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ω-Hydroperfluoroalkylphosphonic Acids, Esters, and Dichlorides

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ω-Hydroperfluoroalkylphosphonic esters (methyl, ethyl, butyl, and 2-ethylhexyl), obtained by telomerization of tetrafluoroethylene with a dialkyl phosphonate in quantitative yield, were hydrolyzed to the telomeric acids and converted to the stable, volatile dichlorides. Properties as a function of chain length were investigated. Surface activity of the acid series reached a maximum at ω-hydroperfluorooctylphosphonic acid. The telomeric acids were stable to heating with the strongly oxidizing aqueous 16% chromic acid solution, and are crystalline, nonvolatile solids, similar in acidity to perfluoropropylphosphonic acid.

Perfluoroalkylphosphonic acids, obtained by the addition of perfluoroalkyl iodides to phosphorus followed by hydrolysis and oxidation, are reported to be unusually stable and very strongly acidic.[1,2] The related ω-hydroperfluoroalkylphosphonic acids are readily prepared by the telomerization of tetrafluoroethylene with dialkyl phosphonates followed by hydrolysis.[3] However, the mixtures obtained have never been separated and the products have only been described as surface-active and oxidation-resistant.

This paper reports the isolation of *individual* ω-hydroperfluoroalkylphosphonic acids, esters, and dichlorides, their properties as a function of alkyl chain length, and a study of the effect of reaction conditions on the telomerization. Unlike the perfluoroalkylphosphonic acids which are nondistillable solids and the alkyl esters which decompose on heating, the dichlorides are both volatile and thermally stable. This discovery made possible an investigation of the entire telomer product spectrum.

Reaction of a dialkyl phosphonate with tetrafluoroethylene occurred rapidly and completely in a pressure reaction vessel using a peroxide as free radical chain initiator. The amount of individual telomer products decreased with molecular weight along an exponential curve, which was made steeper by an increase in temperature or by employing a larger excess of phosphonate ester reactant. Typical product distributions of diethyl phosphonate-tetrafluoroethylene telomers are plotted in Fig. 1 for reaction at 60° and at 130°. The lower reaction temperature clearly produced a larger amount of higher molecular weight telomers; at reactant ratios below 2.9 moles of diethyl phosphonate to one of tetrafluoroethylene a still broader spectrum of products was obtained.

$$CF_2{=}CF_2 + HPO(OR)_2 \xrightarrow{R\cdot} \cdot CF_2CF_2PO(OR)_2 + R'H \xrightarrow{CF_2{=}CF_2}$$

$$\cdot(CF_2CF_2)_nPO(OR)_2 \xrightarrow{HPO(OR)_2} H(CF_2CF_2)_nPO(OR)_2 + \cdot PO(OR)_2$$

The minimum initial reactant ratios which could be employed to give an all-liquid reaction product mixture from reaction at 130° varied with the particular dialkyl phosphonate from about three to one with the methyl ester to 2.6 to one with the ethyl ester and about two to one with the butyl ester. At lower mole ratios, reduced yield resulted and much solid product was obtained. At a reactant ratio of 2.9 to one, however, there appeared to be very little difference in the product distribution observed for the methyl and ethyl esters. The lower molecular weight and boiling point of dimethyl phosphonate suggested that the smaller amount of liquid present at the reaction temperature was a limiting factor. Smooth reaction to clean product mixtures occurred in high yield with this telogen at mole ratios as low as two to one when an inert solvent (1,1,2-trichloro-1,1,2-trifluoroethane) was present in the reaction vessel.

Reactions as usually carried out in a shaker tube actually occurred with a constantly changing reactant ratio. As the telogen was used up, the molecular excess in the reaction mixture was reduced continuously. This factor was eliminated in an experiment in which a liquid mixture of telogen, initiator, and gaseous tetrafluoroethylene were fed continuously at a constant rate and ratio into a reaction vessel kept liquid-full. The product distribution of the telomeric methyl esters which were obtained (Fig. 1) showed that the constantly-maintained high telogen to tetrafluoroethylene reactant ratio (3.4 to one) gave considerably more of the lower molecular weight products than was observed in shaker tube runs at a 2.9 to one initial reactant ratio.

