Aziridinyl Phosphine Oxides Derived from the Radical Addition of Perfluoroheptyl Iodide to Diethyl Vinylphosphonate

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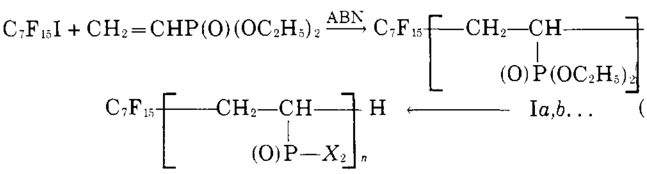
This paper describes the preparation of 10 new compounds derived from the radical addition of perfluoroheptyl iodide to diethyl vinylphosphonate. The free radical reaction is initiated by an azobisnitrile catalyst to give the iodo-adduct and a low molecular weight iodo-telomer. The iodine in the mixed iodo-esters is replaced with hydrogen to give the reduced ester-adduct and ester-telomer. The isolation and identification of these compounds and the respective acid, acid chloride, and aziridinyl derivatives is described. Some infrared and proton magnetic resonance data are also presented. The aziridinyl derivatives are of practical as well as theoretical interest because they contain a variety of functional groups—i.e., phosphoryl, perfluoroalkyl, and aziridinyl.

THE FREE radical addition of short-chain perfluoroalkyl iodides to simple olefins (*16*), vinyl and allyl monomers (*6*), and other unsaturated systems containing a variety of electrophilic and nucleophilic groups (*11, 16*) has been reported extensively. The work was extended to include the addition of long-chain perfluoroalkyl iodides to olefins (*15*) and long-chain ω-alkenoic esters (*7*). There appears to be no previous reference to the free radical addition of perfluoroalkyl iodides to unsaturated compounds containing phosphorus, though similar types of compounds have been prepared by an alternate route in which tetrafluoroethylene has been telomerized in the presence of a dialkyl phosphite to give a mixture of products (*4*). Separation of these mixed telomeric products to give individual ω-hydroperfluoroalkyl phosphoryl compounds was later reported by Brace (*5*).

The object of the work presently reported was to prepare a compound containing various functional groups—i.e., phosphoryl, perfluoroalkyl, and aziridinyl, which might be of practical as well as theoretical interest. Phosphorus-containing compounds have been used in fire-retardant formulations (*8*). Equally known are the low surface energy properties imparted by fluorine-containing compounds, particularly long-chain perfluoroalkanes with terminal CF_3 groups (*10*). Also, aziridinyl derivatives have been investigated extensively for a variety of properties ranging from crosslinking to physiological activity (*1*). The work presently reported describes the preparation of the fluoroalkyl–aziridinyl phosphine oxide derivatives of the adduct and a telomer obtained from the reaction of perfluoroheptyl iodide with diethyl vinylphosphonate. The isolation and identification of the intermediate adduct and telomer derivatives are also presented.

The free radical reaction was initiated by an azobisnitrile catalyst using the addend in slight excess.



$$C_7F_{15}I + CH_2{=}CHP(O)(OC_2H_5)_2 \xrightarrow{ABN} C_7F_{15}\left[-CH_2-\underset{\substack{|\\(O)P(OC_2H_5)_2}}{CH}-\right]_n I$$

$$C_7F_{15}\left[-CH_2-\underset{\substack{|\\(O)P-X_2}}{CH}-\right]_n H \longleftarrow \text{I}a,b\ldots \qquad (1)$$

II*a*, *b*; $X = OC_2H_5$
III*a*, *b*; $X = Cl$
IV*a*, *b*; $X = OH$
V*a*, *b*; $X = \underbrace{N-CH_2-CH_2}$

a, $n = 1$ (adduct)
b, $n = 2$ (telomer)

I*a* and I*b* were isolated only for identification. The normal procedure was to reduce the mixed iodo-esters by replacing iodine with hydrogen, then separate the resulting ester-adduct (II*a*) and ester-telomer (II*b*) by vacuum distillation. No attempt was made to obtain pure materials from the residue, though a crude liquid residue was obtained which had a chemical analysis within the theoretical range of the reduced ester, $n = 3$.

