly *D* (*n* = 4). Fractionation of the products in Column A (see Table III for the record typical of all distillations performed) gave 1-hydro-1,9-dichloroperfluorononyl 9-chloroperfluorononate (*I*) and (isomer) (21%) and *C* (*n* = 4). (66%).

C (*n* = 4) *from I*. Chlorine reacted at a rapid rate with 96 g. (0.1 mole) of *I* (n_D^{25} 1.3324; b.p. 123° (8 mm.)) at 121–130° during 15 min.; the amount of chlorine used was 7.6 g. (0.11 mole). The product (96.0 g.; n_D^{25} 1.3391) was identical to pure *C* (*n* = 4).

Photochlorination of H (*n* = 4) *at 160–170°*. Reaction of 35 g. (0.5 mole) of chlorine with 348 g. (0.386 mole) of *H* (*n* = 4) in the ultraviolet cell heated in an oil bath at 123–165° for 3 hr. gave 25% of the theory of hydrogen chloride. *No chlorine passed through unchanged.* The next day, chlorine was fed in again at 170–172° for 6.5 hr.; a total of 110 g. was used, and 20 g. passed through. A total of 94% of the theory of hydrogen chloride was titrated. The liquid product mixture (370 g.) was distilled in Column A using 2.0 g. of sodium fluoride to catalyze α,α-dichloro ester cleavage. Fraction I-IV contained *D* (*n* = 4), b.p. 115°/200 mm.; n_D^{25} 1.3121; 82.0 g. (22%).

Anal. Calcd. for $C_8F_{16}Cl_2$: Cl, 15.05. Found: Cl, 14.90. (Infrared: No carbonyl band.)

Fractions VI-VIII were *E* (*n* = 4) (which contained a small amount of 9-chloroperfluorononanoylfluoride), b.p. 137° (200 mm.); n_D^{25} 1.3252; 112 g. (32%). The infrared spectrum showed a band at 5.30 μ (carbonyl of the acid fluoride) and at 5.53 μ (COCl carbonyl). Fractions IX, b.p. 140° (1.1 mm.); 44 g.; m.p. 70–80°; and X, b.p. 150–170° (1.1 mm.); 35.5 g.; m.p. 26–30°, were distilled. These materials contained 14.0% chlorine, none of it hydrolyzable. The infrared spectra showed the carbonyl band at 5.47 μ. Fractions XIII and XIV, were tentatively identified as 1,1,1,8-tetrachloroperfluorononane, b.p. 63° (1.1 mm.); m.p. 48–51° (Fisher-Johns Block), 17.0 g. (3.7%). The infrared spectrum showed no CH bands, very weak carbonyl bands at 5.55 to 5.65 μ and intense CF absorption bands.

Anal. Calcd. for $C_9F_{18}Cl_4$: Cl, 24.0. Found: Cl, 24.9 (none of the compound hydrolyzed in alcohol and water).

The waxy residue (65 g.) distilled at 193° (1.2 mm.); 35.1 g., and was not further characterized. The combination of a large sample, too slow chlorine feed, and too high a re-

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(5) A detailed description and drawing of the apparatus is given by M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, 14, 239 (1949).

action temperature was responsible for the preponderance of side reactions.

F (*n* = 4). Acetyl chloride (80.0 g.; 1.0 mole) was added at 20° to 432 g. (0.9 mole) of *A* (*n* = 4) (containing about 0.09 mole of bis(4-hydroperfluorobutyl)carbinol[6] (*J*). The hydrogen chloride evolved was trapped in water. 1,1,9-Trihydroperfluorononyl acetate (*K*) was distilled, b.p. 110° (20 mm.), 463 g.; leaving a residue of 7.0 g. An infrared spectrum showed that some unesterified *J* (OH band at 2.85 μ) was present in the acetate (carbonyl band at 5.64 μ).

Photochlorination of 326 g. (0.6 mole) of *K* in the internal ultraviolet cell, under a reflux condenser cooled to −70°, was begun, using a *rubber tubing* as the connection from the chlorine cylinder. Reaction at 100–115° occurred rapidly at first, but after 2 hr. had essentially stopped; of 192 g. of chlorine fed in, only 67 g. had reacted, and 0.72 equivalents of hydrogen chloride had come out. Eight hours of further reaction at 130–140° gave 1.0 equivalent of hydrogen chloride, while 100 g. of chlorine had been fed. The *rubber tubing connection was replaced* with polyvinyl chloride plastic tubing and chlorination was resumed. In 3 hr. at 130–135° 1.0 equivalent of hydrogen chloride was evolved and 100 g. of chlorine was fed. The chlorine uptake increased from 11.5 g./hr., when rubber tubing was used, to 33 g./hr. with the plastic tubing. A total of 3.73 moles of chlorine was used, and 3.0 moles of hydrogen chloride were evolved. The product weighed 413.5 g. and there was 16 g. in the −80° cold trap. The crude material showed carbonyl bands in the infrared spectrum at 5.45 μ (1,1-dichloro ester) and 5.50 μ (acid chloride), no CH bands, and contained 28.4% Cl; (9.7% hydrolyzable). Distillation in Column A gave *F*(*n* = 4), b.p. 115° (1.4 mm.); n_D^{25} 1.3764, m.p. 30–3°; 240 g. (60%), and several lower-boiling fractions. *F* (*n* = 4) was analyzed.