Dialkyl ω-hydroperfluoroalkylphosphonates listed in Table I are sufficiently stable to be distilled *in vacuo* up to pot temperatures of about 150°. Higher temperatures caused decomposition to olefin and ω-hydroperfluoroalkylphosphonic acid, particularly with di(2-ethylhexyl)phosphonate. *Trans*-esterification with ethanol gave the ethyl esters

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(1) F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 3598 (1954).

(2) H. J. Emeléus and J. D. Smith, *J. Chem. Soc.*, 375 (1959).

(3) J. A. Bittles and R. M. Joyce, U. S. Pat. 2,559,754, June 1951.

TABLE I

Dialkyl ω-Hydroperfluoroalkylphosphonates and ω-Hydroperfluoroalkylphosphonic Acids

$H(CF_2CF_2)_nP(O)(OR)_2$				Calcd.				Found			
n	R	B.P.	n_D^{25}	C	F	H	P	C	F	H	P
1	CH_3	72° (10 mm.)	1.4041		36.2		14.75		36.0		14.75
2[a]	CH_3	58° (1.1 mm.)	1.3521								
3[a]	CH_3	55° (0.60 mm.)	1.3486								
1	C_2H_5	100° (20 mm.)[b]	1.3700	30.3	31.9	4.65	13.0	30.2	32.3	4.75	12.9
2	C_2H_5	95–96° (5.5 mm.)[c]	1.3577	28.4	44.9	3.28	9.2	28.5	45.9	3.25	9.2
3	C_2H_5	80° (0.22 mm.)	1.3507	27.4	52.0	—	7.08	27.4	52.2	—	7.1
1	n-C_4H_9	71–74° (0.45 mm.)	1.3970				10.5				11.5
2	n-C_4H_9	88° (0.5 mm.)	1.3800				7.85				8.1
1	H	—	—	13.2	$4_1.7$	—	17.0	13.2	40.2	—	16.7[d]
2	H	—	—	17.02	$5^1.9$	—	11.0	16.3	51.0	—	10.6[e]
3[f]	H	—	—	—	—	—	7.4	—	—	—	7.7[g]
4[f]	H	—	—	—	—	—	6.2	—	—	—	6.0
5[f]	H	—	—	—	—	—	5.16	—	—	—	5.1

[a] Not completely separated; accurate analyses could not be obtained. [b] Also b.p. 87° (10 mm.); b.p. 54° (1.2 mm.). [c] B.p. 54° (0.2 mm.). [d] Neut. equiv. 91.0; % H_2O, 0.7. [e] Neut. equiv. 137; % H_2O, 1.1. [f] From the ω-hydroperfluoroalkylphosphonic dichloride and 50% aqueous alcohol; the monohydrates were isolated. [g] Neut. equiv., 209.

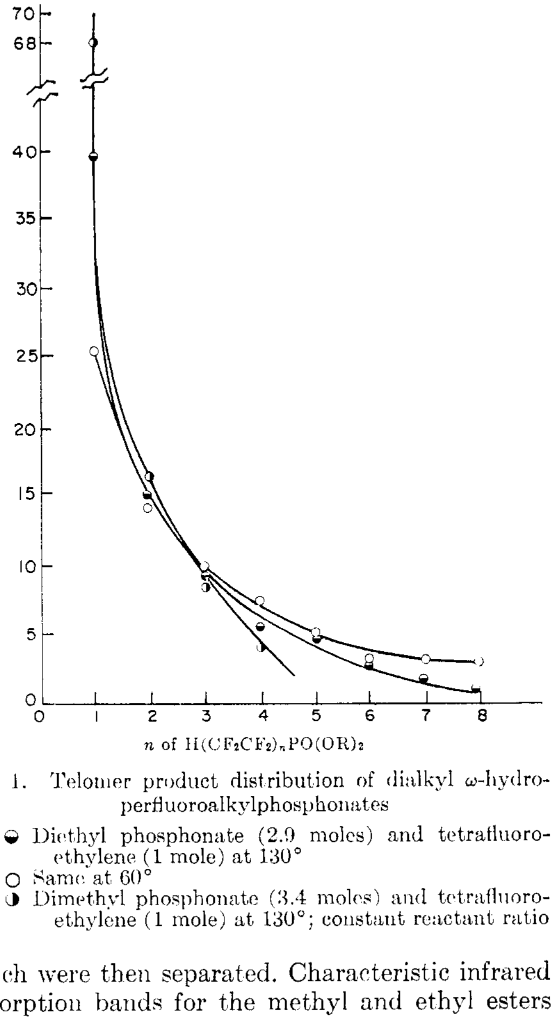

Fig. 1. Telomer product distribution of dialkyl ω-hydroperfluoroalkylphosphonates

◒ Diethyl phosphonate (2.9 moles) and tetrafluoroethylene (1 mole) at 130°

○ Same at 60°

◑ Dimethyl phosphonate (3.4 moles) and tetrafluoroethylene (1 mole) at 130°; constant reactant ratio

which were then separated. Characteristic infrared absorption bands for the methyl and ethyl esters are listed in the Experimental.

