C_6, C_7, and C_8 Perfluoroalkyl-Substituted Phosphinic Acids

Rajendra P. Singh and Jean'ne M. Shreeve*

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343

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Reaction of red phosphorus with R_fI in a 1:2 molar ratio at 230 °C led to the formation of a mixture of $(R_f)_2PI$ and $(R_f)PI_2$ ($R_f = C_6F_{13}$, C_7F_{15}, C_8F_{17}) in about a 70:30 ratio, respectively. These mixtures were separated by vacuum distillation. $(R_f)_2PI$ ($R_f = C_6F_{13}$, C_7F_{15}) are yellow liquids whereas $(C_8F_{17})_2PI$ is a yellow solid. Oxidation of $(R_f)_2PI$ with excess NO_2 led to $(R_f)_2P(O)OH$ ($R_f = C_6F_{13}$, C_7F_{15}, C_8F_{17}) in >90% isolated yields after aqueous hydrolysis of the anhydride intermediates. These highly fluorinated phosphinic acids are white solids with sharp melting points and are highly soluble in methyl sulfoxide (DMSO) and 1,1,2-trichlorotrifluoroethane. However, solubility in chloroform and methylene dichloride is low. These perfluoroalkylphosphinic acids were characterized by IR, NMR (^1H, ^{19}F, and ^{31}P), and mass spectra and elemental analysis.

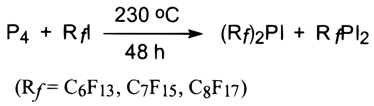
Introduction

Since the pioneering chemistry accomplished by the Emeléus school at Cambridge, the synthesis and utilization of perfluoroalkyl phosphorus compounds have attracted considerable interest. Earlier we reported the synthesis of the lower boiling C_2 perfluoroalkyl-substituted phosphinic and phosphonic acids as well as new routes to the previously known C_1 and C_4 acids.[1] These bis(perfluoroalkyl)phosphorus(V) acids were expected to have potential as electrolytes with good cell characteristics. Prior to and following our work several patents have been issued claiming surface and other applications for both the phosphinic and phosphonic acids.[2−5] Currently, considerable interest in these compounds has arisen for applications to plastic optical fibers for data communications. It seemed appropriate to attempt to synthesize the higher homologues of these compounds with longer perfluoroalkyl groups that would likely be solid. Thus, we would like to report the facile synthesis of $(R_f)_2P(O)OH$ ($R_f = C_6F_{13}$, C_7F_{15}, C_8F_{17}) and their characterization by using spectroscopic and analytical techniques.

Results and Discussion

The compounds $(R_f)PI_2$ and $(R_f)_2PI$ ($R_f = C_6F_{13}$, C_7F_{15}, C_8F_{17}) were prepared[6−8] by heating red phosphorus with a perfluoroalkyl iodide (1:2 molar ratio) at 230 °C in a stainless steel reactor (Scheme 1).

Scheme 1



When $R_f = C_6F_{13}$, the products were liquids. However, when $R_f = C_7F_{15}$, the product mixture was liquid but, after distillation, $C_7F_{15}PI_2$ solidified immediately as a yellow solid whereas $(C_7F_{15})_2PI$ remained as a light yellow liquid. In the case of $R_f = C_8F_{17}$, both the mono and diiodo derivatives were yellow solids before and after distillation. Although earlier workers used H_2O_2,[5] in our work oxidation of $(R_f)_2PI$ ($R_f = C_6F_{13}$, C_7F_{15}, C_8F_{17}) was carried out with nitrogen dioxide in 1,1,2-trichlorotrifluoroethane in a Hoke stainless steel vessel at 25 °C for 12 h. To avoid an exothermic oxidation reaction, NO_2 was condensed into the vessel at liquid nitrogen temperature and then the mixture was allowed to warm slowly to 25 °C. In the case of a liquid substrate no solvent was necessary, but dissolution of the solid substrate is recommended for smooth oxidation. In our earlier synthesis of phosphinic acids with shorter perfluoroalkyl groups, the conversion of the iodophosphine to chlorophosphine was necessary because the iodine that would be formed during the oxidation step was difficult to remove from the product.[1] With the higher perfluoroalkyl iodophosphines, the oxidized and hydrolyzed products were found to have low solubility in chloroform and methylene chloride, which helped enhance the extraction of free iodine. Oxidation of $(R_f)_2PI$ ($R_f = C_6F_{13}$, C_7F_{15}, C_8F_{17}) with excess NO_2 produced the phosphinic acid anhydride,[9] which was easily hydrolyzed by using a quantitative amount of water. The monobasic acids $(R_f)_2P(O)OH$ ($R_f = C_6F_{13}$, C_7F_{15}, C_8F_{17}) were obtained in more than 90% yield (Scheme 2).