The acid chloride–adduct (III*a*) and acid chloride–telomer (III*b*) were prepared from the respective esters by acid hydrolysis to the acids, followed by reaction of the crude acids with phosphorus pentachloride. Since excessive foaming was a problem in the preparation of the crude acid-telomer, particularly upon concentrating the aqueous solutions, the acid was dried in a large evaporating dish.

The pure acid-adduct (IV*a*) and acid-telomer (IV*b*) were obtained by hydrolysis of the respective chlorides. As indicated by chemical analyses, all water was removed by heating the acids in benzene.

The aziridinyl-adduct (V*a*) and aziridinyl-telomer (V*b*) were prepared in carbon tetrachloride by the reaction of the respective acid chlorides with aziridine, using triethylamine as the acid acceptor. Pure V*a* was obtained by precipitation from carbon tetrachloride with petroleum ether.

The infrared (IR) and proton magnetic resonance (PMR) analyses are consistent with the proposed structures, though the spectra were at times complex. In the IR spectra, specific identification of bands between 7.8 and 9.00 microns was difficult because of several intense CF absorptions which occur in this region (*3*). This is complicated by the fact that the phosphoryl (P=O) absorption is known to appear as a doublet and within a wide limit range (*14*). Also, for the aziridinyl compounds, the ring breathing absorption is reported to be in the same region as the phosphoryl group (*13*). In the PMR spectra, the protons of the ester group in compounds I*a* and I*b* were readily assigned. The aziridinyl protons of V*a* and V*b* were identified by comparison with the spectrum of tris-aziridinyl phosphine oxide (APO), which shows only an intense doublet (J = 14 c.p.s.) centered at δ2.07 p.p.m. This is also in agreement with reported results which show the ring protons of an aziridinyl phosphine oxide as a doublet (J_{PH} = 14 c.p.s.) (*2*).

EXPERIMENTAL SECTION

Methods. Proton magnetic resonance spectra were determined in solvents indicated, on a Varian Model A-60A equipped with V-6040 variable temperature probe. Chemical shifts were measured with respect to tetramethylsilane as an internal reference. Infrared spectra were obtained in carbon tetrachloride from a Perkin-Elmer Model 137B spectrophotometer with sodium chloride optics. Elemental analyses and molecular weights (vapor pressure osmometer) were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points are corrected. Aziridinyl assay was determined using a modified sodium thiosulfate titration method (*12*). Ethanol (10 ml.) was used to help dissolve the samples, and a Beckman Zeromatic pH meter, Model 96, was used in conjunction with the indicators for consistency.

Materials. The free radical catalyst used was 2,2′-azobis(2-methylpropionitrile) (ABN) from Eastman Organic Chemicals. Perfluoro-*n*-heptyl iodide (PFHI), obtained from Peninsular Chemresearch, Inc., was purified by washing with a sodium bisulfite solution until colorless. PFHI was then washed with distilled water, dried over sodium sulfate, filtered, and redistilled under vacuum. Copper wool was placed in the distillation head and the receiving flask protected from light to give a clear, colorless distillate. Diethyl vinylphosphonate (DEVP) was prepared by the Arbusov reaction of triethyl phosphite with ethylene bromide, followed by dehydrohalogenation in triethyamine (*9*).

Diethyl 1-Iodo-1H,2H,2H-perfluorononylphosphonate (I*a*) and tetraethyl 1-(1H,1H-Perfluorooctyl)-3-iodo-1,3-trimethylenediphosphonate (I*b*). DEVP (57.8 grams, 0.35 mole) and PFHI (192.1 grams, 0.39 mole) were placed into a three-necked flask equipped with a magnetic stirrer, thermometer, gas inlet tube, and condenser connected to a mercury air trap. Light was excluded by covering the flask with aluminum foil. ABN catalyst (1.15 grams, 0.007 mole) was added and the system flushed with nitrogen. The flask was heated in a water bath to 80° C., at which temperature an exothermic reaction began. An ice bath was used to keep the temperature below 150° C. Reaction temperature was then maintained at approximately 85° C. for 6 hours. Unreacted material (95 grams) was removed by vacuum distillation below 50° C. (0.3 mm.). The residue (153.1 grams) was crude mixed iodo-esters (I). A small amount of I was distilled under vacuum. The iodo-adduct (I*a*) had b.p. 108–14° C. (0.03 mm.); n_D^{20} 1.3930. IR spectrum showed absorption bands at 3.33 microns (w) (CH stretching); 7.93 microns (sh) (may be P=O); 8.07 microns (v.s.), 8.27 microns (s), 8.69 microns (m) (CF); 9.53 microns (m), 9.77 microns (s), (P—O—C); and a broad peak at 10.41 microns (m). The PMR spectrum (CCl_4) showed a triplet at δ1.37 p.p.m., a broad diffuse pattern between δ1.9 and δ3.6 p.p.m., and a multiplet centered at δ4.27 p.p.m. The spectrum integrated 6:2:5, respectively. Anal. Calcd. for $C_{13}H_{13}F_{15}IO_3P$: C, 23.65; H, 1.99; F, 43.17; I, 19.22; P, 4.69; mol. wt., 660. Found: C, 23.81; H, 2.02; F, 43.17; I, 19.09; P, 4.90; mol. wt. (benzene), 650.