Refluxing the esters with concentrated hydrochloric acid for several hours gave complete hydrolysis[4] to the acids (Table I). Extremely stable foams were encountered on attempted distillation; this was avoided by extracting into ether from which most of the water separated out. The phosphonic acids were not soluble in other common water-immiscible solvents. The pure acids and their hydrates were hygroscopic crystalline solids, which would not distill up to 200° (1.0 mm.).

The ω-hydroperfluoroalkylphosphonic dichlorides (Table II) were prepared in high yield from the acids or the ethyl esters by reaction with phosphorus pentachloride. The product distribution of the original ester mixture was then determined by fractional distillation of the dichlorides, which could be heated to 250° without evidence of decomposition. The lower boiling compounds were readily hydrolyzed by atmospheric moisture, and were handled under nitrogen. Hydrolysis gave the pure phosphonic acids.

The surface tension lowering of aqueous solutions of the phosphonic acids is plotted as a function of chain length in Fig. 2. The lower members of the series were more soluble and less effective in

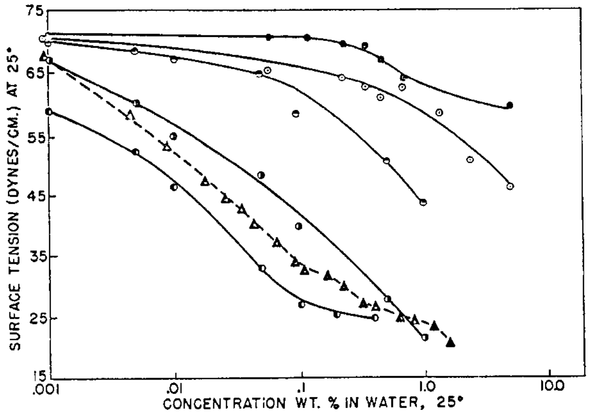

Fig. 2. Surface tension of aqueous solutions of ω-hydroperfluoroalkylphosphonic acids

● $H(CF_2CF_2)_nPO(OH)_2$, $n = 1$; ⊙, $n = 2$; ◓, $n = 3$; ◑, $n = 4$; ◐, $n = 5$; ▲, $n = 2$ to 6

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[4] P. C. Crofts and G. M. Kosolapoff, *J. Am. Chem. Soc.*, 75, 3379 (1953).

TABLE II

ω-HYDROPERFLUOROALKYLPHOSPHONIC DICHLORIDES

$H(CF_2)_{2n}POCl_2$	B.P.	n_D^{25}	Calcd. Cl	Calcd. P	Found Cl	Found P
$n = 1$	95° (300 mm.)	1.3862	32.4	14.15	31.5	14.0
$n = 2$	75° (30 mm.)	1.3670	22.2	9.7	23.2	9.2
$n = 3$	95° (25 mm.) 102° (20 mm.)	1.3560	16.9	7.4	17.3	7.3
		M.P.				
$n = 4$	112° (12 mm.) 120° (20 mm.)	51.5–55.5°	13.7	6.0	14.3	5.9
$n = 5$	132° (12 mm.) 144° (20 mm.)	90–91.5	11.5	5.05	11.1	5.1
$n = 6$	147° (11 mm.)	(109)[a] 111–115°	9.87	4.31	9.7	4.4
$n = 7$	160° (11 mm.) 176° (19 mm.)	(110)[a] 116–127°	8.67	3.78	8.7	3.7
$n = 8$	180° (12 mm.)	(135)[a] 143–147°	7.72	3.37	7.7	3.3
$n = 9$	230° (11 mm.)[b]	158–162°	6.96	3.04	6.2	2.9

[a] Sinter point. [b] Sublimed.

reducing the surface tension of water than the higher acids. A minimum surface tension of 21.7 dynes/cm. was obtained with $n = 4$ at 1%. Acids having longer chains than $n = 5$ were almost completely insoluble in water. The dichlorides ($n = 4$ and 5) and the alkali salts of the phosphonic acids ($n = 1$ to 4) were slightly less effective than the acids themselves in reducing surface tension. Mixtures of the telomeric acids (of $n = 2$ to 6) were of equal or somewhat higher efficiency than the best individual compound. Heating a 0.5% solution of such a mixture for one week at 60° in a 16% by weight chromic acid solution gave no change in appearance or surface tension (25 dynes/cm.).