These acids were found to be very reactive with ethanol, which gave the phosphinic esters, $(R_f)_2P(O)OEt$ ($R_f = C_6F_{13}$, C_7F_{15}, C_8F_{17}) (Scheme 3), when chloroform-containing ethanol as a preservative was used to extract the iodine from the acids. The formation of the esters was confirmed by spectroscopic data. The ^1H NMR spectra showed a triplet due to the CH_3 group at δ 1.2 with $J = 6.4$ Hz and CH_2 as a quartet at δ 3.9. In mass spectroscopic analysis, the molecular ions are observed for the three ethyl esters at *m*/*z* 730, 830, and 930, respectively.

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* Author to whom correspondence should be addressed. Tel: 208-885-6215. Fax: 208-885-6215. E-mail: jshreeve@uidaho.edu.

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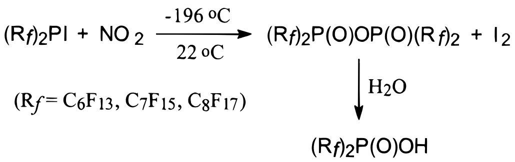
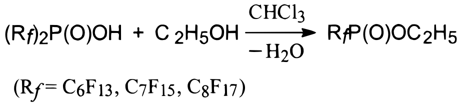
Scheme 2



Scheme 3



The $(R_f)_2P(O)OH$ acids ($R_f = C_6F_{13}, C_7F_{15}, C_8F_{17}$) are white solids with sharp melting points. They are quite stable in air at room temperature and are soluble in dimethyl sulfoxide and 1,1,2-trichlorotrifluoroethane. The IR spectra showed a broad band at about 3200 cm^{-1} due to ν(OH) vibration. The band due to ν(PO) absorption appeared at 1350−1370 cm^{-1}.

The ^{31}P NMR spectra of $(R_f)_2PI$ ($R_f = C_6F_{13}, C_7F_{15}, C_8F_{17}$) showed a multiplet at about δ 24. This multiplicity is due to two-bond and three-bond phosphorus−fluorine couplings. The $^2J_{P-F}$ and $^3J_{P-F}$ were observed to be 34 and 13, respectively.[10] In each of the ^{19}F NMR spectra of R_fI ($R_f = C_6F_{13}, C_7F_{15}, C_8F_{17}$), the peak which appeared at δ −50 due to $I-CF_2$ was found to be shifted to about δ −101 in $(R_f)_2P(O)OH$ ($R_f = C_6F_{13}, C_7F_{15}, C_8F_{17}$). This shift arises from the formation of $P-CF_2$ σ bonds. The ^1H NMR spectra of $(R_f)_2P(O)OH$ ($R_f = C_6F_{13}, C_7F_{15}, C_8F_{17}$) in DMSO-$d_6$ showed a broad band in the region δ 5−7 due to the hydroxyl proton. This shift was found to be solvent dependent and shifted in the region δ 9−12 in a 1:1 mixture of $CDCl_3 + Cl_2FCCF_2Cl$. The peak was found to disappear when D_2O was added to the NMR solution. The ^{31}P NMR of $(R_f)_2P(O)OH$ ($R_f = C_6F_{13}, C_7F_{15}, C_8F_{17}$) showed a clean pentet at about δ 4 with $^2J_{P-F} = 66$ Hz arising from coupling with two equivalent CF_2 groups of the R_f moieties. In ^{19}F NMR spectra the signal due to $P-CF_2$ was found to be shifted to δ −120 with $^2J_{P-F} = 66$.

The acids were also characterized by mass spectroscopy. MS(CI) of $(C_6F_{13})_2P(O)OH$ and FAB (fast atom bombardment) analysis of $(R_f)_2P(O)OH$ ($R_f = C_7F_{15}, C_8F_{17}$) showed the parent ion at *m*/*z* 702 (100% relative intensity), 802 (100% relative intensity), and 902 (90% relative intensity), respectively. The mass spectra of these strong acids show some evidence of dimerization when CIMS is used but only a trace in the FAB analysis.

In summary, we have developed a facile route to the higher bis(perfluoroalkyl)phosphinic acids that should be extendable to a very large number of substituted phosphorus(V) acids.

Experimental Section

Perfluoroalkyl iodides, R_fI ($R_f = C_6F_{13}, C_7F_{15}, C_8F_{17}$), were purchased from Lancaster Chemical Company, red phosphorus from Aldrich, and NO_2 from Air Products and used as received. The perfluoroalkyliodophosphines were protected from light by wrapping the glass vessels with aluminum foil.