The iodo-telomer (I*b*) had b.p. 144–6° C. (0.03 mm.); n_D^{20} 1.4074. IR spectrum showed absorption bands similar to the spectrum of I*a*. The PMR spectrum (CCl_4) was also similar to that of I*a*, showing a triplet at δ1.38 p.p.m., a diffuse pattern between δ1.6 and δ3.3 p.p.m., and a multiplet at δ4.22 p.p.m. The spectrum integrated 12:5:9, respectively. Anal. Calcd. for $C_{19}H_{26}F_{15}IO_6P_2$: C, 27.69; H, 3.18; F, 34.57; I, 15.40; P, 7.52; mol. wt., 824. Found: C, 27.80; H, 3.14; F, 34.55; I, 15.18; P, 7.24; mol. wt. (benzene), 830.

Diethyl 1H,1H,2H,2H-Perfluorononylphosphonate (II*a*) and Tetraethyl 1-(1H,1H-Perfluorooctyl)-1,3-trimethylenediphosphonate (II*b*). A slurry of 30 grams of zinc dust in 200 ml. of ethanol was stirred and heated in a water bath to 60° C. An ethanolic solution of I (153.1 grams) and 75 ml. of concentrated hydrochloric acid were added from separate dropping funnels within 30 minutes. The bath temperature was raised to 70° C.; then 15 grams of zinc and 40 ml. of hydrochloric acid were added in increments over 1 hour. The mixture was heated an additional hour at 80° C., cooled, filtered, and concentrated on a rotary evaporator. The concentrate was washed with distilled water, then taken up in diethyl ether. The ether solution was washed with sodium bicarbonate, then with water to neutrality. The ether solution was dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The reduced esters (113 grams) were distilled under vacuum to give 40.9 grams (22% yield from DEVP) of II*a*, n_D^{20} 1.3538; 9.3 grams of intermediate fraction, n_D^{20} 1.3694; 42.3 grams (35% yield from DEVP) of II*b*, n_D^{20} 1.3857; and 14.2 grams of residue. The residue was stirred with absolute ethanol and filtered to give a fine brown solid (unidentified). The filtrate was concentrated to give a dark brown liquid believed to be another telomer, $n = 3$.

Redistillation of a portion of II*a* gave b.p. 82–4° C. (0.05 mm.).

Anal. Calcd. for $C_{13}H_{14}F_{15}O_3P$: C, 29.23; H, 2.64; F, 53.35; P, 5.80. Found: C, 29.34; H, 2.84; F, 53.18; P, 5.59.

II*b* had b.p. 138–40° C. (0.05 mm.).

Anal. Calcd. for $C_{19}H_{27}F_{15}O_6P_2$: C, 32.68; H, 3.90; F, 40.81; P, 8.87; mol. wt., 698. Found: C, 32.73; H, 4.00; F, 40.88; P, 8.69; mol. wt. (chloroform), 702.

Anal. Solid residue: C, 28.79; H, 3.36; F, 29.35; P, 10.34.

Anal. Liquid residue: Calcd. for $C_{25}H_{40}F_{15}O_9P_3$: C, 34.82; H, 4.67; F, 33.04; P, 10.77. Found: C, 33.37; H, 4.33; F, 31.34; P, 9.79.