Anal. Calcd. for $C_{11}F_6Cl_6O_2$: F, 44.7; Cl, 31.3; Hydrolyzable Cl, 10.4. Found: F, 44.6; Cl, 30.6; Hydrolyzable Cl, 10.1.

An infrared spectrum showed no CH bands, and a single strong carbonyl band at 5.46 μ. Redistillation of the lower-boiling cuts gave 74 g. (26%) of *E* (*n* = 4), b.p. 178–80°; n_D^{25} 1.3303, containing a small amount of trichloroacetic acid (b.p. 197.5°), and 18.0 g. (16%) of trichloroacetyl chloride, b.p. 117–119°; n_D^{25} 1.4201.

Photochlorination of di(1,1,5-trihydroperfluoropentyl)oxalate (*L*). The starting ester was prepared by ester exchange of *A* (*n* = 2) with dimethyl oxalate. Diester in 75% conversion and a small amount of monomethyl ester were isolated. *L*, b.p. 159° (22 mm.); n_D^{25} 1.3398, was analyzed.

Anal. Calcd. for $C_{10}H_6F_{16}O_4$: C, 27.8; F, 58.7. Found: C, 27.4; F, 58.9.

The internal ultraviolet cell was used. At 30° no chlorine was absorbed by 135 g. (0.26 mole) of ester during 1 hr. Very slow reaction occurred at 50–62°. After 2 hr. at 65°, 0.035 mole of hydrogen chloride had evolved and an infrared spectrum of a sample showed very little change from the starting ester. After 7.5 hr. of further reaction at 65–69°, an additional 0.5 mole of hydrogen chloride was evolved (100% of theory for two chlorine atoms substituted). The chlorine fed in amounted to 81 g., but several grams collected in the −80°-cooled exit trap. The weight of the reaction product was 150.8 g. (theory is 152.5 g. for dichloro-substituted compound).

Chlorine analysis (total and hydrolyzable) and infrared spectra showed the product contained α- and ω-chlorine substitution.

Anal. Calcd. for $C_{12}F_{16}H_4O_4Cl_2$: Cl, 12.09 (0.0 hydrolyzable for 5,5′-dichloro *L*). Found: Cl, 14.8 (10.8 hydrolyzable).

The infrared carbonyl absorption bands had shifted from 5.55 and 5.62 μ (starting ester) down to 5.52 and 5.57 μ, which also indicated α-chlorine substitution had occurred.

Distillation of the mixture in Column A under reduced pressure gave a complicated mixture of products by virtue of thermal decomposition. The lower-boiling fractions, b.p. 62–92° (25 to 20 mm.) and the trap liquid were redistilled at 200 mm. (see below). The product (b.p. 150° (20 mm.); n_D^{25} 1.3559 to 1.3549), in four cuts, amounted to 63% of the starting ester and was a mixture of dichloro esters having the possible structures 5,5′-dichloro *L*; 1,5′-dichloro *L* and 1,1′-dichloro *L*.

Anal. Calcd. for $C_6F_{16}H_4O_4Cl_2$: C, 24.55; F, 51.8; Cl, 12.09. Found: C, 24.3; F, 51.67, Cl, 12.8 (9.4 hydrolyzable). The chlorine atoms *alpha* to the ester group only were hydrolyzable in this analysis.

The combined lower-boiling fractions, when refractionated, gave 8.7 g. of 5-hydroperfluoropentanoyl chloride, b.p. 50–53.5° (200 mm.); n_D^{25} 1.3148; 3.4 g. of *E* (*n* = 2), b.p. 57–58.5° (200 mm.); n_D^{25} 1.3220; and 3.2 g. of an acid chloride mixture, b.p. 128–129° (194 mm.); n_D^{25} 1.3631 (infrared C=O bands at 5.55–5.70 μ).

Anal. Calcd. for $C_7F_8H_2O_3Cl_2$: Cl, 19.8. Found: Cl, 18.7 (15.4 hydrolyzable).

In addition, 5.1 g. of a similar product, b.p. 88–90° (25 mm.); n_D^{25} 1.3669 and 1.3646 (found: Cl, 18.8%) was obtained. These properties correspond to a mixed, monochlorinated half ester of oxalyl chloride.