The ^1H, ^{31}P, and ^{19}F NMR spectra were recorded in DMSO-d_6 at 200, 81, and 188 MHz, respectively. Chemical shifts are reported in ppm relative to the standard: tetramethylsilane for ^1H, 80% H_3PO_4 for ^{31}P, and $CFCl_3$ for ^{19}F NMR spectra. IR spectra were recorded as KBr pellets. Mass spectra were taken on an electron impact (70 eV) JEOL JMS AX505HF spectrometer. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ.

General Procedure for the Preparation of $(R_f)_2PI$ ($R_f = C_6F_{13}, C_7F_{15}, C_8F_{17}$). In a typical reaction, perfluoroalkyl iodide (50.0 mmol, 22.3 g of $C_6F_{13}I$ or 24.8 g of $C_7F_{15}I$ or 27.3 g of $C_8F_{17}I$) and red phosphorus (25 mmol, 0.77 g) were placed in a 75 mL Hoke stainless steel vessel and cooled to −100 °C. The reactor was evacuated and heated at 230 °C for 48 h. The ^{31}P NMR showed the formation of diiodo(perfluoroalkyl)phosphine and iodobis(perfluoroalkyl)phosphine in a ratio of about 30:70. The reaction mixture was dissolved in 1,1,2-trichlorotrifluoroethane (10 mL), carefully transferred into a distillation flask under nitrogen, and separated by distillation under vacuum. These iodo and diiodo phosphines must be protected from light. Since these compounds were utilized as intermediates, elemental analyses were not performed. However, elemental analyses are reported for each of the final products.

$(C_6F_{13})_2PI$: light yellow liquid. Yield: 12.1 g (62%). Bp: 62 °C/0.1 mm. ^{31}P NMR ($CDCl_3 + CCl_2FCF_2Cl$): 24.53 (m, $^2J_{C-F} = 34$ Hz, $^3J_{C-F} = 13$ Hz). ^{19}F NMR ($CDCl_3 + CCl_2FCF_2Cl$): −81.7 (t, CF_3, $J_{C-F} = 9$ Hz), −102.2 (d, CF_2), −117.0 (d, CF_2), −122.1 (s, CF_2), 123.3 (s, CF_2), 126.8 (s, CF_2).

$(C_7F_{15})_2PI$: light yellow liquid. Yield: 13.4 g (60%). Bp: 70 °C/0.1 mm. ^{31}P NMR ($CDCl_3 + CCl_2FCF_2Cl$): 24.52 (m, $^2J_{C-F} = 34$ Hz, $^3J_{C-F} = 13$ Hz). ^{19}F NMR ($CDCl_3 + CCl_2FCF_2Cl$): −81.8 (t, CF_3, $J_{C-F} = 9$ Hz), − 101.7 (d, CF_2), −117.1 (d, CF_2), −122.0 (s, CF_2), 122.6 (s, CF_2), 123.4 (s, CF_2), 127.0 (s, CF_2).

$(C_8F_{18})_2PI$: light yellow solid. Yield: 14.9 g (60%). Bp: 90 °C/0.1 mm. ^{31}P NMR ($CDCl_3 + CCl_2FCF_2Cl$): 24.61 (m, $^2J_{C-F} = 34$ Hz, $^3J_{C-F} = 13$ Hz). ^{19}F NMR ($CDCl_3 + CCl_2FCF_2Cl$): −81.8 (t, CF_3, $J_{C-F} = 9$ Hz), − 101.5 (d, CF_2), −117.2 (d, CF_2), 121.9 (s, CF_2) −122.4 (s, CF_2CF_2), 123.3 (s, CF_2), 126.9 (s, CF_2).

General Procedure for the Preparation of $(R_f)_2P(O)OH$ ($R_f = C_6F_{13}, C_7F_{15}, C_8F_{17}$). In a typical reaction, iodobis(perfluoroalkyl)phosphine [10.0 mmol, 7.95 g of $(C_6F_{13})_2PI$ or 8.95 g of $(C_7F_{15})_2PI$ or 9.96 g of $(C_8F_{17})_2PI$] was mixed with 1,1,2-trichlorotrifluoroethane (15 mL), the mixture was placed in a 75 mL Hoke stainless steel reactor, and the reactor was evacuated at room temperature. Nitrogen dioxide (160 mmol) was condensed into the reactor at liquid nitrogen temperature. The reactor was closed, warmed slowly to 25 °C, and repeatedly shaken overnight. The excess NO_2 was recovered under vacuum, and the oxidized product was transferred into a flask. It was stirred for 10 h with 50 mL of methylene chloride (free from preservative and ethanol) and 10 mmol of water. The insoluble bis(perfluoroalkyl)phosphinic acid was filtered and washed with several small portions of methylene chloride until the solid was colorless. Finally the product was dried at reduced pressure.