1H,1H,2H,2H-Perfluorononylphosphonic dichloride (III*a*). II*a* (40 grams, 0.075 mole) was heated with 100 ml. of concentrated hydrochloric acid at gentle reflux for 3 hours. The mixture was concentrated under vacuum to a gelatinous mass. Concentrated hydrochloric acid (75 ml.) was added to the mixture and refluxed overnight. The mixture was again concentrated under vacuum. Benzene was added and the remaining water removed by azeotropic distillation into a Dean-Stark trap. After removal of benzene, the solid residue was dried under vacuum at 105° C. to a constant weight to give the crude acid-adduct. This crude acid was dispersed in carbon tetrachloride and added to a flask equipped with a magnetic stirrer, condenser, and drying tube. The mixture was heated to gentle reflux, then phosphorus pentachloride (36.6 grams, 0.176 mole) was added cautiously in small portions through the condenser. The addition was completed in 30 minutes and the solution refluxed overnight. Sulfur dioxide was bubbled through the warm solution to remove excess phosphorus pentachloride. The solution was concentrated under water aspirator vacuum, and the residue distilled at 69–72° C. (0.04 mm.) to give an 83% yield (32.2 grams, 0.062 mole) of III*a*, a white solid. IR spectrum showed absorption bands at 3.37 microns (w) (CH stretching); 7.80 microns (v.s.) (P=O stretching); and 8.1–8.3 microns (s), 8.68 microns (m) (CF).

Anal. Calcd. for $C_9H_4Cl_2F_{15}OP$: C, 20.99; H, 0.78; Cl, 13.77; F, 55.34; P, 6.01. Found: C, 20.79; H, 0.89; Cl, 13.76; F, 55.13; P, 5.99.

1-(1H,1H-Perfluorooctyl)-1,3-trimethylenediphosphonic Tetrachloride (III*b*). II*b* (57.8 grams, 0.083 mole) was heated at gentle reflux for 6 hours with concentrated hydrochloric acid (300 ml.) in a 1-liter flask equipped with a 500-ml. defoamer-bulb and a condenser. The mixture was cooled in the refrigerator and the liquid decanted from the solid. More hydrochloric acid was added and the procedure repeated. The gel-like material was concentrated in a large evaporating dish on the steam cone using benzene to remove residual water. The solid residue was dried under vacuum at 105° C. to a constant weight to give the crude acid-telomer, which was then reacted with phosphorus pentachloride, as described for the crude acid-adduct above. III*b* was distilled at 125–6° C. (0.01 mm.) to give a 40% yield (21.7 grams, 0.033 mole) of a slightly yellow solid. III*b* had IR spectra bands similar to those of III*a*. The PMR spectrum ($CDCl_3$) showed a multiplet of numerous sharp signals between δ1.9 and δ3.6 p.p.m. The most intense signal occurred at δ2.90 p.p.m.

Anal. Calcd. for $C_{11}H_7Cl_4F_{15}O_2P_2$: C, 20.02; H, 1.07; Cl, 21.49; F, 43.18; P, 9.39; mol. wt., 660. Found: C, 20.16; H, 1.14; Cl, 21.54; F, 43.29; P, 9.21; mol. wt. (chloroform), 673.

1H,1H,2H,2H-Perfluorononylphosphonic Acid (IV*a*). III*a* (2 grams, 0.004 mole) was dissolved in chloroform, then heated with 10 grams of water in an evaporating dish. Residual water was removed by heating with benzene to dryness. The waxy solid residue was dried in a vacuum oven at 105° C. to a constant weight to give a 97% yield of IV*a*, m.p. 155–8° C.

Anal. Calcd. for $C_9H_6F_{15}O_3P$: C, 22.61; H, 1.27; F, 59.61 P, 6.48; mol. wt., 478. Found: C, 22.33; H. 1.26; F, 59.73; P, 6.44; mol. wt. (methanol), 471.

1-(1H,1H-Perfluorooctyl)-1,3-trimethylenediphosphonic Acid (IV*b*). IV*b* was prepared from III*b* as described for IV*a*, except that it was dried to constant weight in a vacuum desiccator at room temperature.

Anal. Calcd. for $C_{11}H_{11}F_{15}O_6P_2$: C, 22.54; H, 1.89; F, 48.62; P, 10.57. Found: C, 22.75; H, 1.95; F, 48.68; P, 10.77.