The pH titration of pure ω-hydroperfluoroalkylphosphonic acids, just as reported[1,2] for the perfluoroalkyl analogs, reveal the enhanced acidity of the dibasic phosphonic acid group having an ω-hydroperfluoroalkyl substituent as compared with the *un*fluorinated alkylphosphonic acids.[4] Two clean breaks were observed. The calculated pK values taken from the titration data are recorded in Table III, together with the reported data.

TABLE III

APPARENT DISSOCIATION CONSTANTS FOR PERFLUORO-, ω-HYDROPERFLUORO-, AND n-ALKYLPHOSPHONIC ACIDS

Phosphonic acid	pK_a (1st Break)	pK_a (2nd Break)
$H(CF_2CF_2)_nP(O)(OH)_2$		
$n = 1$	2.2[a]	4.7[a]
$n = 2$	2.1,[a] 2.04[b], 1.06[c]	4.5[a], 4.51[b], 4.42[c]
$n = 3$	2.3[a]	4.5[a]
$n = 4$	2.1[a], 1.92[b]	4.5[a], 4.30[b]
$n = 5$	2.2[a]	4.3[a]
$H(CH_2CH_2)_nPO(OH)_2$		
$n = 1$[d]	2.43[d]	8.05[d]
$n = 2$[d]	2.59[d]	8.19[d]
$CF_3PO(OH)_2$[e]	1.16	3.93
$C_3F_7PO(OH)_2$	0.9	3.96

[a] The pK_a values were taken directly from the titration curves obtained with a Beckmann pH meter with a glass electrode at 0.013M concentration and are the average of two values which agreed within 0.1 pH unit. [b] Calculated from the data at 0.013M concentration by the method cited in Ref. 1,2. I am indebted to Dr. J. R. Martin for these calculations. [c] At 0.025M concentration. [d] Data reported for 0.005M concentration; See ref. 4. [e] See ref. 1.

EXPERIMENTAL

(*a*) *Dimethyl phosphonate-tetrafluoroethylene telomerization.* Dimethyl phosphonate (redistilled, b.p. 55.5° (10 mm.); n_D^{25} 1.4005; 160 g. (1.46 moles)), di-*tert*-butyl peroxide (2.0 g.) and tetrafluoroethylene (50.0 g.; 0.5 mole; a mole ratio of 2.91) were charged to a 400-ml. silver-lined shaker tube which had been previously "conditioned" by heating three charges of the same materials. (The "conditioning" reactions gave products containing a decreasing amount of brown suspended solid with each repeated experiment and an increasing absorption rate of tetrafluoroethylene). The tube was sealed, attached to a pressure gauge and heated to 130° while shaking. The autogeneous pressure fell from 700 p.s.i. to zero in 20 min. A second run gave identical results. The product (216 g.; 100%) was discharged as a clear liquid containing a small amount of colorless gel.

Fractionation of the product in a 3-ft. platinum spinning band column (Column A) at reduced pressure gave the following materials: Dimethyl phosphonate (111 g.) containing 11.9 g. of dimethyl 2-H-perfluoroethylphosphonate, calculated from the refractive indices; 48.4 g. of dimethyl 2-H-perfluoroethylphosphonate (a total of 59 wt. % of product) b.p. 72–74° (10 mm.); n_D^{25} 1.4041; 17.2 g. of dimethyl 4-H-perfluorobutylphosphonate and dimethyl 6-H-perfluorohexylphosphonate (not completely separated), b.p. 58° (1.1 mm.); n_D^{25} 1.3521; and b.p. 55° (0.60 mm.); n_D^{25} 1.3486; and 34.0 g. (34 wt. % of product) of thick gel products which would not distill at a pot temperature of 173° (0.6 mm.). The approximate composition of the residue based on the ether-soluble phosphonic acids (25 g.) obtained by hydrolysis with concd. hydrochloric acid was $H(CF_2CF_2)_nPO(OH)_2$, n = *average* of 4.