$(C_6F_{13})_2P(O)(OH)$: white solid. Yield: 6.30 g (90% based on oxidation step). Mp: 164−165 °C (sharp). IR (as KBr pellet) cm^{-1}: 3200 (OH), 1358 (P=O), 1200 ($P-CF_2$). ^1H NMR (DMSO-d_6): δ 6.17 (b, 1H, OH). ^{31}P NMR (DMSO-d_6): δ 4.20 (pentet, $J_{P-F} = 66$ Hz). ^{19}F NMR (DMSO-d_6): δ −80.31 (t, CF_3, $J_{C-F} = 9$ Hz), −119.7 (s, CF_2), −121.3 (d, CF_2-P, $J_{P-F} = 66$ Hz), −121.5 (s, CF_2), −122.5 (s, CF_2), −125.7 (s, CF_2). MS (CI) *m*/*z* (species, %): 702 (M^+, 100), 685 ($M^+ - OH$, 1), 383 ($M^+ - C_6F_{13}$, 3), 69 (CF_3^+, 2). Anal. Calcd for $C_{12}HF_{26}O_2P$: C, 20.51; F, 70.37. Found: C, 20.13; F, 69.49.

$(C_7F_{15})_2P(O)OH$: white solid. Yield: 7.36 g (92% based on oxidation step). Mp: 170−171 °C (sharp). IR (as KBr pellets) cm^{-1}: 3200 (OH), 1365 (P=O), 1200 ($P-CF_2$). ^1H NMR (DMSO-d_6): δ 5.47 (b, 1H, OH). ^{31}P NMR (DMSO-d_6): δ 4.05 (pentet, $J_{P-F} = 65$ Hz). ^{19}F NMR (DMSO-d_6): δ −79.9 (t, CF_3, $J_{C-F} = 9$ Hz), −119.6 (s, CF_2), −121.0 (s, CF_2CF_2), 121.4 (d, CF_2-P, $J_{P-F} = 65$ Hz), −122.1 (s, CF_2), −125.4 (s, CF_2). MS (FAB) *m*/*z* (species, %): 702 (M^+, 93), 219 ($CF_3CF_2CF_2CF_2^+$, 11), 169 ($CF_3CF_2CF_2^+$, 100), 119 ($CF_3CF_2^+$, 100), 100 (CF_3CF^+, 100), 93 (CF_3CC^+, 100), 81 (CF_3C^+, 29). Anal. Calcd for $C_{14}HF_{30}O_2P$: C, 20.94; F, 71.07. Found: C, 21.13; F, 69.92. This analysis was on a sample that was very slightly contaminated with $(C_7F_{15})_2P(O)OC_2H_5$.

$(C_8F_{17})_2P(O)OH$: white solid. Yield: 8.56 g (95% based on oxidation step). Mp: 187−188 °C. IR (as KBr pellet) cm^{-1}: 3200 (OH), 1365 (P=O), 1207 ($P-CF_2$). ^1H NMR (DMSO-d_6): δ 5.99 (b, 1H, OH). ^{31}P NMR (DMSO-d_6): δ 4.39 (pentet, $J_{P-F} = 67$ Hz). ^{19}F NMR (DMSO-d_6): δ −80.8 (t, CF_3, $J_{C-F} = 9$ Hz), −119.7 (s, CF_2), −121.5

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(d, $CF_2{-}P$, $J_{P-F} = 67$ Hz), −121.7 (s, $CF_2CF_2CF_2$), −122.7 (s, CF_2), −126.1 (b, s, CF_2). MS (FAB) *m*/*z* (species, %): 902 (M^+, 67), 219 ($CF_3CF_2CF_2CF_2^+$, 11), 169 ($CF_3CF_2CF_2^+$, 40), 119 ($CF_3CF_2^+$, 85), 100 (CF_3CF^+, 53), 93 (CF_3CC^+, 100), 81 (CF_3C^+, 10). Anal. Calcd for $C_{16}HF_{34}O_2P$: C, 21.28; F, 71.61. Found: C, 21.01; F, 72.10. This analysis was on the sample that was very slightly contaminated with $(C_8F_{17})_2P(O)OC_2H_5$.

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