1H,1H,2H,2H-Perfluorononylbis(1-aziridinyl)phosphine Oxide (V*a*). Redistilled triethylamine (12.6 grams, 0.124 mole) and redistilled aziridine (5.4 grams, 0.124 mole) in carbon tetrachloride (100 ml.) was added to a 4-necked flask equipped with a mechanical stirrer, thermometer, dropping funnel, and condenser with drying tube. The flask was cooled to 5° C. in an ice bath. III*a* (29 grams, 0.056 mole) in 75 ml. of carbon tetrachloride was added from the dropping funnel at such a rate as to keep the reaction temperature below 10° C. After the addition, the reaction temperature was allowed to rise to room temperature. The reaction mixture was heated at 35–40° C. with stirring for 1 hour. The copious white precipitate was removed by vacuum filtration, rinsed thoroughly with carbon tetrachloride, and dried to give 14.7 grams (95% yield) of triethylamine hydrochloride. The filtrate was cooled at 0° C. overnight, then filtered by gravity through sodium sulfate. The clear filtrate was concentrated to approximately 125 ml. on a rotary evaporator below 40° C. The solution was treated with decolorizing carbon and sodium sulfate, then filtered by vacuum through diatomaceous earth. The filtrate was again concentrated to approximately 75 ml.; then 150 ml. of petroleum ether (30° to 60° C.) was added. The solution was stored at −20° C. for 1 hour. The liquid was decanted through filter paper (filtrate No. 1). The slurry of white precipitate was redissolved in 100 ml. of petroleum ether and stored at −20° C. overnight. The white waxy precipitate was filtered by vacuum, washed thoroughly with cold petroleum ether and dried in a desiccator to give 8.9 grams of V*a*, m.p. 49–50° C.; average aziridinyl assay of duplicate samples, 99.7%. The concentrated filtrate was diluted with petroleum ether and a second crop of crystals (10.1 grams) was obtained; m.p. 42–4° C., average aziridinyl assay of duplicate samples, 97.7%. The filtrate was combined with filtrate No. 1 and concentrated to a yellow solid residue (7.1 grams). The first and second crop of crystals gave a 64% yield of V*a*.

The IR spectrum of V*a* showed absorption bands at 7.90 microns (sh), 7.98 microns (sh) (may be ring breathing and P=O); 8.09 microns (v.s.), 8.27 microns (s), 8.70 microns (m) (CF), 10.53 microns (m); 10.71 microns (s) (P—N—C ring stretching).

The PMR spectrum (CCl_4) showed an intense doublet, coupling with phosphorus (J_{PH} = 14 c.p.s.), centered at δ2.08 p.p.m. and assigned to the aziridinyl protons.

Anal. Calcd. for $C_{13}H_{12}F_{15}N_2OP$: C, 29.59; H, 2.29; F, 53.95; N, 5.30; P, 5.86; mol. wt., 528. Found: C, 29.50; H, 2.41; F, 54.00; N, 5.33; P, 5.78; mol. wt. (methanol), 530.

1-(1H,1H-Perfluorooctyl) - 1,3-trimethylenebis[di(1-aziridinyl)phosphine Oxide] (V*b*). V*b* was prepared from IV*b* as described for V*a* to give a 64% yield; m.p. 103–7° C.; aziridinyl assay 97.3%. (V*b* was obtained as a slightly purer product when dissolved in carbon tetrachloride and a polymeric material removed by filtration; aziridinyl assay, 100.2%). IR spectrum showed absorptions similar to those for V*a*, except for degree of intensity and resolution. The absorption at 7.98 microns was stronger and more distinctive than a shoulder, whereas the adsorption at 10.56 microns appeared as a shoulder. The P—N—C ring stretching band at 10.71 microns was very strong. The PMR spectrum (CCl_4) showed an intense doublet (J = 14 c.p.s.) at δ2.03 p.p.m. and a doublet of doublets (J = 14 c.p.s.) of less intensity, centered at δ2.10 p.p.m.

Anal. Calcd. for $C_{19}H_{23}F_{15}N_4O_2P_2$: C, 33.25; H, 3.38; F, 41.52; N, 8.16; P, 9.03; mol. wt., 686. Found: C, 33.07; H, 3.14; F, 41.42; N, 8.08; P, 9.15; mol. wt. (chloroform), 691.

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