Anal. Calcd. for $C_8H_{16}H_3PO_3$: P, 6.44; N.E. 241. Found: P, 6.7; N.E. 236.

The ether-insoluble acid weighed 2.4 g.

At 2.56 and 2.36 mole ratios of dimethyl phosphonate to tetrafluoroethylene, a much slower reaction occurred and the products contained a brown solid. At mole ratios of 2.30 to 1.82 using 100 g. of 1,1,2-trifluoro-1,2,2-trichloroethane as solvent, pressure drops and yield of telomer product corresponding to about 80–90% utilization of tetrafluoroethylene were obtained during an 8-hr. reaction time. The product mixtures consisted of a light gray colored gel and a liquid of increasing thickness as the reactant ratio of telogen to tetrafluoroethylene was reduced.

(*b*) *Dimethyl phosphonate-tetrafluoroethylene telomerization in an overflow autoclave.*[5] A 1.4-l. "Magna Dash" stainless-steel autoclave was charged with a 1 wt. % solution of di-*tert*-butyl peroxide in dimethyl phosphonate and heated to 130°. A total of 4633 g. (41.6 moles) of dimethyl phosphonate solution and 1217 g. (12.2 moles) of tetrafluoroethylene (3.41 mole ratio) were fed into the autoclave at 400 p.s.i. (gauge) pressure over a 2.5-hr. period at the rate of 454 g. of tetrafluoroethylene per hr. The tetrafluoroethylene was completely absorbed. The product (5850 g., 100%) was a clear liquid.

Fractionation in Column A gave an $n = 1$ and $n = 2$ telomer; the residue was hydrolyzed to a mixture of acids which was converted to dichlorides by reaction with phosphorus pentachloride and fractionated (see below). The products totaled: $n = 1$, 1560 g. (7.4 moles; 61% yield based on tetrafluoroethylene); $n = 2$, 397 g. (1.21 moles; 20%); $n = 3$, 200 g. (0.49 mole; 12%); $n = 4$, 96 g. (0.16 mole; 5.2%); $n = >4$, 38 g. The corresponding wt. % of total product (2300 g.) were $n = 1$, 68%; $n = 2$, 16.4%; $n = 3$, 8.7%; $n = 4$, 4.2%.

Diethyl phosphonate–tetrafluoroethylene telomerizations. (*a*) *At 130° using 1.45 moles of diethyl phosphonate and 0.5 mole of tetrafluoroethylene.* The product from the reaction done as in (a) above was a clear liquid (252 g.; 100% conversion of tetrafluoroethylene) with a small amount of suspended floc which passed through filter paper. It was distilled in Column A. There was recovered 141.9 g. of diethyl phosphonate, 37 g. (40 wt. %) of $n = 1$ telomer and 10 g. of $n = 2$ telomer (not completely separated from each other) before decomposition in the pot forced shut-down of distillation. The residue was 45.7 g. of telomeric esters which was hydrolyzed by refluxing with 100 cc. of concd. hydrochloric acid for 19 hr. The water and alcohol were distilled. A white gel collected in the downward condenser which was extracted into ether and the ether evaporated. The oil weighed 1.3 g. and showed strong OH and C-F bands in the infrared spectrum. Its infrared spectrum and analysis corresponded to a telomeric alcohol mixture of the *average* composition $H(CF_2CF_2)_3CH(OH)CH_3$.

Anal. Calcd. for $C_8H_6F_{12}O$: C, 30.0; F, 63.4. Found: C, 29.4; F, 64.2.

The pot residue (52.9 g.) was extracted into ether, leaving 4.2 g. of insoluble phosphonic acids. The ether was removed and water evaporated down to 15 mm. pressure at 145° pot temperature. The residue of mixed phosphonic acids weighed 37.8 g. The total product distribution as determined by subsequent distillation of dichlorides was $n = 1$, 39.6% (by wt.); $n = 2$, 15%; 3, 9.6%; 4, 5.9% 5, 5.3%; 6, 7, and 8, 3 7%; >8, 4.5%.