Photochlorination of 1,1,7-trihydroperfluoroheptyl perfluorobutyrate (*M*) *at 70°*. *M* (154.9 g.; 0.29 mole) b.p. 93.5° (20 mm.); n_D^{25} 1.3033 was placed in the ultraviolet cell, heated to 70° in an oil bath, and chlorine was passed in at an 8 g./hr. rate for a total of 4 hr. After 2 hr. of reaction, a sample was removed for analysis and at 0.5-hr. intervals thereafter. A total of 0.25 mole of hydrogen chloride was evolved during the reaction. Hydrolyzable chlorine content of the samples increased from 1.25% to 3.4%, while total chlorine rose from 2.3% to 5.9%. The ratio of hydrolyzable to total chlorine rose from 0.54 to 0.58. The theory for α-chlorine substitution is 6.3% total and hydrolyzable chlorine; that for ω-chlorine substitution is 6.3% total, 0% hydrolyzable chlorine. The ratio of α- to ω-hydrogen atoms in *M* is 0.66. At the slow chlorine feed rate and low temperature used, clean-cut monosubstitution did not occur; a small amount of dichloroproduct and a significant amount of coupled product were also isolated. (*Cf.* Table I, 120°, 82% yield (*n* = 3)). The product recovered from the reaction was 152.4 g. (99%). Distillation in Column A gave the following fractions:

I, b.p. 109–171° (650 mm.); 12.5 g.; n_D^{25} 1.300–1.3107, contained perfluorobutyric acid and unchanged starting material. II, a monochloro ester mixture, had a b.p. of 183° (650 mm.); n_D^{25} 1.3110–3125; 67.4 g.

Anal. Calcd. for $C_{11}F_{19}ClH_2O_2$: Cl, 6.3. Found: Cl, 6.6 (3.4 hydrolyzable).

III, monochloro and dichloro ester mixture, had a b.p. of 93–100° (20 mm.); n_D^{25} 1.313–1.316; 25.0 g.; found: Cl, 8.1 (4.0 hydrolyzable). IV, "coupled" monochloro ester mixture, b.p. 100–112° (0.5–1.0 mm.); n_D^{25} 1.3255; 11.0 g. The residue amounted to 4.4 g.

The starting material gave an infrared spectrum having CH bands at 3.37, 6.85, and 7.12 μ, and carbonyl absorption at 5.54 μ. Fraction III had an infrared spectrum showing carbonyl band absorption at 5.50 to 5.52 μ, and CH bands at 3.35, 6.85, and 7.12 μ. The carbonyl band absorption indicated α-chlorine substitution had occurred. I gave an infrared spectrum having CH bands at 3.37 and 7.12 μ, but not at 6.85 μ, and carbonyl absorption at 5.50 μ only. An absorption band at 9.80 μ which was present in III was absent in IV. IV was analyzed.

Anal. Calcd. for $C_{22}F_{19}Cl_2H_2O_4$: Cl, 6.2; mol. wt., 762. Found: Cl, 5.6 (0.7 hydrolyzable), mol. wt. (ebulloscopic in alcohol), 813.

The principal constituent of IV appeared to be

$$\begin{matrix} CF_3(CF_2)_2COO\overset{\mathrm{H}}{\mathrm{C}}-(CF_2)_6Cl \\ | \\ CF(CF_2)_2COO\underset{\mathrm{H}}{\mathrm{C}}-(CF_2)_6Cl \end{matrix}$$

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[6] C. D. Ver Nooy, to be published.

which would be consistent with the position of the infrared carbonyl absorption and the analyses.

Chlorination of bis(α,α,ω-trihydroperfluoroalkyl)carbonates. Carbonates of α,α,ω-trihydroperfluoroalkanols (A) were made by the route used by Blodgett.[7] Treating equivalent amounts of alcohol and pyridine with a small excess over 0.5 equivalents of phosgene at 30–50° gave a brie of carbonate and pyridine hydrochloride. Decomposing by addition of ice, water, and methylene chloride or chloroform, washing and drying the organic phase, followed by concentration and distillation gave pure carbonate. Results are given in Table IV.

TABLE IV

Carbonates of α,α,ω-Trihydroperfluoroalkanols

n	Yield, %	B.P.	n_D^{25}	d_4^{20}
1[a,b]	91.2	85 (18 mm.)	1.3368	1.592
2[b]	86.8	127 (17 mm.) 85–88 (1.3 mm.)	1.3267	1.718
3[b]	90.4	90–92 (0.2 mm.) 110–116 (1.0 mm.)	1.3240	1.793
4[b]	81	143–148 (1 mm.; m.p. 50–53°, from ethanol) 285 (1 atm.)		

[a] *Anal.* Calcd. for $C_6H_5F_4O_3$: C, 29.0; H, 2.1; F, 52.4. Found: C, 29.3; H, 2.2; F, 53.2. [b] All these esters showed the carbonyl band at 5.62 μ in the infrared.

Bis(1,1,5-trichloroperfluoropentyl)carbonate. A sample of 30.03 g. (0.0614 mole) of bis(1,1,5-trihydroperfluoropentyl)-carbonate in a "Pyrex" flask was irradiated with a sun lamp as an ultraviolet light source, while passing a slow stream of chlorine gas through it. The sun lamp maintained the liquid system at 65–70°. Chlorine flow rate was adjusted so that a pale yellow color of dissolved chlorine was maintained in the liquid, with negligible chlorine gas color in the off gases which were scrubbed through a concentrated aqueous solution of potassium iodide. Initial chlorine absorption was rapid, with slowing of the absorption rate after 7 hr. Absorption was called complete when, with no chlorine feed, appreciable yellow color of chlorine remained after 2 hr. of heating and irradiation.