(*b*) *Reaction at 60° using succinic acid peroxide initiator.* The reaction done as in (a) above of 180 g. (1.3 moles) of redistilled diethyl phosphonate, 50.0 g. (0.5 mole) of tetrafluoroethylene (a 2.6 to one mole ratio) and 2.0 g. of "Lucidol" succinic acid peroxide at 60° gave 50% of the total pressure drop in 1 hr. The temperature rose exothermically to 64°. In 4 hr. the pressure had dropped to 37 p.s.i. The product (227 g.; 90% conversion of tetrafluoroethylene) was a viscous light gray gel (neutral *p*H). Distillation from an oil bath heated up to 180° gave 26.1 g. of distillable telomeric esters ($n = 1$ about 14 g.; $n = 2$, 9.0 g., and $n = 3$. 6.0 g.) and 38.5 g. of solid residue.

The residue contained 11.9 g. of a solid *insoluble* in 100 cc. of boiling alcohol. Hydrolysis of 24.0 g. of soluble esters was carried out by refluxing with 75 cc. of concd. hydrochloric acid for 8 hr. at 86°. The ether-soluble phosphonic acids which separated on cooling weighed 19.4 g. They were converted to a mixture of dichlorides, $n = 4$ to 8 (about 1.5 g. each).

(*c*) *Reaction at 60° of 1.45 moles of diethyl phosphonate and 0.5 mole of tetrafluoroethylene (2.9 to one mole ratio).* The reaction was repeated two times as in (a) above giving 251 g. and 252 g. of telomer product mixture as a thick gray gel. Distillation of the combined material in a 16 × 1-in. column filled with stainless steel protruded packing gave the following fractions: I, diethyl phosphonate, b.p. 68–70° (11 mm.); n_D^{25} 1.405; 306.8 g., II, b.p. 72–81° (10 mm.); n_D^{25} 1.3964; 18.6 g.; III, diethyl 2-H-perfluoroethylphosphonate, b.p. 83–92° (10 mm.); n_D^{25} 1.3720; 34.3 g.; IV, b.p. 95–105° (10 mm.); n_D^{25} 1.3659; 11.2 g.; V, diethyl 4-H-perfluorobutylphosphonate, b.p. 105–107° (10 mm.); n_D^{25} 1.3612; 8.7 g.; leaving a solid residue of 125.3 g.

The residual mixture of esters was hydrolyzed by refluxing with 300 cc. of concd. hydrochloric acid for 9 hr.; the alcohol, alkyl chloride, and water mixture was distilled and the process was repeated. After refluxing of the thick and foamy mixture for 22 hr., water was removed through a 16-in. column. The gray gel remaining weighed 251.5 g. Ether extraction removed most of the soluble phosphonic acids and the gel which remained separated into a water layer and solid. The solid was dried in air, and the water evaporated. Thorough ether extraction left 17.8 g. of insoluble solid phosphonic acids which were analyzed.

Anal. Found: C, 22.0; F, 70.2; P, 2.1.

The soluble phosphonic acids (95.2 g.) were converted to dichlorides and fractionated. The total products were: $n = 1$, 24.8% 2, 14.3%; 3, 10.0%; 4, 7.4%; 5, 5.1%; 6, 3.2%; 7, 3.2%; 8, 3.0%; > 8, 9.7%.

Di(2-ethylhexyl)phosphonate-tetrafluoroethylene telomerization. Reaction of 50 g. (0.5 mole) of tetrafluoroethylene, 2.0 g. of di-*t*-butyl peroxide, and 200 g. (0.6 mole) of "Dioctyl" (actually 2-ethylhexyl) phosphonate (mole ratio 1.19) in a shaker tube at 134–130° for 3 hr. gave 251 g. of liquid clear product (100%). Attempted distillation in Column B at 0.40 mm. pressure gave much gas evolution. The product was collected in the Dry Ice trap. The pressure rose to 1.2 mm., as only 7.5 g. liquid, b.p. 47–53° (0.7 mm.); n_D^{25} 1.4232 was collected. The residue weighed 213.5 g. A change to a straight take-off still was made, and 22.5 g. of liquid, b.p. 87–130° (1.2–5.0 mm.); pot temperature 158–171°; n_D^{25} 1.4165 was obtained. The trap liquid, 39.1 g.; n_D^{25} 1.4111 was primarily 2-ethyl-1-hexene which was redistilled (see below). The liquid residue (135.1 g.) had n_D^{25} 1.4106 and was strongly acidic. It was composed primarily of $H(CF_2CF_2)_n$-$P(O)(OH)_2$, $n =$ *average* of 4, according to titration.

Anal. Found: Neut. equiv., 215.