Analysis of the absorber solution showed 0.365 equivalent of hydrogen chloride had evolved (theory = 6 × 0.0613 = 0.368 eq.), with 0.5 mole of free chlorine passing through the system unchanged. Weight of the bis(1,1,5-trichloroperfluoropentyl)carbonate was 40.61 g. (95%). It solidified on cooling to 47–50°, to give a white solid.

The crude 1,1,5-trichloro ester was distilled directly under reduced pressure through an 18-in. spinning band column (about ten plates). A marked decomposition occurred at a heating bath temperature of about 140°, to give three cuts condensing at room temperature and two fractions condensing in a second receiver at solid carbon dioxide temperatures, as follows:

Cut	Receiver Temp.	B.P. (Press.)	Wt., G.	n_D^{25}
1	Room temp.	44–58 (8 mm.)	9.25	1.3683
2	Solid CO_2	—	8.48	1.3280
3	Room temp.	27–48 (1 mm.)	1.51	1.3782
4	Room temp.	65–96 (1 mm.)	13.51	1.3638
5	Solid CO_2	—	6.69	1.3379
Residue			0.5	

The two volatile fractions (cuts 2 and 5) smelled strongly of phosgene. Combination of the volatile fractions and redistillation of 14.1 g. give 12.6 g. of E (n = 2) with an acrid odor, b.p. 93° (760 mm.); n_D^{25} 1.3283; with 1.02 g. of residue from run-back, n_D^{25} 1.3305. The residue had a saponification equivalent of 151.

Fractions 1, 3, and 4 were combined (22.2 g. total) and redistilled at 1.5–2.5 mm. to give 19.2 g. of crude E (n = 2), n_D^{25} 1.3346, smelling strongly of phosgene, and 0.08 g. of residue. Redistillation of 18.6 g. of the crude acid chloride gave 15.4 g., b.p. 96°; n_D^{25} 1.3280, and 0.64 g. of residue. Isolated yield of distilled E (n = 2) was 28.0 g. or 76.5% yield.

Bis(1,1,7-trichloroperfluoroheptyl)carbonate. Bis(1,1,7-trihydroperfluoroheptyl)carbonate (430.4 g.; 0.623 mole) in a "Pyrex" glass flask was irradiated with a sun lamp as an ultraviolet light source, while passing a slow stream of chlorine gas through it. The temperature of the liquid system was maintained at 85–135°. Off gases were scrubbed through water, analysis of which indicated that at least 3.06 equivalents of hydrogen chloride were evolved (82%). The resulting bis(1,1,7-trichloroperfluoroheptyl)carbonate was a white solid melting at about 47°.

Anal. Calcd. for $C_{15}F_{24}Cl_6O_3$: Cl, 23.7. Found: Cl, 23.0.

The bis(1,1,7 - trichloroperfluoroheptyl)carbonate was pyrolyzed at heating-bath temperatures of 165–225° at atmospheric pressure to give 476.3 g. of E (n = 3). Redistillation gave 431.2 g. (86% yield) of pure E (n = 3), b.p. 142°, n_D^{25} 1.3267.

Displacement reactions. Ethyl 5-chloroperfluoropentanoate. Absolute alcohol (25.0 g.; 0.54 mole) was added slowly from a syringe over a period of 25 min. to 119.5 g. (0.2 mole) of C (n = 2). Hydrogen chloride very rapidly evolved, and a slow reflux of alcohol occurred in a 16-in. tantalum spinning band column (Column B) connected to a −80° trap. The reaction mixture was kept at 83° for 2 hr. Distillation gave 12.2 g. of excess alcohol and 122 g. of ethyl 5-chloroperfluoropentanoate, b.p. 146°, n_D^{25} 1.3347 (97%). An infrared spectrum showed a C=O band at 5.59 μ.

Anal. Calcd. for $C_7F_8H_5O_2Cl$: C, 26.7; F, 48.3; Cl, 11.3. Found: C, 27.0; F, 48.8; Cl, 11.7.

Ethyl 11-chloroperfluoroundecanoate. 1,1,11-Trihydroperfluoroundecyl alcohol (A, n = 5) (585.2 g.; 1.1 moles) with acetic anhydride (224 g.; 2.2 moles) and pyridine (85 g.; 1.1 moles) gave 1,1,11-trihydroperfluororoundecyl acetate, b.p. 80–81° (0.5 mm.); m.p. 43–49°. It recrystallized from methanol-water (93/17); yield, 81%, m p. 50–50.5°. Photochlorination of 513 g. of the acetate (0.89 mole) in the ultraviolet reactor at 80–152° gave F (n = 5), m.p. 143–148° (recrystallized from *o*-dichlorobenzene). Addition of ethanol (110.6 g.; 2.4 moles) was carried out at 135° in the ultraviolet cell under an efficient reflux condenser over a 5-hr. period, and refluxing continued for 8 hr. at 85°.