Glassware which had contained the acid solution was highly repellent to benzene or carbon tetrachloride, showing that a fluorocarbon compound had been strongly absorbed on the surface. The above combined trap and distillates (68.0 g.) was fractionated in a 2-ft. spinning band column to give 37.0 g.; b.p. 120–120.5°; n_D^{25} 1.4156 which had the infrared spectrum and properties reported for 2-ethylhexene-1, (b.p. 119°; n_D^{20} 1.4155).[6] Fractions, b.p. 42.5–43° (40 mm.); n_D^{25} 1.4162; 2.6 g. and b.p. 103–100° (40 mm.); n_D^{25} 1.4239; 12.2 g. were also obtained.

The product from a second telomerization reaction using the same conditions was extracted with 100 cc. of 5% sodium bicarbonate solution in order to remove the free acid prior to the distillation of the neutral ester. An emulsion formed that was not broken by the addition of salt, ether, ethanol,

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(5) Assistance by Dr. D. R. Baer is gratefully acknowledged.

(6) J. P. Wibaut and A. J. Van Pelt, Jr., *Rec. trav. chim.*, **57**, 1055 (1938); **60**, 55 (1941).

or aluminum sulfate on standing 48 hr. Filtration on cloth on a Buchner funnel merely plugged the cloth; 100 cc. of chloroform was added to the liquid emulsion filtrate which stood for several days. The chloroform layer which separated was washed with 100 cc. each of 5% sodium bicarbonate solution and 5% sodium carbonate solution and fractionated in Column A. The distilled products were the *ethyl* esters formed by ester exchange as shown by infrared spectra and analyses: $H(CF_2CF_2)_nPO(OC_2H_5)_2$, $n = 1$, 20.6 g.; $n = 2$, 14.0 g.; $n = 3$, b.p. 74–76° (0.22 mm.); n_{D}^{25} 1.3515; 7.0 g.; $n = 3$ (4), b.p. 79–107° (0.25 mm.); n_{D}^{25} 1.3466; 8.3 g.; $n > 3$, 5.0 g.

2-H-Perfluoroethylphosphonic acid. In a flask containing a polytetrafluoroethylene-covered magnetic stirring bar, and fitted with a reflux condenser and an exit line connected to a trap to quench hydrogen chloride fumes, was placed 35 g. (0.147 mole) of redistilled diethyl 2-H-perfluoroethylphosphonate and 100 cc. of concd. hydrochloric acid. The mixture was refluxed at 78–110° for 5 hr. The acid went into solution in 1 hr. The volatile products were distilled by downward distillation and the residue of slightly yellow liquid (32.5 g.) was heated to 192° (0.8 mm.) with no signs of vapors distilling after removal of the water. The liquid residue crystallized on standing (25.6 g.; 95.6%). It was very hygroscopic and liquefied at room temperature in the air when pressed between cover plates.

In like manner *4-H-perfluoro-n-butylphosphonic acid* was obtained as large, colorless crystals (97% of theory) which were transferred to vials in a nitrogen-filled box for analysis. A sealed capillary gave m.p. (sinters at 39.5°) 40.5–43.5° (sample contained 1.1% water).

6-H-Perfluorohexylphosphonic acid. To 6.2 g. (0.015 mole) of the dichloride (b.p. 102° (28.0 mm.); n_{D}^{25} 1.3560) was added 3 cc. of 50% aqueous alcohol solution. The temperature rose to 82° and fell to room temperature as 7 cc. of additional 50% aqueous alcohol was added. A homogeneous solution was obtained. Water, alcohol, and hydrogen chloride were evaporated out by heating, which left 5.7 g. (99.6%) of white crystalline solid. The acid contained one molecule of water of hydration as indicated by phosphorus and neutral equivalent analysis. *8-Hydroperfluorooctylphosphonic acid and 10-hydroperfluorodecylphosphonic acid* were prepared in an analogous fashion, and isolated as monohydrates, unchanged by heating for 3 hr. at 115°.

ω-Hydroperfluoroalkylphosphonic dichlorides. (*a*) *From telomeric phosphonic acids.* A typical mixture of ω-hydroperfluoroalkylphosphonic acids (47.0 g.) was dried by azeotropic distillation with benzene. Phosphorus pentachloride (60.0 g.; 0.29 mole) was added in portions by means of a powder addition tube at 45–118° while the mixture was stirred. Hydrogen chloride (which came out vigorously) was trapped in water. Phosphorus oxychloride refluxed towards the end of the reaction. A preliminary distillation gave 38.0 g. of phosphorus oxychloride, b.p. 62–115°, and 33.0 g. of mixed ω-hydroperfluoroalkylphosphonic dichlorides, b.p. 62–115° (20 mm.), leaving a solid residue of 7.7 g. The phosphonic acid chloride fraction was redistilled in Column A operated at reduced pressure and high reflux ratio. An azeotrope, b.p. 108° or b.p. 80° (300 mm.); n_{D}^{25} 1.4418 containing 76% of phosphorus oxychloride and 2-H-perfluoroethylphosphonic dichloride was obtained in Column A.

(*b*) *From a telomeric ester mixture.* Reaction of 86.6 g. (Calcd. 0.33 mole) of a "telomer" ester mixture with phosphorus pentachloride (146 g., the calculated amount for 0.33 mole of ester) was carried out as above using a Dry Ice trap to condense volatile products. After initial vigorous reaction, the material reacted more slowly, and the flask was heated. Addition required 1.5 hr. at 75–105°. The mixture was refluxed further for 1.5 hr. at 110–120°. Ethyl chloride and a small amount of higher boiling chloro compounds collected in the trap. Distillation of the reaction product in Column A gave a series of dichloride fractions with some color-forming impurities contaminating the higher boiling cuts.

Infrared spectra. The spectra were taken in a Perkin-Elmer Model 21 Infrared Spectrometer using rock salt prisms. The solid compounds gave poorly defined spectra, but the liquid compounds showed several features of interest relating to their unique structures. $H(CF_2CF_2)_nPOCl_2$ ($n = 1,2,3$) had a single CH (stretching) band at 3.35 μ, CH deformation bands at 7.20 and 7.35 μ, a single P → O (stretching) band at 7.70–7.72 μ, and several CF bands and CH skeletal vibration bands. 2-H-Perfluoroethylphosphonic dichloride had CF bands at 8.20, 8.75–8.90, and 9.75 μ only and a single band at 12.25 μ. 4-Hydroperfluorobutylphosphonic dichloride had CF bands at 8.25 (weak), 8.50, 8.80, 9.50, and 9.70 μ; and bands at 10.75, 11.25, 11.55, 11.80, 12.40, 12.65, 13.08, and 14.40 μ.

6-H-Perfluorohexylphosphonic dichloride had CF bands at 8.30–8.75, 9.40, and 9.60: and bands at 10.65, 11.08, 12.00, 12.25, 13.00, 13.70, 14.40 and 14.85 μ.

$H(CF_2CF_2)_nP(O)(OCH_3)_2$ ($n = 1,2$) had CH (stretching) bands at 3.35, 3.40, and 3.50 μ; CH (deformation) bands at 6.85–6.90 μ (CH_3) and of the $H(CF_2)_n$ group at 7.20, and 7.40 μ; P → O (free) at 7.78 μ and P → O $(OCH_3)_2$ at 8.45–8.50 μ and at 9.50–9.70 μ. Dimethyl 2-H-perfluoroethylphosphonate had CF bands at 8.20 and 9.00 μ and skeletal vibration bands at 10.95, and 11.85 μ; dimethyl 4-H-perfluorobutylphosphonate had CF bands at 8.25 and 9.00 μ and skeletal bands at 10.70, 11.85, 12.50, 13.25, 13.50, 13.95, and 14.50 μ. $H(CF_2CF_2)_nP(O)(OC_2H_5)_2$ $n = 1,2,3$) had CH (stretching) bands at 3.35, 3.40, and 3.50 μ (weak); CH (deformation) bands at 6.75, 6.90, and 7.30 μ ($C{-}CH_3$); and at 7.20 and 7.40 μ ($H(CF_2)_n$); P → O (free) at 7.80–7.82 μ; P → O $(OC_2H_5)_2$ at 8.40 and 9.60 μ and various CF and skeletal bands. Diethyl 2-H-perfluoroethylphosphonate had CF bands at 8.25, 8.45, 9.00, and 9.75 μ; and bands at 10.50, 12.25 (strong), 12.55, and 13.20–13.40 μ. Diethyl 4-H-perfluorobutylphosphonate had CF bands at 8.30, 8.75, 9.00, and 9.75 μ, and bands at 11.10, 11.50, 13.00, 13.75, and 14.50 μ.

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