The reaction mixture was distilled in a 2-ft. spinning brush column to give 434.7 g. (80%) of *ethyl 11-chloroperfluoroundecanoate*, b.p. 94° (2.8 mm.). An NMR spectrum showed only ω-chloro atoms present. The forerun fractions contained ethyl trichloroacetate, b.p. 167–167.5° (lit.[8] b.p. 167–168°) and an unknown crystalline solid.

Ester exchange reaction of 1,1,5-trihydroperfluoropentanol with C (n = 2). In a 50-ml. flask were placed 5.00 g. (0.00836 mole) of C (n = 2) and 3.88 g. (0.0167 mole) of 1,1,5-trihydroperfluoropentyl alcohol. No heat of reaction and no evolution of gas was observed. When the mixture was heated in an oil bath under Column B, however, a liquid slowly refluxed, b.p. 98°, and hydrogen chloride was evolved when the bath temperature reached 168°. The product (3.25 g.; n_D^{25} 1.3257; 130% of theory for displacement reaction alone) was removed over a 5-hr. period at a very high reflux ratio and was identified as E (n = 2) by its infrared spectrum, analysis and conversion to the amide. Evidently, some (about 15%) thermal cleavage of the α,α-dichloro ester to acid chloride also occurred during the reaction.

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(7) F. W. Blodgett, private communication.

(8) *Beilstein*, 2, 209.

Further distillation gave 2.10 g. of 1,1,5-trihydroperfluoropentan-1-ol, b.p. 57–58° (20 mm.); n_{D}^{25} 1.3168; (54% of the alcohol charged); an intermediate fraction (1.17 g.) containing alcohol and ester, b.p. 63–89° (20 mm.); n_{D}^{25} 1.3219; and 1.16 g. of *H* ($n = 2$), b.p. 99° (20 mm.); n_{D}^{25} 1.3225, (74%), leaving 0.3 g. of liquid residue and hold-up.

Anal. Calcd. for $C_{10}F_{10}H_3ClO_2$: C, 24.3; H, 0.61; F, 61.5; Cl, 7.17. Found: C, 24.2; H, 0.82; F, 61.6; Cl, 7.3.

An infrared spectrum showed a CH band at 3.37 μ and an ester carbonyl band at 5.55 μ. The reaction was repeated two times with identical results.

Heating the α,α-dichloro ester alone gave 10% cleavage in 3 hr., 18% in 4 hr., 27% in 4.5 hr., and 36% in 5.25 hr. under the above conditions. With the bath at 200°, 83% total cleavage in 2.5 more hr. of distillation was obtained.

Ester exchange reaction of 1,1,5-trihydroperfluoropentanol with 1,1-dichloroperfluorobutyl 5-chloroperfluoropentanoate. 1,1-Dihydroperfluorobutanol (Columbia Org. Chem. Co.) was dried with calcium sulfate several days and fractionated in Column A. Material distilling at 95°; n_{D}^{25} 1.296 was used for the preparation of 1,1-dihydroperfluorobutyl 5-chloroperfluoropentanoate (*N*). *E* ($n = 2$) (30 g.; 0.10 mole) and 1,1-dihydroperfluorobutanol (20 g.; 0.1 mole) were heated at 100–148° for 8 hr. under total reflux in Column A. Unchanged alcohol (6.4 g.) was recovered, b.p. 51° (100 mm.); plus an intermediate cut, 5.3 g.; b.p. 84–104° (100 mm.); n_{D}^{25} 1.3147; and *N*, in two cuts of 14.8 g. and 7.2 g.; b.p. 105–106°; n_{D}^{25} 1.3117 and 1.3108. *N* had the C=O band in infrared spectra at 5.52 μ, and was analyzed.

Anal. Calcd. for $C_9H_2F_{15}O_2Cl$: C, 23.4; H, 0.4. Found: C, 23.7; H, 0.7.

Photochlorination of *N* (21.0 g.; 0.046 mole) in the manner described above at 120–140° during 5 hr. with an excess of chlorine present gave 78% of hydrogen chloride and 18.7 g. (82%) of distilled *1,1-dichloroperfluorobutyl 5-chloropentanoate* (*O*), b.p. 72° (13 mm.); n_{D}^{25} 1.335 (Column B). An infrared spectrum showed no CH bands, and C=O at 5.40 μ.

Anal. Calcd. for $C_9F_{15}O_2Cl_3$: C, 20.4; H, 0.0; Cl, 20.0 (hydrolyzable, 13.4). Found: C, 20.4; H, 0.4; Cl, 20.4 (hydrolyzable, 13.4).

Ester-exchange of (*O*) (10.6 g., 0.02 mole) with 1,1,5-trihydroperfluoropentanol (9.28 g., 0.04 mole) in Column A occurred smoothly at a pot temperature of 144–150° (bath 177–200°) over a 5.5-hr. period. A distillate (I), 2.8 g., collected in a Dry Ice-cooled trap at atmospheric pressure. Fractionation of the residue (Column A) gave 4.5 g. of *A* ($n = 2$), b.p. 58° (20 mm.); n_{D}^{25} 1.3151 (97%); an intermediate cut, 0.82 g., b.p. 79–87° (20 mm.); n_{D}^{25} 1.3197; and 8.6 g. of *H* ($n = 2$), b.p. 85° (10 mm.); n_{D}^{25} 1.3222 to 1.3218 (three cuts, 87%). The residue was 0.1 g. Liquid (2) (1.3 g.) collected in the −70° trap during the beginning of the distillation. Analysis of the trap liquids by vapor-liquid chromatography on a 1-m. silicone-on-"Chromasorb" column showed that only perfluorobutyroyl chloride was present in (1) and that it was the principal material present in (2). About 25% of *E* ($n = 2$) was present in (2), or less than 10% total. The total trap liquids comprised 83% of the theory for ester-exchange reaction. Not more than 10% 1,1,5-trihydroperfluoropentyl perfluorobutyrate was formed during reaction.

Attempted reaction of C (n = 2) with silver cyanide. A mixture of 5.98 g. (0.010 mole) of *C* ($n = 2$) and 2.68 g. (0.020 mole) of silver cyanide in a round-bottom flask was stirred under Column B while heating with an oil bath. When the temperature of the bath reached 214°, a slow reflux of *E* ($n = 2$) occurred; the liquid, b.p. 98°; wt., 5.40 g.; n_{D}^{25} 1.3260 (90%) was removed under high reflux over a 1-hr. period with the bath at 221–235°. The residue was apparently dry solid, 3.10 g., including the hold-up in the column. Thermal cleavage rather than replacement occurred under these conditions.

Catalytic cleavage of C (n = 2) to E (n = 2). A mixture of 5.0 g. (0.084 mole) of *C* ($n = 2$) 1.7 g. (0.17 mole) of sodium fluoride (1/8-in. pellets) and 5 cc. of tetramethylenesulfone in a small short path distilling flask was heated in an oil bath previously heated to 100°. Reaction around the sodium fluoride pellets occurred immediately. The pellets were crushed with a stirring rod, and the liquid-collecting cup and condenser returned in place over the reaction mixture. Liquid collected in the cup with the bath at 107–115°. The cup filled (*ca.* 1.5 g.) in 0.5 hr. The liquid was transferred to a small distilling pot, and the process repeated two times. The total *E* ($n = 2$) recovered was 3.8 g.; n_{D}^{25} 1.3270 (76%). (Some of the volatile acid chloride was lost when the vessel was opened.) Further heating at atmospheric pressure up to 134° bath temperature or under reduced pressure down to 17 mm. gave a great deal of foaming, but no more liquid distillate. Fractionation of the liquid in Column B gave 3 8 g. of *E* ($n = 2$), b.p. 95–101°; n_{D}^{25} 1.3271. The infrared spectrum (carbonyl band at 5.52 μ) and analysis confirmed its identity.

Anal. Calcd. for $C_5F_8Cl_2O$: C, 20.1; F, 50.9; Cl, 23.7. Found: C, 20.6; F, 54.2; Cl, 24.0.

9-Chloroperfluorononanoyl fluoride from sodium fluoride and C (n = 4). A slurry of 80 g. of tetramethylenesulfone, 47 g. (0.047 mole) of *C* ($n = 4$), and 8.6 g. (0.20 mole of sodium fluoride in a flask was heated under Column A in an oil bath at 150° for 3 hr. while stirring. Distillation gave *9-chloroperfluorononanoyl fluoride*, b.p. 112° (200 mm.); n_{D}^{25} 1.3040, in 85% yield. The infrared spectrum showed the COF band at 5.32 μ.

Anal. Calcd. for $C_9F_{17}ClO$: Cl, 7.7. Found: Cl, 7.3.

7-Chloroperfluoroheptanoyl fluoride from cobaltic fluoride and C (n = 3). In a Hastelloy shaker tube, a mixture of 50.0 g. (0.062 mole) of *C* ($n = 3$) and 15.1 g. (0.13 mole) of cobaltic (III) fluoride was heated at 150° for 4 hr. Chlorine was vented off and 7-chloroperfluoroheptanoyl fluoride distilled in 97% yield. (See Table II for analyses.)

Reaction of ethyleneimine with C (n = 3). A solution of 1.08 g. (0.025 mole) of ethyleneimine and 2.55 g. (0.025 mole) of triethylamine in 25 cc. of dry benzene was stirred under nitrogen atmosphere while 10.0 g. (0.0125 mole) of *C* ($n = 3$) was added over a 0.5-hr. period at 0–4°. A thick white paste formed. An additional 16 cc. of benzene was added and the mixture stirred for 2 hr. at 0–10°. The solid (*G*) was collected under nitrogen, washed with benzene and dried in a nitrogen atmosphere box; 10.0 g.; m.p. (sinter 157°) 162–165° dec. The solid was washed with dry tetrahydrofuran, collected again and dried in nitrogen; wt., 8.3 g. (65% yield) m.p. 176–177° dec. *G* was recrystallized from tetrahydrofuran containing a small amount of methanol; needles, m.p. 176.4–177.2° dec.

Anal. Calcd. for $C_{15}F_{12}H_{20}N_2Cl_2O$: Cl, 13.05; N, 5.16. Found: Cl, 13.8; N, 5.4.

G was readily soluble in water and was strongly surface active. Values of surface tension at 25° determined by means of a du Nuoy tensiometer were: 0.0%, 72.2 dynes/cm.; 0.1%, 31.1; 0.2%, 26.3; 0.5%, 22.9; 1.0%, 24.7 dynes/cm. The critical micelle concentration appeared to lie somewhere between 0.5 and 1.0%.

The benzene filtrate (above) was evaporated under reduced pressure at 25–20°, leaving 3.00 g. of yellow viscous oil. The tetrahydrofuran filtrate likewise gave 2.1 g. of viscous oil (35% total yield). This polymeric product contained much more chlorine than that calculated for the 1-(7-chloroperfluoroheptyl)aziridine polymer alone and is formulated as a low molecular weight "telomer" having triethylammonium chloride and hydrogen end groups. (A "telomer" having an average number of 2-ethyleneimine units would account for the observed chlorine content.)

Anal. Calcd. for $C_9F_{12}H_4NOCl$: Cl, 8.75; N, 3.45. Found: Cl, 11.4; N, 3.4.

Trichloromethyl perfluorooctanoate. Methyl perfluorooctanoate (n_{D}^{25} 1.3049; 30.0 g.; 0.071 mole) was photochlorinated in an internal ultraviolet cell at 42° for 3 hr., at 50–80° for 1.5 hr., and at 90–125° for 1.5 hr. A total of 28 g. (0.39 mole) of chlorine was used, and 0.086 mole of volatile acid was titrated. The crude product weighed 36.0 g. including 1.3 g. of liquid in the −80° trap (95% crude yield). Distillation in

Column B of trichloromethyl perfluorooctanoate occurred with some decomposition, at 28 mm. of mercury pressure (b.p. 95°), but the compound distilled smoothly at 5.0 mm., (b.p. 60°); $n_{\rm D}^{25}$ 1.3351 (69% yield).

Anal. Calcd. for $C_9F_{15}Cl_3O_2$: Cl, 20.0. Found: Cl, 19.5.

The infrared spectrum showed a single strong carbonyl band at 5.47 μ.

The trap liquid (3.1 g.), which smelled of phosgene, was redistilled in Column B and gave *perfluorooctanoyl chloride,* b.p. 128–30°; $n_{\rm D}^{25}$ 1.3011; 2.0 g. (lit.[9] b.p. 130°).

9-Chloroperfluorononanoic acid (*P*). A solution of 25.0 g. (0.05 mole) of *E* ($n = 4$) in 100 cc. of carbon tetrachloride was stirred while 0.80 g. (0.045 mole) of water was added at 25°. A layer of white solid formed on top. The mixture was heated to 42°, 5 cc. of ether was added as a co-solvent, and the clear solution stood overnight. (Without solvent present very little reaction occurred. Acetone gave a yellow product, but was otherwise satisfactory.) Part of the solvents were evaporated off at 70–80° over a 4-hr. period. Upon cooling, 9-chloroperfluorononanoic acid (*P*) crystallized out. The hygroscopic acid was collected under a nitrogen blanket on a Buchner funnel and dried in a vacuum oven at 40°; wt., 11.2 g.; m.p. 83–84° (Fisher-Johns Block); 81–84.2° (capillary, corrected thermometer). Evaporation of the solution gave an additional 11.8 g. of *P*, m.p. 83–84°, making a total of 23.0 g. (95%). *P* was recrystallized from carbon tetrachloride solution (98% recovery), m.p. 84–85° (Fisher-Johns Block); m.p. 81.8–82.6° capillary, corrected; resolidified 81°; remelted 82.5–83.1°.

Anal. Calcd. for $C_9F_{16}ClO_2H$: C, 22.5; F, 63.2; Cl, 7.38; neut. equiv., 481. Found: C, 22.4; F, 63.1; Cl, 7.46; neut. equiv., 486; H_2O, 0.05.

P from C ($n = 4$). Reaction of 1.70 g. (.095 mole) of water with 47.4 g. (0.0475 mole) of *C* ($n = 4$) ($n_{\rm D}^{25}$ 1.3391, infrared spectrum, single C=O at 5.44 μ) in a heated flask did not occur up to 130°. The mixture was stirred by a magnetic stirrer over a 1-hr. period at 130–200° while a total of 0.046 mole of hydrogen chloride was evolved. Some *P* sublimed up into the condenser. Carbon tetrachloride (100 cc.) was added and the solution cooled; *P*, m.p. 83.5–85° (Fisher-Johns Block), 29.8 g.; and an additional 2.0 g. of impure P crystallized. The oil remaining was fractionated to give 7.0 g. of *E* ($n = 4$), b.p. 80° (20 mm.); $n_{\rm D}^{25}$ 1.3263 (15% of the starting material) and 1.8 g. of impure *P*.

5-Chloroperfluoropentanamide (*Q*). A solution of 2.0 g. (0.0033 mole) of *C* ($n = 2$) in 10 cc. of ether was cooled in ice and saturated with dry ammonia gas. Ether was evaporated, and the white solid was washed with water. *Q*, 1.47 g. (80%), was recrystallized from benzene, m.p. 124° (capillary, corrected). An infrared spectrum showed NH bands at 3.00 and 3.15 μ, carbonyl bands at 5.8–5.95 μ, and a strong band at 6.15 μ.

A solution of 1.38 g. (0.046 mole) of *E* ($n = 2$) in 10 cc. of dry benzene was saturated with ammonia. The temperature rose to 50°; the benzene solution of the amide was filtered hot, and on cooling deposited long needles, 1.2 g. (93%) of *Q*, m.p. 124.5°. A mixed melting point with the product, m.p. 124° above, was not depressed.

Preparation of B ($n = 4$) *by direct esterification. B* ($n = 4$) was prepared in 45% conversion by heating an equimolar mixture (0.05 mole) of 9-hydroperfluorononanoic acid and *A* ($n = 4$) in a flask immersed in an oil bath at 160° for 6 hr. A small amount of water came out of the mixture. A preliminary distillation gave 42.0 g. of a crude mixture (95% recovery), and careful fractionation gave *B* ($n = 4$), b.p. 151.5° (5.0 mm.); m.p. 46.7–47°. An infrared spectrum showed only one carbonyl band at 5.56 μ, no OH band, but CH bands at 3.42 and 3.50 μ.

Anal. Calcd. for $C_{18}F_{32}H_4O_2$: C, 25.2; F, 70.6. Found: C, 24.1; F, 71.4.

Preparation of 1,1,9-trihydroperfluorononyl 9-chloroperfluorononanoate (*H*) *from E* ($n = 4$). A mixture of 110 g. (0.22 mole) of *E* ($n = 4$), b.p. 135–137° (200 mm.); $n_{\rm D}^{25}$ 1.3251 (contained a small amount of 9-chloroperfluorononanoyl fluoride) and 175 g. (0.41 mole) (an excess) of *A* ($n = 4$), b.p. 155.5–155.6° (200 mm.); melting range 32–57° (containing above 20% of *J*[8]), was heated in a flask fitted with a nitrogen inlet, a condenser leading to an empty trap and a water trap. The hydrogen chloride which came out overnight at 156° amounted to 0.2 mole (99%). The solid ester mixture (287.2 g.) was fractionated in Column A. There was recovered 80.0 g. (0.19 mole) of mixed alcohols, b.p. 82–92° (10 mm.) (mostly *J*) and 190 g. (96%) of *H*, b.p. 151–152° (5 mm.); m.p. 55°. The reaction was repeated three times with identical results.

Anal. Calcd. for $C_{18}F_{32}H_3O_2Cl$: C, 24.18; F, 68.0; Cl, 3.96. Found: C, 24.1; F, 67.7; Cl, 3.8.

Preparation of H from C ($n = 4$) *and A* ($n = 4$). *C* ($n = 4$) (166 g.; 0.16 mole, containing an estimated 19% of *I*) and 195 g. (0.45 mole) of *A* (ω-H, $n = 4$) (an excess) in a flask heated in an oil bath at 136–192° for 45 min. gave no evolution of hydrogen chloride. A slow nitrogen stream was bubbled into the liquid. A small pellet (0.5 g.) of sodium fluoride was added and heating continued at 170° overnight. Some reaction occurred (about 30% of theory of hydrogen chloride evolved). In order further to speed up the reaction, 10 drops of triethylamine was added and the reaction mixture was heated to a higher temperature with a heating mantle. The outside surface temperature reached 240° as a slow reflux occurred, and hydrogen chloride up to 72% of the theory was evolved in 1 hr. Distillation in Column A gave a 19% yield of 9-chloroperfluorononanaldehyde (from *I*); b.p. 76–7° (19 mm.); $n_{\rm D}^{25}$ 1.3165; (which had a C=O band at 5.65 μ), 1.15 times the theoretical amount of recovered alcohols and 234 g. (78%) of *H*, b.p. 152° (5 mm.). The loss as residue was only 1.5%.

WILMINGTON, DEL.

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(9) A. M. Lovelace, D. A. Rausch, and W. Postelnek, *Aliphatic Fluorine Compounds,* Rheinhold Publishing Company, New York, page 224 (1958).